BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

SEPTEMBER, 1933.

General, Physical, and Inorganic Chemistry.

Blue and violet spectra of hydrogen molecule. D. Chalonge and E. Vassy (Compt. rend., 1933, **196**, 1979—1981; cf. A., 1931, 991).—By a method similar to that of Freeman (cf. A., 1927, 81) with p.d. of 80 and 82 volts, respectively, the blue and violet spectra of H_2 were obtained. The blue spectrum is continuous; the violet shows, superposed on a continuous spectrum, the lines of the secondary spectrum and faint first lines of the Balmer spectrum. C. A. S.

Doppler effect in hydrogen at high voltages. K. Lion (Z. Physik, 1933, **83**, 442—443).—Discharge potentials above 100 kv. produced no limit of line displacement. A. B. D. C.

Wave-mechanical calculation of the Rydberg correction for helium terms. E. A. Hylleraas (Z. Physik, 1933, 83, 739—764). A. B. D. C.

Zeeman effect for perturbed N_2^+ terms. A. E. Parker (Physical Rev., 1933, [ii], **44**, 84—89).—Data and explanations of the Zeeman patterns at field strengths up to 27,000 gauss are given. N. M. B.

Rotational analysis of the perturbed (13, 15) $^2\Sigma$—$^2\Sigma$ N_2^+ band. A. E. Parker (Physical Rev., 1933, [ii], **44**, 90—91; cf. preceding abstract). N. M. B.

Multiplets in the spectra of O III, O IV, O V, and C III. P. G. Kruger and W. E. Shoupp (Physical Rev., 1933, [ii], **44**, 105—108).—New and revised multiplet data are given from photographs of spectra in the region 100—650 Å. N. M. B.

Lowest excited state of neon according to Slater's method. S. Rozental (Z. Physik, 1933, 83, 534—542).—Theoretical. A. B. D. C.

Pressure effects of foreign gases on the sodium *D* lines. H. Margenau and W. W. Watson (Physical Rev., 1933, [ii], **44**, 92—98).—True line contours were photographed and photometrically evaluated for the effect on the Na *D* lines, at low pressure of Na vapour, of A, N_2, and H_2 at 0—17 atm. pressure. The red shift of the absorption max. varies linearly with the density of the perturbing gas; asymmetries to the red for A and N_2, and slightly to the blue for H_2, are found; both *D* lines show the same broadening and shift; results can be accounted for by assuming a distance of closest approach of about 9 Å. between excited Na and the foreign gas mols. N. M. B.

Measurements of the intensity distribution and width of predissociation lines of the AlH molecule. L. Farkas and S. Levy (Z. Physik, 1933, **84**, 195—207).—Width and intensity distribution of the rotation lines of AlH, investigated with a Fabry–Perot étalon, agree with Kronig's theory of predissociation. A. B. D. C.

Arc spectrum of chlorine. C. C. Kiess (Bur. Stand. J. Res., 1933, **10**, 827—839).—Using new type plates for the long and short wave-length regions, the no. of lines previously known has been approx. doubled. Data for 441 lines are tabulated; the analysis of Cl I is revised, new terms are given, and previous classifications are corr. N. M. B.

High-frequency discharges in argon. II. Spectral properties. S. P. McCallum, L. Klatzow, and J. E. Keyston (Phil. Mag., 1933, [vii], **16**, 193—197; cf. this vol., 439).—The high-frequency discharge in A gives rise to a continuous spectrum from 6100 to 2200 Å. in addition to line spectra. Similar continuous spectra are observed with He and Ne. The distribution of energies of the electrons in A about the mean energy is much narrower than in He. An explanation is offered. A. J. M.

Spectrum of the A^{++} ion, A III. V. von Keussler (Z. Physik, 1933, **84**, 42—55).—The energy of ionisation of A^{++} is 4·7 volts. A. B. D. C.

Series of alkaline atoms in an electric field. E. Segrè and G. C. Wick (Proc. K. Akad. Wetensch. Amsterdam, 1933, **36**, 534—542).—The intensities of K lines of both permitted and forbidden series are calc. for the spectrum excited in an electric field, the results agreeing with experiment (cf. following abstract). J. W. S.

Influence of electric fields on the absorption spectrum of potassium. C. J. Bakker (Proc. K. Akad. Wetensch. Amsterdam, 1933, **36**, 589—594).—With increasing field strength the absorption limit is moved to longer wave-lengths. New absorption lines which appear are interpreted as "forbidden" lines. J. W. S.

Arc spectra of chromium, manganese, cobalt, and nickel. H. Slevogt (Z. Physik, 1933, **84**, 136).—A correction (cf. this vol., 547). A. B. D. C.

Spark spectrum of copper between 400 and 240 Å. L. Bloch and E. Bloch (Compt. rend., 1933, **197**, 132—134; cf. this vol., 2).—86 lines have been measured between λ 383·33 and 322·85 Å., and 57 more (311·99—240·40) determined by extrapolation. C. A. S.

Band spectrum of copper hydride. A. Heimer and T. Heimer (Z. Physik, 1933, **84**, 222—235).—Dissociation energies for CuH are 3·2 for $^1\Sigma$, 1·8 for $^1\Sigma^*$, and 0·8 volts for $^1\Sigma^{**}$. A. B. D. C.

First spark spectrum of arsenic. A. S. Rao (Indian J. Physics, 1933, **7**, 561—584; cf. A., 1932, 668).—The spectrum of As has been studied under varying conditions of excitation in the region 8400—4000 Å.; 280 lines have been ascribed to As II, many of them being classified. Higher members of the mp^3P terms have been identified and combinations involving the transition of one of the inner group of s^2p^2 electrons have been detected. Cases of interpenetration of different sub-levels indicating a strong tendency towards *JJ* coupling are pointed out. The largest term is $4p^3P_0$ (ν=162,788 cm.$^{-1}$), *i.e.*, ionisation potential about 20·1 volts for the singly-ionised As atom. J. W. S.

Nuclear spin of arsenic. A. S. Rao (Z. Physik, 1933, **84**, 236—247).—Nuclear moment is 3/2. A. B. D. C.

Nuclear moment of krypton. H. Kopfermann and N. Wieth-Knudsen (Naturwiss., 1933, **21**, 547—548).—The $1s-mp$ lines of Kr under high dispersion show a strong central component and several weak ones. The central line is due to the sum of the components of the even isotopes of Kr; the weak components are due to Kr^{83}. The lines previously discovered now fall into a simple hyperfine structure term scheme, giving for the mechanical moment of Kr^{83} the val. $I \nless 7/2$. A. J. M.

Intensity measurements with the members of the principal series of rubidium and cæsium. H. J. Hübner (Ann. Physik, 1933, [v], **17**, 781—815).—The determinations were made by introducing salts of Rb and Cs into O_2–H_2 (I) or coal gas–compressed air (II) flames, temp. being 2850° and 2176° abs., respectively. The intensities were determined by a photographic–photometric method. The intensity ratio of the components of the second and third members of the principal series of Cs for an "infinitely thin" thickness of the light source was determined. For the second Rb member the val. for (I) was 2·55, and for (II) 2·58. In (II) the ratio for the third Rb member was 3·25 and for the third Cs member 8·0. A. J. M.

Hyperfine structure and nuclear moment of rubidium. H. Kopfermann (Z. Physik, 1933, **83**, 417—430).—The mechanical moment of Rb^{87} is 3/2, and of Rb^{85} 5/2, whilst the magnetic moment of 87 is nearly double that of 85. A. B. D. C.

Absence of fine structure in the arc spectrum of silver. S. Tolansky (Proc. Physical Soc., 1933, **45**, 559—564).—No fine structure in the region 8300—4000 Å. was detected. Its absence is attributed to electron configuration rather than to smallness of nuclear magnetic moment. N. M. B.

Mean life of cadmium atom in state 2^3P_1. P. Soleillet (Compt. rend., 1933, **196**, 1991—1993; cf. A., 1932, 439).—Direct measurement of the mean life of the Cd atom in state 2^3P_1 by means of radiation of λ 3261 Å. gives $2{\cdot}45\times10^{-6}$ sec. C. A. S.

New resonance series in antimony vapour. R. Siksna (Compt. rend., 1933, **196**, 1986—1987).—Mg II λ 2929 and 2937 Å. give rise each to a resonance series in Sb vapour at 950°; one anti-Stokes and 15 positive terms of both series were observed (cf. this vol., 200). C. A. S.

Atomic fluorescence of antimony. R. Siksna (Compt. rend., 1933, **197**, 134—136; cf. A., 1926, 776).—In the fluorescence spectrum of Sb excited by strongly condensed sparks of Cd and Zn, 2 and 11 at. lines, respectively, were observed. C. A. S.

Width of absorption lines of I_2. I. I. Agarbiceanu (Compt. rend., 1933, **197**, 38—39).—Examination of the absorption spectrum of I_2 alone and in presence of O_2 indicates that the enlargement of the lines is due to the mutual interaction of mols. during collision and to the instability of the two levels by the passing of the mols. between which the line is produced. The O_2 depolarises the fluorescence light of I_2 (cf. this vol., 201). C. A. S.

Recombination radiation in the cæsium positive column. F. L. Mohler (Bur. Stand. J. Res., 1933, **10**, 771—780).—Radiation emitted along the axis of the positive column was measured spectrophotometrically, and electrical measurements were made with small probe surfaces. Data for at. consts. determining the rate of interaction of electrons, ions, and atoms in a discharge are obtained. N. M. B.

Arc spectrum in air at normal pressure of neodymium for λλ 2400—3100 Å. S. Piña de Rubies (Compt. rend., 1933, **197**, 33—35).—184 new lines are tabulated (cf. A., 1931, 890). C. A. S.

Polarisation phenomena in the stepwise excitation of mercury fluorescence. E. F. Richter (Ann. Physik, 1933, [v], **17**, 463—464).—A correction (cf. A., 1931, 8). W. R. A.

Non-Ritzian nature of the ^3S terms of mercury. I. Walerstein (Nature, 1933, **132**, 139). L. S. T.

Variation in intensity in radiation emitted by a mercury vapour arc during lighting. L. Grillet (Compt. rend., 1933, **197**, 311—313).—The ratios of the intensities of various lines in the spectrum of a Hg-vapour lamp with a.c. to those for a similar lamp with d.c. vary from about 4·5 for λ 5461, 4358, and 4046 to 11 for λ 4077, and 12·5—13 for λ 5791—5770; the ratios increase in all cases to about unity in 1·5— 2·5 min., and attain the above approx. steady vals. in about 5 min. C. A. S.

Determination of the excitation function for some mercury terms. R. Seiler (Z. Physik, 1933, **83**, 789—805).—Excitation functions were determined from the energy lost by an electron beam exciting the Hg vapour. A. B. D. C.

Optical potentials of the mercury atom. So-called ultra-ionisation potentials. R. G. Loyarte and M. H. de Bose (Physikal. Z., 1933, **34**, 589—592).—Priority is claimed in the determination of ultra-ionisation potentials of the Hg atom. A table of potentials is given and analysed. A. J. M.

Continuous gas spectra. II. W. Finkelnburg (Physikal. Z., 1933, **34**, 529—560).—A summary. A. J. M.

Gas breakdown at normal pressure. J. J. Sämmer (Z. Physik, 1933, 83, 814—831).—Theoretical, showing why the discharge is conc. in a narrow column. A. B. D. C.

Calculation of extent of polarisation of resonance radiation. P. Soleillet (Compt. rend., 1933, **197**, 316—318; cf. A., 1929, 120; 1932, 891).—Mathematical. C. A. S.

Hyperfine structure of perturbed series. E. G. Jones (Proc. Physical Soc., 1933, **45**, 501—506).—Theoretical. N. M. B.

Forbidden lines in astrophysical sources. J. C. Boyce, D. H. Menzel, and (Miss) C. H. Payne (Proc. Nat. Acad. Sci., 1933, **19**, 581—591).—From a survey, based on the analysis of spectra, of the metastable states of the atoms from H to A, tables are given of calc. and observed forbidden transitions, wave-lengths of lines and their sources, and relative intensities of nebular pairs, and of auroral and nebular lines. The newly observed line λ 4725 is attributed to Ne iv. N. M. B.

Night light and Northern lights. L. A. Sommer (Z. Physik, 1933, 84, 268—270).—Vegard's measurements of wave-lengths of Northern lights (A., 1932, 1187) are in good agreement with those of the night sky (cf. this vol., 332). A. B. D. C.

Spontaneous absorption of radiation and deviation of spectral lines of nebulæ. E. Sevin (Compt. rend., 1933, **197**, 26—28). C. A. S.

Excitation of *X*-rays by collision of high-velocity positive ions. K. Lion (Z. Physik, 1933, 83, 431—441).—Soft *X*-rays with wave-lengths $>$ 6 Å. are excited by positive rays of 150 kv. A. B. D. C.

Crystalline diffraction spectrography of γ- and *X*-rays of the radium family. M. Valadares (Compt. rend., 1933, **197**, 144—145; cf. this vol., 443).—The strong lines 138·9, 143·0, 160·7, and 165·8 X of Ra-$B+C$ agree well with the K lines of Bi experimentally determined, and with those calc. from the energies of the electronic levels of element 83. They are therefore lines of fluorescence, as also are probably the weak lines of this region. The line 232·7 X may be identical with Ellis and Skinner's line 53·6 kv. of Ra-$B+C$ (cf. A., 1924, ii, 137; 1932, 556). C. A. S.

Wave-length determinations in the very soft *X*-ray region. F. C. Chalklin and L. P. Chalklin (Phil. Mag., 1933, [vii], **16**, 363—389).—A grating *X*-ray spectrograph is described. Measurements for soft radiation from C, N, O, Mo, Rh, Pd, Ag, Ta, W, Pt, and oxidised W and Ta are recorded, and the origin of the lines is discussed. H. J. E.

Quadrupole and other weak lines in the *K*-spectra of the elements 37 Rb to 42 Mo. II. E. Carlsson (Z. Physik, 1933, 84, 119—130; cf this vol., 332). A. B. D. C.

Natural widths of the $K\alpha$ *X*-ray doublet from Fe (26) to Ag (47). S. K. Allison (Physical Rev., 1933, [ii], **44**, 63—72).—Data are given for the full widths at half max. of the $K\alpha_1$ and $K\alpha_2$ lines of Fe, Co, Ni, Cu, Zn, Ge, Sr, Zr, Nb, Mo, Ru, Rh, Pd, and Ag. N. M. B.

Precision measurements of the *L* series of molybdenum and silver. P. Haglund (Z. Physik, 1933, 84, 248—259).—A new vacuum tube spectrometer is described. A. B. D. C.

***L*-, *M*-, and *N*-absorption in the ultra-soft *X*-ray region.** J. A. Prins and A. J. Takens (Z. Physik, 1933, 84, 65—74).—Measurements are in agreement with energy levels deduced from the harder region, except for the $M_{\text{IV V}}$-level of 52 Sn, 48 Cd, and 47 Ag, and the deviations are similar to those observed for 74 W to 90 Th. A. B. D. C.

Absorption effect in the *M*-series [of tungsten and tantalum]. V. Kunzl (Nature, 1933, **132**, 139). L. S. T.

***M*-level of magnetised iron.** Privault (Compt. rend., 1933, **197**, 140—142; cf. this vol., 441).—Application of a field of 15,500 gauss to an Fe cathode had no effect on λ of $K\beta_1$ and $K\beta_2$ $>$ 0·03 and 0·06 X, or on the energies of levels M_3 and M_5 $>$ 0·2 and 0·4 ev., respectively. C. A. S.

Determination of the *J*-discontinuity by a condition of matter. *J*-Phenomena. X. C. G. Barkla and J. S. Kay (Phil. Mag., 1933, [vii], **16**, 457—472).—Only certain specimens of a given substance show *J*-phenomena. There are also optimum working conditions of the *X*-ray tube for its appearance. H. J. E.

Electron configuration in metallic phases. U. Dehlinger (Z. physikal. Chem., 1933, **B**, 22, 45—59).—From the colours of Ag, Cu, and Au and their disappearance when these metals are alloyed with metals of the Fe and Pt groups, and from the miscibility relations in such alloys, it is concluded that in the body-centred cubic phase CuPd there is in the electron gas one electron per atom and a further electron oscillates between every two atoms, so that in Hume-Rothery's body-centred phases (A., 1926, 356) there are 3/2 electrons per atom involved in the linking. The nos. of electrons in Hume-Rothery's β, γ, and ε phases seem to be a consequence of a principle according to which those phases are especially stable, at least at high temp., in which only those terms necessary for the lattice construction are each occupied by a single electron in so far as they are not equiv. in respect of energy. R. C.

Electron microscope images of surfaces exposed to electrons. E. Ruska (Z. Physik, 1933, 83, 492—497). A. B. D. C.

Electron microscope observations of the barium evaporation cathode. E. Brüche and H. Johannson (Z. Physik, 1933, 84, 56—58).—The grains of Ba on the surface of a Ni cathode are conveniently photographed by the electron microscope. A. B. D. C.

Scattering of electrons by heavy atoms. W. Henneberg (Z. Physik, 1933, 83, 555—580).—Theoretical treatment of elastic scattering, particularly by Hg, Kr, and A at 100—800 volts. A. B. D. C.

Inelastic electron scattering by helium atoms. A. L. Hughes and J. H. McMillen (Physical Rev.,

1933, [ii], 44, 20—24).—Data and angular distribution curves, for the primary electron energy range 27·5—400 volts and angular range 6—150°, are given for electrons scattered by He atoms when the electrons have lost 21·12 volts energy, thereby exciting the atom to the 2^1P state. Results agree with theory.
N. M. B.

Small-angle inelastic scattering of electrons in helium. R. Whiddington, T. Emmerson, and J. E. Taylor (Nature, 1933, 132, 65). L. S. T.

Electron diffraction by liquids. L. R. Maxwell (Physical Rev., 1933, [ii], 44, 73—76).—Diffraction patterns were obtained for interference by the transmission of 14—30 kv. electrons through thin films of phytol and three oils. N. M. B.

Arrangement for producing rapid ions. H. Kallmann (Sitzungsber. Preuss. Akad. Wiss., Phys. Math. Klasse, 1933, 12, 1—12).—H^+, Li^+, Li^{++}, and Li^{+++} ions were accelerated by successive passage through a series of oppositely directed fields, part of the charge being removed before the ion passed into the reverse field. The apparatus is described. A max. kinetic energy of $1{\cdot}65 \times 10^6$ volts was obtained.
H. J. E.

Effect of neutral gas molecules on slow protons (total action, scattering, charging). C. Ramsauer and R. Kollath (Ann. Physik, 1933, [v], 17, 755—780).—The effective cross-sections of Kr, Xe, and CH_4 with respect to protons were determined, and scattering measurements were carried out with Kr and Xe. In the scattering process positively-charged gas mols. are produced. With respect to their charging capacity, the inert gases form a series from He to Ne in the order of the periodic table, and CH_4 also falls into the series. A connexion between charge and ionisation potential can be traced only in the inert gas series. From the behaviour of protons scattered elastically, the velocity and directional distribution of the gas mols. collided with are calc. A. J. M.

Influence of magnetic field on stream of cadmium atoms. Lande factor, g, for state 2^3P_1. P. Soleillet (Compt. rend., 1933, 197, 46—47).—A horizontal beam of light of λ 3261 Å. was passed through a vertical stream of Cd atoms at 600° abs. A magnetic field of 0·025 gauss was applied perpendicularly to both beam and jet and the effect on the polarisation of the fluorescence light observed in the same direction. From the result the Larmor rotation, ω_0, being $3{\cdot}67 \times 10^5$, the Lande factor, g, was deduced as 1·75, *i.e.*, nearly the theoretical 1·50. C. A. S.

Formation of negative ions in mercury vapour. U. Stille (Ann. Physik, 1933, [v], 17, 635—653).—Negative ions are not produced when the discharge is passed through pure Hg vapour. Negative ions with e/m of the order of that of Hg ions are produced when a trace of H_2 is admitted to the discharge tube, and these are probably HgH^- ions. A. J. M.

Production and behaviour of negatively-charged metallic particles in electrical discharges. K. Sommermeyer (Physikal. Z., 1933, 34, 582—589).—The conditions under which a transport of negatively-charged metallic particles formed by vaporisation or sputtering in the neighbourhood of the cathode in a discharge tube containing the inert gases takes place towards the anode are investigated. Where the vaporisation or sputtering was rapid, the metal followed the lines of force. The explanation of this is discussed. Ions of at. or mol. size may be formed, but probably the particles are larger.
A. J. M.

Radiation from canal-ray impact. F. L. Verwiebe (Physical Rev., 1933, [ii], 44, 15—19).—The beam from a metal target on which H canal rays impinged contained at. H, neutral particles, and protons. A radiation of wave-length 1216 Å., agreeing with that of the first Lyman line, was detected.
N. M. B.

Conditions for the occurrence of the Ramsauer effect. W. Voss (Z. Physik, 1933, 83, 581—618).—Theoretical. A. B. D. C.

Determinations of effective cross-sections of gas molecules. H. L. Bröse (Ann. Physik, 1933, [v], 17, 816—820).—The principal differences between the methods of Townsend and Ramsauer for determining the effective cross-section of gas mols. are discussed. A. J. M.

Quantum mechanical cross-section for ionisation of helium by electron impact. W. W. Wetzel (Physical Rev., 1933, [ii], 44, 25—30).—Mathematical. Results indicate that the max. probability of ionisation occurs when the energy transfer is about 3·5 volts > the ionisation potential.
N. M. B.

Revision of the at. wt. of thallium. Analysis of thallous chloride. G. P. Baxter and J. S. Thomas (J. Amer. Chem. Soc., 1933, 55, 2384—2387).—From determinations of the ratio TlCl : Ag, the at. wt. of Tl is 204·40. J. G. A. G.

At. wt. of lead from Katanga pitchblende. G. P. Baxter and C. M. Alter (J. Amer. Chem. Soc., 1933, 55, 2785—2792).—Full details are given of work previously reported (cf. this vol., 659).
J. G. A. G.

Isotopes. F. W. Aston (Science, 1933, 78, 5—6).—A lecture. L. S. T.

Arrangement of at. nuclei and the prediction of isotopes. S. B. L. Mather (J. Amer. Chem. Soc., 1933, 55, 3053—3056).—The existence of a no. of isotopes is predicted by means of Gamow's classification of at. nuclei. J. G. A. G.

Radioactivity of some rare-earth elements. W. Yeh (Compt. rend., 1933, 197, 142—143; cf. this vol., 4, 442).—Examination of the oxalates of La, Nd, and Sm by means of a Geiger–Müller counter indicated slight emission (1/15th that of Sm) of α-particles by Nd, but complete absence of activity in La. C. A. S.

Radium solutions. A. Becker (Z. Physik, 1933, 83, 701—710).—Ra in solution gives a const. emission of its emanation over 18 years (cf. A., 1922, ii, 810); the effect of sulphates and carbonates on this emission has been determined. A. B. D. C.

Investigation of wave radiation from radium-*D* by the Wilson chamber method. G. F. von D. zu Vischering (Z. Physik, 1933, **84**, 17—41).—Secondary electrons due to γ-rays were investigated in a Wilson chamber, and the ranges of these electrons were used to determine the energy of the rays. A. B. D. C.

Diminution of velocity of α-particles in hydrogen. G. Mano (Compt. rend., 1933, **197**, 47—49; cf. A., 1932, 671).—The velocities of slower α-particles from Th-*C*+*C'* after passage through lengths varying up to 12 cm. of H_2 at n.t.p. have been determined. The results agree with those deduced from Bethe's formula as corrected by Bloch (cf. A., 1930, 972; Ann. Physik, 1933, **16**, 285), if the mean energy of excitation be taken as 16·0 volts. C. A. S.

Retardation of α-particles. G. Mano (Compt. rend., 1933, **197**, 319—322; cf. A., 1928, 104; 1930, 659; also above).—Experimental results regarding retardation and the vals. of *E*, the mean energy of excitation of the atom, deduced therefrom, are compared with the results of Bethe's and Bloch's theories (cf. A., 1932, 789; this vol., 443). Bethe's theory applies to elements of low, Bloch's to those of high, at. wt. C. A. S.

Proton emission by excitation of the boron nucleus by α-rays. H. Pose and F. Heidenreich (Naturwiss., 1933, **21**, 516—517).—The determinations of Bothe and Fränz, who investigated the no. of H particles liberated from B with a Geiger–Müller tube, were repeated using an electrometer. Absorption curves for protons released by α-rays of range 3·72, 2·67, and 2·32 cm., respectively, agree with those of Bothe and Fränz. A. J. M.

Collisions of α-particles with fluorine nuclei. N. Feather (Proc. Roy. Soc., 1933, **A**, **141**, 194—209).—Stereoscopic photographs have been taken of the tracks of nearly $0{\cdot}5\times10^6$ α-particles in a CF_4–He mixture. No proton disintegration was obtained. The range–velocity curve for F recoil atoms has been constructed, and less complete data establishing the range–velocity relation for C recoil atoms have been obtained. L. L. B.

Photographic method of determining absorption of β-rays. (Mlle.) R. Macaigne (Compt. rend., 1933, **196**, 1993—1995).—The absorption by Al of β-rays from Ra-*D*+*E* determined photographically agrees with that determined by an ionisation chamber and supports the val. 16·9 for μ/ρ of Al for β-rays from Ra-*E* (cf. A., 1927, 915). C. A. S.

β-Ray magnetic spectrum of Ac-*B*+*C*+*C'*+*C''*. T. Graf (Compt. rend., 1933, **197**, 238—241; cf. this vol., 4).—The *HR* (referred to that of Th-*B* as 1382·6) energies, origins, intensities, and energies of the γ-radiation have been determined for eight new lines with *HR* and origins: 767·10, L_2; 857·60, M_1; 879·55, N_1; 2245·3, *K*; 2301·3, N_1; 2548·1, L_1; 2597·0, M_1, and 3796·0, *K*. The max. *HR* for the β-rays of Ac-*C''* is 6000 (cf. A., 1930, 8). C. A. S.

Emission of positive electrons by γ-rays of Ra-*B*+*C*. Grinberg (Compt. rend., 1933, **197**, 318—319).—γ-Rays from Ra, filtered through 3·5 cm. Pb, falling on 2 mm. thick Pb gave rise to four positive electrons (energies 0·089, 0·38, 0·38, and 0·62 $\times10^6$ ev.) for 129 negative electrons (max. energy 1·7 $\times10^6$ ev.). These results agree with those of Curie and Joliot (cf. this vol., 658). C. A. S.

Scattering of short-wave γ-rays. L. Meitner and H. Kösters (Z. Physik, 1933, **84**, 137—144).—A study of the undisplaced component of radiation of wave-length 4·7 X scattered by the nuclei of Fe and Pb. A. B. D. C.

Transmutation of elements by protons. M. L. E. Oliphant and (Lord) Rutherford (Proc. Roy. Soc., 1933, **A**, **141**, 259—281).—An apparatus is described by means of which the disintegration of such active elements as Li and B may be examined at low voltages (20,000—200,000 volts) and in the form of very thin films. Li gave particles at 30 kv. with protons bombarding the target, whilst the effect from B was negligible below 60 kv. Very thin films of Li and B were studied, as well as thick films. Mol. H_2 ions gave particles at about twice the energy required for protons, and the yield increased at twice the rate as the energy increased. Fe, O, Na, Al, N, Au, Pb, Bi, Tl, U, and Th gave no observable effect when bombarded with protons or mol. ions at energies up to 200 kv. Be and F gave small effects. The disintegration of the B^{11} nucleus by proton capture is discussed. L. L. B.

Complexity of the proton and mass of the neutron. (Mme.) I. Curie and F. Joliot (Compt. rend., 1933, **197**, 237—238; cf. this vol., 762).—It is suggested that the emission by Al and B under the influence of α-particles of protons, neutrons, and positive electrons may be simultaneous, and that the proton, π, may consist of a neutron, ω, and a positive electron, ε^+, associated together with condensation of mass. The transmutation of $B^{10}+\alpha$ would then be to $C^{13}+\omega+\varepsilon^+$ and to $C^{13}+\pi$ simultaneously; whence is deduced the val. 1·011 (He=4) as the mass of ω, instead of 1·0065 (cf. A., 1932, 790). This val. agrees better with 9·011 for Be^9 (cf. this vol., 442), indicating that Be^9 consists of $2\alpha+\omega$; also with 8×10^6 ev. as the energy of the neutron from Po+Be, and with the emission of low-energy neutrons by Po+Al and Po+Na, although not on the present val. of the mass of Li^7, with that of those from Po+Li. C. A. S.

Emission of neutrons. (Mme.) I. Curie and F. Joliot (J. Phys. Radium, 1933, [vii], **4**, 278—286).—Under bombardment by Po α-radiation, F, Na, and Al emitted neutrons and probably γ-radiation; the emission of neutrons by these nuclei, which are known to emit protons also, shows that a nucleus can undergo two types of transmutation by α-rays. For H, C, O_2, N_2, P, and Ca no penetrating radiation was detected. Resonance energies of the α-radiation corresponding with the emission of neutrons are: Be $2{\cdot}6\times10^6$, and B $2{\cdot}2\times10^6$ ev.; emission of neutrons from Li begins at 5×10^6 and of γ-rays at 3×10^6 ev. N. M. B.

Positrons and atomic nuclei. G. W. Todd (Nature, 1933, **132**, 65).—Evidence against the view (this vol., 658) that the proton consists of a neutron and positron is advanced. L. S. T.

Cosmic radiation measurements with a new tube-counter. L. Tuwim (Compt. rend., 1933, **197**, 79—81; cf. *ibid.*, **196**, 350).—The advantage of the new tube-counter is that it distinguishes between the actions of cosmic rays on different elements, and facilitates counting collisions. The nos. of collisions per c.c. per sec. for air and H_2 are, respectively, 3·3 and 0·42 unprotected, and 2·4 and 0·33 behind 10 cm. of Pb. The ratio of the nos. for air and H_2 indicates that the action of cosmic rays on matter consists of two distinct effects: ionisation affecting the extra-nuclear electrons, and absorption affecting the nucleus. Of 10^8 collisions between cosmic particles and mols. of air only 1 is nuclear (cf. this vol., 551). C. A. S.

Very soft radiation from insulators. G. Reboul (Compt. rend., 1933, **196**, 1987—1989; cf. A., 1932, 672).—The loss of electrification by insulating material, *e.g.*, resin, paraffin, etc., electrified by friction is accompanied by emission of very soft radiation capable of affecting a photographic plate after prolonged exposure, due perhaps to electric discharges at the surface, or to re-establishment of the electronic equilibrium of the insulating material. C. A. S.

Electricity released from matter. K. K. Darrow (Science, 1933, **77**, 591—595).—A lecture. L. S. T.

Electron theory of metallic conduction. J. C. Slater (Science, 1933, **77**, 595—597).—A lecture. L. S. T.

Most probable values of *e*, *e*/*m*, and *h*. II. K. Shiba (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1933, **21**, 128—137; cf. A., 1932, 1187).—The most probable vals. of these consts. are recalc. taking into account the most recent determinations, including the determination of abs. wave-length of *X*-rays (Witmer and Cork), *e*/*m* by Dunnington, and experiments with photo-electrons by Kretschmar. The most probable vals. are: $e=(4{\cdot}804\pm0{\cdot}003)\times10^{-10}$ e.s.u., $e/m=(1{\cdot}7602\pm0{\cdot}0005)\times10^{7}$ c.g.s./e.m.u., $h=(6{\cdot}626\pm0{\cdot}006)\times10^{-27}$ erg/sec. A. J. M.

Wave equation of electrons in the general relativity theory. L. Infeld and B. L. van der Waerden (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1933, No. 9, 25 pp.). A. J. M.

Comparison of the nuclear theories of Heisenberg and Wigner. I. C. Eckart (Physical Rev., 1933, [ii], **44**, 109—111; cf. this vol., 334).—Mathematical. N. M. B.

Magnetic interaction of a valency electron with inner shells. M. H. Johnson, jun., and G. Breit (Physical Rev., 1933, [ii], **44**, 77—83).—Mathematical. N. M. B.

Passage of photons through atoms. V. Trkal and F. Zaviska (J. Phys. Radium, 1933, [vii], **4**, 269—277; cf. Posejpal, A., 1932, 1187).—Polemical. N. M. B.

Does the negative energy spectrum influence nuclear phenomena? G. Beck (Z. Physik, 1933, **83**, 498—511).—Dirac's wave equation and the resulting negative energy levels are applied qualitatively to Klein's paradox, collisions, and the continuous β-ray spectrum. A. B. D. C.

Statistics of diatomic gases. K. Széll (Z. Physik, 1933, **84**, 112—119).—Fermi–Dirac and Bose–Einstein statistics are applied to the rotation of a rigid diat. mol. A. B. D. C.

Spectrographic examination of radiation from resistance cells. G. Déchêne (Compt. rend., 1933, **196**, 1989—1991).—The radiation emitted at an electrode when a high-tension current is passed through a semi-conducting substance, *e.g.*, yellow HgO or effloresced Na_2CO_3 (cf. A., 1926, 1072), consists usually of a band at 50—170 Å. sometimes extending to 10—200 Å., and occasionally a narrow band at about 20 Å., with a diffuse one at 250—700 Å. C. A. S.

Absorption of metallic and colloidal silver. P. Maréchal (Compt. rend., 1933, **196**, 1984—1985).—The absorptions for λ 2600—3730 Å. of metallic Ag cathodically sputtered and of colloidal Ag are identical for equal thicknesses of metal. The light traversing the colloidal solution therefore passes through and not between the metallic particles. C. A. S.

Structure and Zeeman effect of the CO_2 emission doublet band at 2900 Å. R. Schmid (Z. Physik, 1933, **83**, 711—738). A. B. D. C.

Position of absorption bands of coloured alkali halide crystals. J. H. de Boer and W. de Groot (Z. Physik, 1933, **83**, 517—520).—Fröhlich's theoretically deduced relation of frequency of absorption max. and grating const. (this vol., 446) applies to excited states of the coloured lattice, whereas Mollwo's apparently equiv. empirical relation (A., 1932, 673) applies to absorption by alkali atoms bound to vacant spaces within the crystal. A. B. D. C.

Intensity distribution in the spectrum of beryllium oxide. R. C. Johnson and E. G. Dunstan (Phil. Mag., 1933, [vii], **16**, 472—478).—Microphotometer peak intensity measurements were made for the $'\Sigma \longrightarrow {}'\Sigma$ system of BeO, and the transition probabilities were calc. H. J. E.

Infra-red arc spectra of manganese and rhenium. W. F. Meggers (Bur. Stand. J. Res., 1933, **10**, 757—769).—Using new type ultra-sensitive plates for the region 7200—11,000 Å. data are recorded for about 200 lines of Mn and 300 lines of Re. New lines disclose new spectral terms or at. energy levels. Lines of both spectra show hyperfine structure. N. M. B.

Absorption spectrum of sulphur dioxide in ultra-violet. A. Jonescu (Compt. rend., 1933, **197**, 35—37).—Some 500 absorption bands of SO_2 to about 2500 Å. have been examined and a formula for their frequencies is deduced. Their relation to the states of activation of the mol. and its predissociation and dissociation, and the heats thereof, are discussed (cf. A., 1932, 1075; this vol., 660). C. A. S.

Example of the influence of the nature of chemical linkings on absorption of light. J. P. Mathieu (Bull. Soc. chim., 1933, [iv], **53**, 426—429).—The absorption spectrum of a tartaric acid solution of $Cr(OH)_3$ shows a change from the normal heteropolar compound to a complex homopolar compound. This view is confirmed by comparison of the absorption curves of the heteropolar $CrCl_3,6H_2O$ and the homopolar $H_3Cr(C_2O_4)_3$. E. S. H.

Ultra-violet absorption of binary liquid mixtures. II. System allylthiocarbimide–piperidine in ethyl alcohol. R. Kremann and R. Riebl (Z. physikal. Chem., 1933, **165**, 372—378; cf. this vol., 207).—The extinction at the max. of the ultra-violet absorption band of allylthiocarbimide, at which wave-length the absorption of $C_5H_{10}N$ is negligible, is a max. for an equimol. mixture, which is ascribed to the formation of an equimol. compound. R. C.

[Ultra-violet] absorption of certain classes of organic molecules. D. Biquard (Ann. Chim., 1933, [x], **20**, 97—151).—Absorption has been measured from 2780 to 2300 Å. The absorptions of inactive diphenylsuccinic acid and of its Et ester are > those of the stereoisomeric racemic compounds. There is no definite difference between the absorptions of the racemic and active forms of phenyl- and benzyl-lactic acids and their Me esters. The absorption spectra of the H sulphite and cyanohydrin of $CH_2Ph{\cdot}CHO$ and of $Ph{\cdot}[CH_2]_2{\cdot}CHO$ are the same as that of PhMe, the ·CHO band being absent. The spectra of the acids $Ph{\cdot}[CH_2]_n{\cdot}CH(OH){\cdot}CO_2H$ become progressively closer to that of PhMe as n increases from 0 to 2. *α-Hydroxy-β-phenylbutyric acid*, m.p. 121—122°, is formed by treatment of $CHPhMe{\cdot}CH(OH){\cdot}SO_3Na$ with KCN followed by hydrolysis with HCl. A. G.

Absorption and fluorescence spectra of the acid sulphates of quinine and ten of its derivatives in water and aq. sulphuric acid solution. L. J. Heidt and G. A. Forbes (J. Amer. Chem. Soc., 1933, **55**, 2701—2709; cf. this vol., 792).—Absorption spectra are recorded for the range 480—220 mμ. As the size of the group attached to position 6 of the quinoline nucleus of cinchonidine, cinchonine, hydrocupreine, optochin, eucupine, and vuzin increases, the absorption max. are broadened and shifted towards the red. A similar effect occurs when the *sec.*-OH at position 4 of quinine is replaced by CO (quinicine) or by CO_2H (quininic acid). The fluorescence spectra excited by λ 366 mμ in aq. or 0·9*M*-H_2SO_4 solutions have no fine structure and are substantially identical. The results are correlated with the photochemical reduction of chromate in the presence of these alkaloids. J. G. A. G.

Change of light absorption and refraction in the formation of artificial resin masses. J. H. de Boer, R. Houwink, and J. F. H. Custers (Rec. trav. chim., 1933, **52**, 709—718).—Polystyrene (I) absorbs less light than monostyrene and the bands are displaced in the direction of shorter wave-length. The absorption curve of (I) is in accordance with an alkylbenzene structure. The absorption curve of CH_2O–PhOH resin is typical of a phenol; on condensation the whole curve is displaced towards the red end to an extent agreeing with a substitution of Me in PhOH. Polymerisation of styrene is accompanied by a decrease in mol. refraction, but mol. refraction increases during the condensation of CH_2O with PhOH or $C_6H_4Me{\cdot}OH$. The increase of refraction and the displacement towards the red are related quantitatively. E. S. H.

Photographic–photometric method of measuring absorption by solutions in the visible. F. W. Beyer (Z. Physik, 1933, **83**, 806—813).—The method described was used to determine the absorption spectra of $[Co(NH_3)_6]Cl_3$ and $[Co\ 3\ en]Cl_3$. A. B. D. C.

Absorption in the ultra-violet of some β-arylacrylic acids and their derivatives. (Mlle.) R. M. da Costa.—See this vol., 822.

Absorption spectra of *m*-bromophenol-indophenol, 2 : 6-dibromophenol-indophenol, and guaiacol-indophenol. M. M. Brooks (J. Amer. Chem. Soc., 1933, **55**, 2434—2435).—Extinction coeffs. for 0·0001*M* solutions at p_H 11·7 are recorded for the range 510—680 mμ. J. G. A. G.

Infra-red spectrum of carbon dioxide. II. A. Adel and D. M. Dennison (Physical Rev., 1933, [ii], **44**, 99—104; cf. this vol., 661).—Mathematical. Consideration of the interaction between the vibration and rotation of the CO_2 mol. leads to the complete potential function for CO_2. N. M. B.

Infra-red absorption spectrum of pyridine and of some of its derivatives. I. Spectrum from about 0·80 to about 2·5 μ of pyridine and of some of its homologues. L. Passerini (Gazzetta, 1933, **63**, 305—319).—The absorption spectra of C_5H_5N, α- and β-picoline, αα′-lutidine, and collidine have been determined for λ 0·80—2·5 μ. The principal bands of C_5H_5N are also given by its homologues, with similar intensity, but the positions of the max. differ slightly. O. J. W.

Infra-red absorption spectra of organic compounds containing two chromophores. P. Lambert and J. Lecomte (Compt. rend., 1933, **197**, 234—235; cf. A., 1932, 55).—The absorption spectra between λ=6 and 16 μ have been examined of 17 compounds $A{\cdot}[CH_2]_n{\cdot}B$, where A is Ph and B is Ph or CO_2Et, or A=B=OPh, and n=0—10. The spectra when $n=0$ differ entirely from those when $n=1$, and both from those for $n > 1$. These last show substantial but smaller progressive differences, and the spectrum of $Ph{\cdot}[CH_2]_3{\cdot}CO_2Et$ only distantly resembles that of an equimol. mixture of PhEt and EtOAc. These differences from the results in the ultra-violet are due to absorption in the infra-red of the CH_2 group and of C chains. C. A. S.

Intensity relations in the Raman spectrum of hydrogen. II. S. Bhagavantum (Indian J. Physics, 1933, **7**, 549—559; cf. this vol., 548).—All the rotation lines in the Raman spectrum of H_2 gas are depolarised to the same extent, $\rho=0{\cdot}85\pm0{\cdot}05$. The relative intensities are in agreement with theory. The discrepancy with theory in the relative intensities of the *Q* and *R* branches of the vibration scattering is confirmed, and also, contrary to theory, it is found that the line arising from mols. in zero rotation state in the *Q* branch is depolarised to some extent. J. W. S.

Two new Raman lines of water. M. Magat (Compt. rend., 1933, **196**, 1981—1983).—Using Hg light filtered through a solution of Victoria-blue, the following observations of a band which would include Ellis' hypothetical 510 cm.$^{-1}$ (cf. A., 1931, 1211) were made: in H_2O 396—796 (with 4358 Å.), and 465—766 (with 2537 Å.), in aq. $Ca(NO_3)_2$+LiCl 350—740, and in aq. $MgCl_2$ 350—785 (cf. A., 1932, 983). This band is perhaps due to a forbidden frequency of the H_2O mol. On this basis a revised interpretation of these bands is given (cf. this vol., 445). A new band was found at 152—225 cm.$^{-1}$, corresponding with 600 g.-cal. per mol. C. A. S.

Comparative intensity measurements on Raman lines of inorganic complexes. I. Hansen-Damaschun (Z. physikal. Chem., 1933, **B**, **22**, 97—113).—The results show that the linking is very similar in SO_4'', ClO_4', CO_3'', and NO_3' and approximates to the homopolar type, whilst the complexes $[Zn,6NH_3]^{\cdot\cdot}$ and $[Cd,6NH_3]^{\cdot\cdot}$ are far removed from the homopolar type of linking. R. C.

Raman spectrum of calcium nitrate. E. Bauer, M. Magat, and A. da Silveira (Compt. rend., 1933, **197**, 313—315; cf. A., 1932, 983).—The ratios of the intensities of the Raman lines 720 and 740 cm.$^{-1}$ of NO_3' have been determined for various concns. of $Ca(NO_3)_2$ without and with addition of LiCl. The results do not support Grassmann's theory (cf. A., 1932, 1075). C. A. S.

Raman effect of some complex cyanides. R. Samuel and M. J. Kahn (Z. Physik, 1933, **84**, 87—91).—Raman effect due to complex cyanides of Cr, Co, Ni, Ru, and Rh was observed. Those with co-ordination no. 6 gave two frequencies, corresponding with the C–N vibration and with the vibration of this group and the central atom; the second was absent from complexes with other co-ordination nos. The C–N frequency appears to increase with the homopolarity of the linking. A. B. D. C.

Raman spectra of iodides. II. Ethyl, propyl, and *iso*butyl iodides. N. G. Pai (Indian J. Physics, 1933, **7**, 519—529; cf. A., 1932, 1189).—A no. of new Raman frequencies are reported for these compounds and are compared with infra-red absorption data. J. W. S.

Raman spectrum of some heterocyclic organic compounds. I. M. Milone and G. Müller (Gazzetta, 1933, **63**, 334—338).—The Raman spectra of dimethyl- and methylethyl-furazan and of dimethyloxdiazole have been determined. They show lines characteristic of the groups CH, CH_2, C·C, C⋮N, and N·N. O. J. W.

Raman spectra of pinene, thiophen, salol, and thymol. S. Venkateswaran and S. Bhagavantam (Indian J. Physics, 1933, **7**, 585—593).—The frequencies observed and the extent of their depolarisation are given in tabular form, and are discussed in relation to the results with analogous compounds. J. W. S.

Raman spectrum of pyrrole and some derivatives. G. B. Bonino, R. Manzoni-Ansidei, and P. Pratesi (Z. physikal. Chem., 1933, **B**, **22**, 21—44).—The Raman spectra of pyrrole, *N*-acetylpyrrole, 2-methylpyrrole, opsopyrrole, kryptopyrrole, 2 : 4-dimethyl-3-propylpyrrole, and 2-methylpyrrolidine have been examined. A model of the pyrrole mol. is discussed. R. C.

[Raman effect and] acetylenic linking: Δ^{β}-acetylenes. (Mlle.) B. Gredy (Compt. rend., 1933, **197**, 327—328; cf. this vol., 553).—The Raman spectra of CMe⋮CR (R=Me, Et, Pr^{α}, and Bu^{α}) all show the pair of lines near 2236 and 2304 cm.$^{-1}$ (2238 and 2316 for R=Me, 2235—2238 and 2303—2304 for the others), and the two lines near 376 (373—380) and 1381 (1380—1383). Δ^{β}-*Heptinene*, b.p. 111·5—112·5°, is obtained in 70% yield by the action of Me_2SO_4 on Na-hexinene (cf. A., 1888, 929). C. A. S.

Raman spectra of oximes. G. B. Bonino and R. Manzoni-Ansidei (Z. physikal. Chem., 1933, **B**, **22**, 169—180).—The frequency 1630 cm.$^{-1}$ is assigned to the C⋮N linking. The results support the usual structural formula for the oximes and the formula with the semipolar double linking for the Na salts of the aromatic oximes. R. C.

Fluorescence of sulphur dioxide. W. Lotmar (Z. Physik, 1933, **83**, 765—785).—Powerful fluorescence is produced by Zn 2100 Å. line. Quenching and the effect of foreign gases indicate that the life period of the mol. thus excited is shortened by the presence of a predissociation limit. Observed bands are given in a term scheme. A. B. D. C.

Extinction of fluorescence in solutions by organic substances. J. Eisenbrand (Z. physikal. Chem., 1933, **B**, **22**, 145—168; cf. A., 1932, 1188, 1189).—The extinction of the fluorescence of quinine sulphate in MeOH solutions containing H_2SO_4 has been studied. Since the dihydric phenols have effectively the same extinguishing power as their ethers, theories of extinction depending on the reducing properties of the phenols (*ibid.*, 578) are untenable. Hydrocarbons containing incompletely saturated conjugated double linkings have extinguishing power; hydrocarbons with completely saturated conjugated double linkings, *e.g.*, C_6H_6, or with only a single double linking have none. Introduction into C_6H_6 of such substituents as impair the saturation of the conjugated system, *e.g.*, Me, OH, OMe, confers extinguishing power. There is no simple relation between extinguishing power and optical absorption, dipole moment, mol. refractivity, or ionic charge of the foreign substance, but in general a hydrocarbon exhibiting exaltation of mol. refraction has extinguishing power. The principal part in such extinctions as the above is probably played by the particularly loosely held electron associated with unsaturated conjugated double linkings. R. C.

Efficiency of the chemiluminescence accompanying oxidation of Grignard compounds. C. D. Thomas and R. T. Dufford (J. Opt. Soc. Amer., 1933, **23**, 251—255).—Heats of oxidation for 11 aliphatic and 5 aromatic Grignard compounds, and total luminous efficiencies of chemiluminescence for MgPhBr, *p*-C_6H_4Me·MgBr, *p*-C_6H_4Br·MgBr, and *p*-C_6H_4Cl·MgBr are given. N. M. B.

Phosphorescence of solid nitrogen and its relation to crystal structure. L. Vegard (Science, 1933, **77**, 588—589).—A summary. L. S. T.

Bands in the thermoluminescence spectrum of fluorite from Obira, Japan. E. Iwase (Nature, 1933, **131**, 909—910). L. S. T.

Fluorescence of solutions and gases. A. Boutaric and J. Bouchard (J. Phys. Radium, 1933, [vii], **4**, 324—332).—Mathematical. N. M. B.

Emission from oxide-coated cathodes. II. M. Benjamin and H. P. Rooksby (Phil. Mag., 1933, [vii], **16**, 519—525; cf. this vol., 446).—Emission from a simple mixture of BaO and SrO is governed by that from each oxide separately. Solid solutions of the oxides give increased emission. The emission–composition curve has an optimum val. H. J. E.

Thermal and photo-electric emission of cæsium–cæsium oxide cathodes and the influence of cæsium atoms in the dielectric. J. H. de Boer and M. C. Teves (Z. Physik, 1933, **83**, 521—533).—Emission is increased by the presence of Cs atoms in the oxide layer, due to readier transmission of the electrons. A. B. D. C.

Theory of thermo-electric cells consisting of combinations of semi-conductors. C. Wagner (Z. physikal. Chem., 1933, **B**, **22**, 195—198).—From the sign of the thermo-e.m.f. of a cell consisting of two pieces of the same material with different electronic conductivities, *e.g.*, Cu_2O at 1000° in equilibrium with different O_2 pressures, it can be decided whether electron excess or electronic deficiency conduction predominates (cf. this vol., 888). R. C.

Thermal and voltaic potential of cuprous oxide. G. Mönch and S. Stechhöfer (Z. Physik, 1933, **84**, 59—64).—E.m.f. due to unequally tempered ends of Cu_2O amounted to 0·1 volt, and that due to a temp. difference of 100° to 0·4 volt. A. B. D. C.

Internal photo-electric absorption in halide crystals. R. W. Gurney (Proc. Roy. Soc., 1933, **A**, **141**, 209—215).—Theoretical. In the quantum-mechanical model of an insulating crystal, bands of electron levels are separated by wide zones of disallowed energies. Throughout an imperfect crystal are distributed numerous submicroscopic cracks, on and near the surfaces of which are localised levels with energies lying in the disallowed zones. Various inter-related phenomena are discussed in terms of transitions between the allowed electron levels. L. L. B.

Crystal photo-effect with photo-electric conducting sodium chloride. S. Pelz (Naturwiss., 1933, **21**, 517).—If a crystal of NaCl coloured yellow by exposure to Ra is illuminated over half its surface, a current flows without the application of an external field, the phenomenon being similar to that observed with cuprite and galena. If the crystal is intensively illuminated a secondary effect occurs. The primary effect occurs also with coloured KCl, and although not previously observed, the possibility of its occurrence has been demonstrated theoretically by Fowler. A. J. M.

Photo-electric effects of crystals of argentite, proustite, and pyrargyrite. G. Athanasiu (Compt. rend., 1933, **197**, 42—44).—On inserting a crystal of argentite in a circuit and illuminating the contact with one electrode a negative e.m.f. is observed with light of λ 0·5—1·4 μ, max. for 1·15 μ. Proustite and pyrargyrite with a Pt electrode give a positive current, max. for 0·58 and $< 0{\cdot}45\ \mu$, and 0·62—0·65 and $< 0{\cdot}45\ \mu$, respectively, but sometimes negative with a Cu electrode for red light; an auxiliary current of 0·6 volt is required to reverse the effect. In all cases the $\lambda\lambda$ of the light giving max. e.m.f. are those giving max. conductivity at low temp. (—110° to —137°) (cf. A., 1920, ii, 212; 1924, ii, 82). C. A. S.

Electrical conductivity of zinc and cadmium oxides. H. H. von Baumbach and C. Wagner (Z. physikal. Chem., 1933, **B**, **22**, 199—211).—The conductivity, κ, of a rod of ignited ZnO or CdO at about 450—650° decreases at any given temp. with increasing O_2 pressure, p, according to $\kappa = kp^{-1/n}$, where k and n are consts. For ZnO in H_2O–H_2 mixtures and CdO in Cd vapour κ is abnormally great. The suggested explanation of these observations is the presence in the oxide phase of an excess of metal, varying regularly with p and probably consisting of cations in lattice interstices and excess electrons. Thermo-e.m.f. measurements indicate that the conductivity of the ZnO is of the electron excess type. R. C.

Misplacement phenomena in cuprous oxide and their effect on electrical properties. H. Dünwald and C. Wagner (Z. physikal. Chem., 1933, **B**, **22**, 212—225; cf. A., 1931, 793).—The sp. conductivity of Cu_2O at 800—1000° is approx. proportional to $p^{1/7}$, where p is the O_2 pressure in the gas phase, which is qualitatively explained by the assumption that the transport of electrons occurs mainly by electron deficiency conduction (cf. Wagner, this vol., 888), a theory confirmed by thermo-e.m.f. measurements at various O_2 pressures. The share of $Cu^{\cdot}$ ions in the conduction at 1000° is about 4×10^{-4}. The variation of the excess of O in the Cu_2O above the stoicheiometric ratio with p and temp. has been measured. Assuming that in the Cu_2O lattice there are electron deficiency centres and empty places in the $Cu^{\cdot}$ partial lattice, the experimental observations at 800—1000° are explained. The diffusion coeff. for the formation of a film of Cu_2O on Cu in $O_2/<100$ mm. at 1000° has been calc. R. C.

Electrical conductivity of cupric oxide. H. H. von Baumbach, H. Dünwald, and C. Wagner (Z. physikal. Chem., 1933, **B**, **22**, 226—230).—The conductivity of compact CuO at 600—1000° increases only very slightly with the partial pressure of O_2 in the gas atm., and is practically entirely electronic. The interpretation is that the misplacements in the lattice consist of equiv. nos. of $Cu^{\cdot\cdot\cdot}$ ions and electrons, $Cu^{\cdot\cdot} \rightleftharpoons Cu^{\cdot\cdot\cdot} + \ominus$. Burnt rods of finely-divided CuO behave anomalously in conductivity. R. C.

Electronic properties of conductors and insulators. R. H. Fowler (Proc. Roy. Soc., 1933, **A**, **141**, 56—71).—A crit. survey of current views on the nature of cryst. insulators and their electronic properties. Tamm's theory of surface levels on an insulator is analysed, and the view that the existence of these surface levels in cryst. insulators is one fundamental reason for their insulating properties is abandoned. L. L. B.

Theory of ordered mixed phases. III. Misplacement phenomena in polar compounds as the basis of ionic and electronic conduction. C. Wagner (Z. physikal. Chem., 1933, **B, 22**, 181—194; cf. A., 1931, 1223).—Electronic conduction in semiconductors may depend either on the presence of effectively free electrons, corresponding with the classical electron gas theory ("electron excess conduction"), or on the presence of electron deficiency centres, *i.e.*, lattice constituents which have lost some of their normal complement of electrons and are therefore able to participate in exchange of bound electrons ("electron deficiency conduction"). The deviation from the stoicheiometric composition often gives the concn. of misplacements in the lattice, and therefore determines conduction. With predominant electronic conduction, the conductivity decreases with increasing partial pressure, *p*, of the electronegative lattice component if the conduction is of the electron excess type, and increases if it is of the electron deficiency type, whilst it is independent of *p* if free electron and electron deficiency centres are present in equiv. amounts. With cationic conduction predominating, the concn. of interstitial cations is equiv. to that of empty places in the cation partial lattice, and similarly for predominating anionic conduction. R. C.

Influence of surface charge on conductivity measurements of insulators. A. D. Goldhammer (Z. Physik, 1933, 84, 212—217). A. B. D. C.

Dependence of dipole moment on solvent, infra-red terms, and linking moments. O. Fuchs and H. L. Donle (Z. physikal. Chem., 1933, **B, 22**, 1—20).—The principal errors in the determination of dipole moment by the method of dil. solutions are the effect of the solvent and the uncertainty of the infra-red terms. The measured moment is always influenced by the solvent, particularly with mols. containing polar groups which can rotate towards each other, but by a suitable choice of solvent its effect may be rendered negligible. From an examination of data for the infra-red terms of the displacement polarisation of various dipole-free aromatic mols. it has been possible to calculate the vals. for various simple polar C_6H_6 derivatives more accurately than hitherto, and thus recalculate the dipole moments. A review of linking moments shows that exact data are still lacking. The dipole moments of various ketones have been redetermined. R. C.

Composition of electric moments of polyalcohols: moments of associated dipoles. P. Girard and P. Abadie (Compt. rend., 1933, **197**, 146—148).—The statical dielectric const., ε_1, is proportional to *c*, the no. of dipoles per unit vol., *d*, and γ, the polarisability of the mol., *i.e.* $=Acd\gamma$, where *A* is a const.; $\gamma=\gamma'+\gamma''$, where γ' is the induced polarisability and negligible compared with $\gamma''(=\mu^2/3kT)$, the permanent polarisability (μ is the permanent moment of the dipole, *k* Boltzmann's const., and *T* the abs. temp.). As ε_1 and *d* for the polyalcohols considered are practically const., $c\mu^2$ is so also if *T* is; or if μ_1 is the elementary moment due to one alcohol function ($=1{\cdot}6\times10^{-18}$ e.s.u.), $\mu=\mu_1\sqrt{n}$, *n* being the no. of alcohol functions, and *c* varies as *n*. These conclusions are verified for (figures are vals. of ε_1 at the temp. noted): glycol 37·6, 20°; glycerol 40, 20°; 32·5, 80°, 26·6, 120°; 22, 170°; erythritol 28·2, 120°; xylitol 40, 20°; sorbitol 33·5, 80°; mannitol 24·6, 170°; glucoheptitol 27·4, 120°; and glucoheptulitol 27·1, 120°. C. A. S.

Relation between dipole moment and cohesion forces. II, III. A. E. van Arkel and J. L. Snoek (Rec. trav. chim., 1933, **52**, 719—732, 733—741; cf. A., 1932, 983).—II. Theoretical. The influence of Debye's attraction term on the relative b.p. of simple aliphatic halogen and nitro-derivatives is discussed. From the properties of CCl_3Me, CCl_2Me_2, $CClMe_3$, and $CCl_3{\cdot}NO_2$ a lower limit 3·2 Å. is deduced for the at. diameter of Cl, whilst the val. obtained from salts is 3·6 Å. Debye's formula does not lead to a satisfactory derivation of dipole moment from b.-p. data for mols. which deviate widely from the spherical form; better agreement is obtained by introducing a form factor. Qual. agreement is obtained in the isomeric groups cyanide–carbylamine and nitro–nitrite. With mols. showing association, such as alcohols, acids, and amines, the moments are probably peripheral, so that the dipoles of such mols. approach each other closely.

III. The former theoretical considerations are applied to numerous derivatives of C_2H_6, C_3H_8, C_5H_5N, diazine, thiophen, and $C_{10}H_8$. E. S. H.

Free rotation and the electrical moments of diacetyl, acetylacetone, acetic anhydride, and ethyl acetate. C. T. Zahn (Physikal. Z., 1933, **34**, 570—574).—Ac_2 shows a much smaller moment (1·25—1·48) than it would have if there were complete rotation (3·2). Moreover, it is dependent on temp., which indicates either completely free rotation, or complete hindrance. The *trans*-position is taken up. With CH_2Ac_2 there was no temp. effect. The tautomerism of this compound is discussed, and vals. for the moments of the different forms are calc. The experimental val. (3·0) makes the compound a mixture of the diketone and the enol form. In the case of Ac_2O there was no dependence on temp. The mol. can be the ordinary free mol. or the linked form, there being little difference in the calc. vals. of the moments of the two forms. Similarly, EtOAc can also be either the free mol. or the linked form. It is clear that strong intermol. forces exist between groupings, and that this is not confined to mols. containing double linkings. The hindrance may be due simply to the electrostatic action of the polarised atoms. A. J. M.

Dipole moments of *p*-chloro- and *p*-bromophenol. M. A. G. Rau (Physikal. Z., 1933, **34**, 575).—The method used by Williams and by Donle (this vol., 448) in evaluating the dipole moments of these compounds is subject to error, giving rise to the differences between their vals. The method of Hedestrand (A., 1929, 647) applied to their data yields results agreeing with each other. The vals. of dielectric const. and density of both observers plotted against concn. give linear curves, showing the absence of association in the concn. range used. A. J. M.

Dielectric constants of some organic liquids. S. Sugden (J.C.S., 1933, 768—776).—A simple resonance method of measuring dielectric consts. of liquids is described. Errors due to the form of the cell and consts. of the circuit are discussed and evaluated. The following vals. are obtained for the dielectric const. at 25°: C_6H_6, 2·272 ± 0·001; PhCl, 5·612 ± 0·006; $[CH_2Cl]_2$ 10·36 ± 0·02; COPhMe, 17·39 ± 0·02; PhCN, 25·19 ± 0·04, $PhNO_2$, 34·75 ± 0·07. No variation of the dielectric const. with frequency is found over the range 60—1500 kilocycles per sec. J. W. S.

Refractive power of some gaseous fluorides. W. Klemm and P. Henkel (Z. anorg. Chem., 1933, **213**, 115—125).—Vals. of n for BF_3, CF_4, SiF_4, GeF_4, SF_6, SeF_6, and TeF_6 were measured interferometrically for wave-lengths 5876 and 5461 Å. The mol. refractions for 5876 Å. were calc. The position of the absorption bands of each compound was calc. from its dispersion curve. All lie in the far ultra-violet. H. J. E.

Double refraction of oriented surface layers. A. M. Taylor and A. King (Nature, 1933, **132**, 64).—Evidence of the double refraction of the interfacial layer between melted normal fatty acids and glass has been obtained. The birefringence is small, usually < 0·0001, and exists for a few degrees of temp. just above the f.p. of the acid. The mols. of acid are thus oriented at a glass–liquid interface to a depth comparable with a wave-length of visible light. The sharpness with which birefringence disappears at a crit. temp. may indicate that the anisotropic layer is a new phase and that the fatty acid behaves as a liquid crystal immediately above its m.p. L. S. T.

Optical rotatory power. IV. Rotatory dispersion of bornyl and menthyl xanthates, especially in the region of absorption. T. M. Lowry and H. Hudson (Phil. Trans., 1933, **A**, **232**, 117—154).—The series of xanthates studied show two absorption bands, one at about 3600 Å. being attributed to the ·CS·S· group, and a stronger about 2800 Å., to the :CS group. A new equation has been developed to which both conform closely. The circular dichroism is of opposite signs in the two bands, and in the first follows a similar course to the absorption. In the region of transparency the anomalous rotatory dispersion can be expressed with exactness by two terms of Drude's equation, and a new equation has been devised to represent that in the absorption region. F. L. U.

Rotatory power of active dilactamide. P. Vièles (Compt. rend., 1933, **197**, 40—42).—The rotatory dispersion of *l*-dilactamide (cf. A., 1932, 253) between λ 5893 and 4047 Å. (given by a single Drude term), and the variation of the power with temp. (linear between 10° and 32·75°) and concn. (parabolic), have been determined. The two latter are mutually independent. Measurements with mixtures of *d*- and *l*-dilactamide indicate non-existence of a racemic compound in solution. C. A. S.

Nature and space extension of scattering moments for optically active molecules. W. Kuhn and K. Bein (Naturwiss., 1933, **21**, 529).—Theoretical. A. J. M.

Optical and thermodynamic activity of camphorsulphonic acid in solutions of neutral salts. C. Drucker (Z. physikal. Chem., 1933, **165**, 411—419).—The effect of alkali salts, $BaCl_2$, and $La(NO_3)_3$ on the optical rotation, activity coeff., f, conductivity, and f.-p. depression of the acid in aq. solution has been examined. The mol. rotation is depressed by salts in varying degree, the decrease for NaCl alone being almost proportional to the salt concn., c. f increases with, but much more rapidly than, c. R. C.

Rotatory dispersion of organic compounds. XXI. Cyclic derivatives of tartaric and malic acids. B. Jones (J.C.S., 1933, 788—796).—The rotatory dispersions of *Me*, m.p. 74°, and Et benzylidenetartrate, dibenzylidenetartrate, *acetylmalic anhydride*, m.p. 58°, and Et β′β′β′-trichloro-α′-hydroxyethyl-α-anhydrotartrate have been studied for solutions in EtOH, $COMe_2$, and Ac_2O, and for the wave-length range 6708—4358 Å. Measurements with the first two compounds were extended to 3239 Å. It is concluded that although ring formation tends to simplify the dispersion, the anomalies disappear completely only when free rotation is inhibited. J. W. S.

Magnetic-optic minima of organic compounds. J. L. McGhee and M. Lawrenz (J. Amer. Chem. Soc., 1933, **55**, 2614—2615; cf. A., 1930, 1541).—For each of the homologous series alkyl bromides, alkyl acetates, and alcohols, the scale readings for the min. increase with increasing wt. of alkyl. The scale readings decrease for the fatty acids. J. G. A. G.

Magnetic birefringence in liquid mixtures. S. W. Chinchalkar (Indian J. Physics, 1933, **7**, 491—518).—The deviation of the magnetic birefringence in liquid mixtures from theoretically calc. vals. has been investigated. The results are correlated with the existing data on the variation of magnetic birefringence with temp., the variation of mol. optical anisotropy with temp., and optical anisotropy in the vapour and liquid phases. It is suggested that the variation in the effective optical anisotropy of the mols. with dilution is at least one, and probably the main, cause of the deviations observed. J. W. S.

Abnormal electric and magnetic birefringence. R. Lucas and M. Schwob (J. Phys. Radium, 1933, [vii], **4**, 287—300).—Anomalies of change of sign of birefringence under the influence of solvents or of temp. effect contrary to theory were shown by camphor, fenchone, and Et phenylsuccinate. Results are explained by the theory of mol. polymorphism. N. M. B.

Electrical Kerr effect and association in liquids. I. Kerr effect in liquids and solutions and its dependence on temperature. II. Orientation in liquids and its influence on molecular refraction, molecular polarisation, degree of depolarisation due to molecular light scattering, and on the Kerr effect. H. A. Stuart and H. Volkmann (Z. Physik, 1933, **83**, 444—460, 461—482).—I. An abs. method was used to determine the temp. variation of the Kerr const. of C_6H_6, C_7H_{14}, and CCl_4, and the concn. variation of the molar Kerr const. of solutions of $PhNO_2$ in these liquids. The results disagree with the Langevin–Born theory even for dil. solutions on account of orientation within the liquid.

II. The phenomena were investigated for non-dipole liquids, and show that deviations due to orientation of the mols. occur when the density of the mols. is so large that disordered orientation of the mol. axes is unlikely. A. B. D. C.

Molecular structure of polyalcohols deduced from their dispersion and absorption for radio frequencies : molecular association. P. Girard and P. Abadie (Compt. rend., 1933, 196, 1995—1997; cf. A., 1932, 899).—Absorption and dispersion curves for λ 20—5000 cm. for glycerol (at 25° and 37°) and sorbitol (at 80°) compared with the corresponding curves deduced from the vals. of the at. radius, *a* (depending on the expression $4\pi\eta a_3/3kT$ for the time of relaxation), that give the nearest similar curves, indicate in glycerol two kinds of dipoles, simple and associated 2 and 2, united laterally, probably all becoming simple at 50°, and in sorbitol simple mols. and mols. associated 2 and 2, 3 and 3, and perhaps 4 and 4. $[CH_2{\cdot}OH]_2$ and xylitol at 20° show respectively slight and strong association. It is shown that the time of relaxation decreases proportionally to the no. of elementary dipoles in the mol. of a polyalcohol, which implies the probability of a cylindrical or an ellipsoidal shape for such a mol. C. A. S.

Structure of crystallised platinocyanides. H. Brasseur (Compt. rend., 1933, 196, 2015—2017).—Pauling has shown that the CN groups (regarded as units) in the platinocyanides are in one plane with the Pt. From a comparison of the optical properties of the platinocyanides with those of cyanuric triazide (cf. this vol., 559) and Wooster's deductions as to the connexion between double refraction and structure (cf. A., 1932, 10) it is concluded that the line joining the C and N atoms in each CN group is perpendicular to the above plane. C. A. S.

Determination of molecular structure by means of electron diffraction. VI—VIII. Ethyl chloride, bromide, and iodide. L. Brú (Anal. Fís. Quím., 1933, 31, 115—121).—The distances between the C and Cl, C and Br, and C and I atoms are $1{\cdot}81 \pm 0{\cdot}08$, $2{\cdot}02 \pm 0{\cdot}07$, and $2{\cdot}32 \pm 0{\cdot}04$ Å., respectively. H. F. G.

Constitutional factors controlling phototropic changes in carbonyl compounds. V. Relationship between the polar characters of substituent groups and the activation energies of proton addition. W. S. Nathan and H. B. Watson (J.C.S., 1933, 890—895; cf. this vol., 505).—A quant. relationship exists between the critical increment of the reaction of oxonium ion with $COMe{\cdot}C_6H_4X$ and the dipole moment of PhX. The relationship applies also to new data for the speed of phototropic change of substituted ω-chloroacetophenones. Almost identical connexion is observed between the dipole moment of MeX and the difference in the crit. increments of dissociation and association of the acid $CH_2X{\cdot}CO_2H$. These relationships indicate the absence of electromeric displacements in the cases considered. J. W. S.

Free radicals of organic radicals. Quantum-theoretical contributions to the problem of aromatic and unsaturated compounds. IV. E. Hückel (Z. Physik, 1933, 83, 632—668).—Free radicals with C^{III} and N^{II} occur only with aromatic and unsaturated substituents of these atoms; this is due to the four C valencies assuming the tetrahedral directions in the mol., and their assuming three directions oriented at 120° in a plane together with a free valency normal to the plane (*i.e.*, a single electron proper function with this plane as a node exists containing one electron, a $[p]_h$-electron) in the radical; the $[p]_h$-electron for these radicals can give resonance with similar electrons in the neighbouring C atoms, and the corresponding gain in energy gives a small resultant energy of dissociation. Transition from one structure to the dissociated structure is discussed from the point of view of energy of activation. Finally, the discrepancy between an equilibrium const. for the gas phase and that observed for solutions is shown to be due to change in phase vol. of the solvent due to dissociation of the solute (cf. A., 1931, 1000; Pauling and Wheland, J. Chem. Physics, 1933, 1, 362). A. B. D. C.

Diamagnetic susceptibility of the hydrogen molecule. K. Honda and T. Hirone (Z. Physik, 1933, 84, 208—211).—Paramagnetism of diat. mols. due to thermal rotation gives a susceptibility independent of temp., and the sum of this for H_2 and Van Vleck's diamagnetic susceptibility gives good agreement with the observed susceptibility. A. B. D. C.

Electric polarisability and diamagnetic susceptibility of molecules. S. Bhagavantam (Indian J. Physics, 1933, 7, 617—621).—Vinti's relation (A., 1932, 1191) is tentatively applied to simple mols., using Van Vleck's formula for diamagnetic susceptibility. The results are discussed. J. W. S.

Variation of the magnetic properties of barium with temperature. C. T. Lane (Physical Rev., 1933, [ii], 44, 43—45).—The susceptibility–temp. curve for a range of 400° showed a discontinuity at 350°, similar to that occurring at the Curie point in ferromagnetics, and supporting evidence for α and β modifications as given by the resistivity–temp. curve. N. M. B.

Magnetic properties of artificially anisotropic substances. W. König (Ann. Physik, 1933, [v], 17, 736—746).—The susceptibilities of solutions of $MnCl_2$, $MnSO_4$, $CoSO_4$, $MgSO_4$, and $NiSO_4$ in gelatin, moulded into cylindrical form and under definite deformations, were determined. A. J. M.

Magnetic properties of celloidin, agar-agar, and celluloid under artificial anisotropy. K. Weisel (Ann. Physik, 1933, [v], 17, 747—754; cf. preceding abstract).—Celloidin and agar-agar were found unsuitable. The susceptibility of celluloid plates under various deformations was determined. A. J. M.

Paramagnetism and chemical linking. E. Rabinowitsch (Z. Elektrochem., 1933, 39, 702—715).—A review.

Photometric determination of *X*-ray quality. W. H. Love (J. Cancer Res. Comm. Sydney, 1933, 5, 11—15).—The evaluation of the relative energy associated with the various wave-lengths, and the determination of the wave-length–energy curve, are described. N. M. B.

Determinations of the signs of the Fourier terms in complete crystal structure analysis. K. Banerjee (Proc. Roy. Soc., 1933, A, 141, 188—193).—Mathematical. It is shown that the signs of the Fourier terms can be found with the help of the equations developed by Ott (A., 1928, 821). The method is used to find the signs of the terms S_{00l} of anthracene crystal, for the different vals. of l. L. L. B.

Quartz as a standard for accurate lattice-spacing measurements. A. J. Bradley and A. H. Jay (Proc. Physical Soc., 1933, 45, 507—522).—With Cu $K\alpha$ radiation, sharp and accurately measurable $K\alpha$ doublets were obtained. Determination of the axial ratio from an X-ray powder photograph gave c/a 1·10002$\pm$0·00004, whence $a=$ 4902·9 and $c=$5393·3X. Data for quartz from different sources are given. N. M. B.

Origin, first appearance, and growth of crystal nuclei: influence of H. F. current. D. Samuracas (Z. Krist., 1933, 85, 474—478; cf. A., 1932, 567).—An over-cooled molten (*e.g.*, salol) or a supersaturated solution of a substance [*e.g.*, aq. $Pb(NO_3)_2$] is cooled slowly from θ to θ' in time t, and then suddenly to θ'', the temp. being so adjusted that the sudden fall renders visible the nuclei formed by the slow cooling. With θ and θ'' const. the no. of nuclei increases with $\theta-\theta'$. Each nucleus is surrounded by a "crystallisation field" in which more nuclei tend to appear. With t, θ, θ'' const. the time before nuclei become visible increases with θ'. High-frequency current increases the no. but decreases the size of the nuclei, which arrange themselves along the lines of force. C. A. S.

The $\alpha \rightleftharpoons \beta$ transformation of calcium. F. Ebert, H. Hartmann, and H. Peisker (Z. anorg. Chem., 1933, 213, 126—128; cf. Rinck, A., 1931, 416).—X-Ray photographs show that face-centred cubic α-Ca is transformed reversibly at 450° into hexagonal β-Ca (a 3·98, c 6·52 Å.; $c:a=1·639$; 2 atoms of Ca in unit cell). This explains the observed change in reactivity of Ca with N_2 at this temp. H. J. E.

Structural peculiarities of bismuth and antimony. A. Schulze (Z. physikal. Chem., 1933, 165, 188—194; cf. this vol., 116).—The electrical resistance–temp. curve of polycryst. Sb is discontinuous at 105—110°. This anomaly seems to be due, not to polymorphic transformation, of which X-ray examination gives no indication, but to mechanical deformation, for it is absent with single crystals of Sb or polycryst. Sb which has been heated at 600° and slowly cooled. Dilatometric measurements gave similar results. R. C.

Modifications of phosphorus pentoxide. K. Boratyński (Rocz. Chem., 1933, 13, 340—345).—Commercial P_2O_5, d 2·288, consists of cryst. (I), d 2·284, amorphous (II), d 2·207, and vitreous, d 2·382—2·422, modifications. 50% yields of (I) are obtained by sublimation at 300°/760 mm., and 80% at 250°/15 mm. (I) readily dissolves in H_2O, whilst (II) imbibes H_2O and forms a gel, the velocity of dissolution of which is proportional to the temp. R. T.

***X*-Ray study of modifications of phosphorus pentoxide.** A. Nowakowski (Rocz. Chem., 1933, 13, 346—350).—X-Ray spectra of commercial P_2O_5 indicate that this consists chiefly of the cryst. modification, part of which is converted into vitreous non-volatile P_2O_5 during sublimation, as is shown by the diminished anisotropy of the product. R. T.

Perfection of crystal laminæ. W. N. Bond (Phil. Mag., 1933, [vii], 16, 410—422).—By examining the banded spectrum of white light reflected from mica laminæ 0·01 mm. thick, the latter were found to be uniform in thickness to 8×10^{-8} cm. H. J. E.

Crystallisation of ingots. R. G. Heggie (Trans. Faraday Soc., 1933, 29, 707—721).—Experiments with stearic acid show that equiaxial crystallisation is promoted by slow cooling and by motion of the melt. Under still conditions, equiaxial crystallisation of solid solutions is possible only below a crit. rate of cooling dependent on the temp. of freezing range. For a pure substance (*e.g.*, Sn) this is zero, so that only columnar crystallisation can occur. Matuschka's theory of a dynamic heat balance (B., 1931, 1012) is upheld. J. S. A.

Evidence for the cybotactic group view of the interior of a liquid. G. W. Stewart (Indian J. Physics, 1933, 7, 603—615).—Fifteen different experimental results are quoted which support the cybotactic view of liquids, in which the latter are regarded as consisting of aggregates which crudely simulate cryst. orderliness and of mols. approx. at random. J. W. S.

Diffraction of *X*-rays by liquid sulphur. A. H. Blatchford (Proc. Physical Soc., 1933, 45, 493—500).—Data for the range 130—260° are given. Results indicate that the diffraction is due to an unstable grouping of S atoms becoming less pronounced with rise of temp. At 220° a sudden alteration corresponds with the change from the form S_λ to S_μ. N. M. B.

Crystal structure of borides of the type MB_6. F. Laves (Z. physikal. Chem., 1933, B, 22, 114—116).—An error in Stackelberg and Neumann's paper (this vol., 116) is corrected. The lattice of these borides consists of a three-dimensional structure of B atoms in the interstices of which are the metal atoms. R. C.

Crystallography of some compounds of gadolinium and samarium. A. Pabst (Amer. J. Sci., 1933, [v], 26, 72—79).—Crystals of $Gd(CO_2H)_3$, $Gd(OAc)_3,4H_2O$, $Gd(CO_2Et)_3,3H_2O$, $Gd(CO_2Pr^\alpha)_3,2H_2O$, $Sm(BrO_3)_3,9H_2O$, and $Gd(BrO_3)_3,9H_2O$ are described. C. W. G.

Correct setting of crystals. [Structure of methylammonium cuprichloride and dimethylammonium chlorostannate.] G. Greenwood (Z. Krist., 1933, 85, 420—424).—The selection as unit cell of that of which the angles are nearest right angles gives results in agreement with Fedorov's method. This is illustrated by *X*-ray examination of $(NH_3Me)_2CuCl_4$ d_4^{20} 1·719, unit cell *a* 7·30, *b* 7·535, *c* 18·55, containing 4 mols., and $(NH_2Me_2)_2SnCl_4$, with *a* 14·00, *b* 7·20, *c* 7·08, and 2 mols. (cf. A., 1902, i, 747). C. A. S.

Crystal structure of ammonium hydrogen fluoride. L. PAULING (Z. Krist., 1933, **85**, 380—391; cf. this vol., 13).—The unit cell of NH_4HF_2 has *a* 8·33, *b* 8·14, *c* 3·68 Å., and contains 4 mols., space-group V_h^7—*Pman*. Each N is attached to four F ions at a distance of 2·76 Å. by H linkings (cf. A., 1928, 690; 1932, 1191), the proton being probably nearer N than F; each F ion is attached to two N and one F ion, the F–H distance in the linear HF_2 group being 1·184 Å. C. A. S.

Crystal structure of cæsium, thallium, and rubidium perrhenates. F. M. JAEGER and J. BEINTEMA (Proc. K. Akad. Wetensch. Amsterdam, 1933, **36**, 523—528).—$RbReO_4$, like $KReO_4$ and $AgReO_4$ (A., 1930, 20), is tetragonal-bipyramidal in structure, $a_0 : c_0 = 1 : 2·2707$, whereas $CsReO_4$ and $TlReO_4$ are orthorhombic with a definite pseudo-tetragonal character, $a_0 : b_0 : c_0 = 0·961 : 1 : 2·3901$ and 0·970 : 1 : 2·2985, respectively. These results are compared with those for corresponding osmiamates (cf. this vol., 13). J. W. S.

Structure of sanidine and other felspars. W. H. TAYLOR (Z. Krist., 1933, **85**, 425—442; cf. A., 1929, 749).—Sanidine, *d* 2·57, *n* 1·52, $(KNa)AlSi_3O_8$, has *a* 8·4, *b* 12·9, *c* 7·1 Å., β 116°, with 4 mols. in the unit cell, space-group C_{2h}^3. A structure based on a framework of linked SiO_4 and AlO_4 tetrahedra is suggested, and the analogy to that of danburite illustrated (cf. A., 1931, 415). C. A. S.

***X*-Ray examination of garnet from the gorge of the Lieser near Spittal (Carinthia).** H. HERITSCH (Z. Krist., 1933, **85**, 392—403).—The garnet contains SiO_2 36·91, TiO_2 0·22, Al_2O_3 19·24, Fe_2O_3 5·04, FeO 19·58, MnO 0·42, MgO 1·93, CaO 16·61, corresponding with $(Ca,Mg,Fe^{II},Mn^{II})_3(Al,Fe^{III})_2Si_3O_{12}$; *d* 3·877, *n* 1·777. The unit cell has *a* 11·668 A., and contains 8 mols. The properties and structure agree with those calc. from Menzer's classification (cf. Z. Krist., 1928, **69**, 300), the garnet filling a gap between his grossular-andradite and almandine-pyrope. C. A. S.

***X*-Ray examination of bauxites and mullites.** M. E. NAHMIAS (Z. Krist., 1933, **85**, 355—369).—There is no stable cryst. compound of Al_2O_3 and SiO_2 between sillimanite (I) and mullite (II). For (II) the formula $3Al_2O_3,2SiO_2$ is proved by the fact that all excess of SiO_2 or Al_2O_3 beyond that formula appears as tridymite or corundum. Kaolinite at 450° passes into a mixture of γ-Al_2O_3 and amorphous SiO_2 (sometimes regarded as metakaolinite; cf. B., 1929, 172), which continues as such to 950°, when (II) begins to be formed, and is completely so at 1050°, with no formation of (I) at any stage. (I) and (II) are both rhombic with respectively *a* 7·52, *b* 7·65, *c* 5·78 Å., and *a* 7·52, *b* 7·65, *c* 2·89 Å., space-groups V^h_{16} and (perhaps) V_h^1, but the structure of (II) is doubtful; variations in (II) of different origins are perhaps due to the presence in solid solution of varying amounts of TiO_2 and Fe_2O_3. Eleven analyses of bauxites are given (cf. B., 1933, 147). C. A. S.

Crystal structure of nacrite. J. W. GRUNER (Z. Krist., 1933, **85**, 345—354).—Nacrite, $Al_2(OH)_2Si_2O_5$, is monoclinic hemihedral; the unit cell has *a* 5·16, *b* 8·93, *c* 28·60 Å., β 91° 43′, and contains 8 mols., $d_{calc.}$ 2·581, space-group C_s^4. The structure resembles that of dickite and kaolinite (cf. A., 1932, 987; this vol., 45), but each alternate layer is rotated through 180° relatively to its neighbours, thus explaining the different optical properties. Varying amounts of dickite were present in the specimens examined. C. A. S.

Crystal structure of the dihalides. J. M. BIJVOET [with NIEUWENKAMP] (Chem. Weekblad, 1933, **30**, 479—483).—Principally a review, with particular reference to the Cd and Hg halides. Sublimed $CdBr_2$ yields an *X*-ray diagram of similar type to that of $CdCl_2$, but when cryst. from aq. solutions and dehydrated at room temp. it yields a simpler diagram, which, however, reverts to the normal slowly at room temp. or more rapidly at 400°. H. F. G.

Crystal structure of hydrohalides of ephedrine and ψ-ephedrine. B. GOSSNER and H. NEFF (Z. Krist., 1933, **85**, 370—379).—The following are given for *d*, *a*, *b*, *c* (in Å.), β, no. of mols. in unit cell: *r*-ephedrine hydrochloride 1·231, 13·27, 7·04, 13·44, 118° 24′, 4; hydrobromide 1·444, 13·15, 7·11, 14·00, 119° 25′, 4; hydriodide 1·586, 13·40, 7·23, 14·70, 120° 24′, 4; *r*-ψ-ephedrine hydrochloride (I) 1·186, 24·48, 9·97, 18·58, 90°, 16; hydrobromide 1·403, 13·87, 6·80, 14·04, 116° 51′, ?; hydriodide 1·550, 13·49, 6·97, 14·62, 114° 26′, ? (cf. A., 1930, 470). All are monoclinic prismatic, space-group C_{2h}^5, except (I), which is rhombic dipyramidal, V_h^{15}. The bearing of the foregoing on mol. and crystal structure of racemic compounds is discussed. C. A. S.

Crystal structure of sugar derivatives. E. G. COX and T. H. GOODWIN (Z. Krist., 1933, **85**, 462—473; cf. A., 1932, 1192).—The following data are given: for *d*, *a*, *b*, *c* (in Å.), and no. of mols. in the unit cell: α-methyl-*d*-glucoside (cf. A., 1922, i, 128), 1·48, 11·21, 14·57, 5·29, 4; β-methyl-*d*-glucoside hemihydrate (I), 1·49, 7·32, 7·32, 33·6, 8; α-methyl-*l*-arabinoside, 1·47, 9·32, 16·92, 4·68, 4; β-methyl-*l*-arabinoside (II), 1·44, 16·56, 7·74, 5·89, 4; β-*d*-glucosan, 1·64, 6·65, 13·14, 7·46, 4; γ-monoacetylmethyl-*l*-rhamnoside (cf. A., 1932, 45), 1·41, 7·98, 18·25, 7·08, 4; *d*-chitosamine hydrochloride (III) (cf. A., 1932, 271), 1·55, 7·68, 9·18, 7·11, 2. Except (I), tetragonal trapezohedral, $P4_12_12$—D_4^4, and (III), monoclinic sphenoidal, $P2_1$—C_2^2, all are rhombic bisphenoidal, $P2_12_12_1$—Q^4. (II) also occurs in monoclinic crystals, $a : b : c = 1·154 : 1 : ?$, β 115·5° approx.; both forms crystallise together from EtOH. C. A. S.

Minute structure of cotton fibre. K. ATSUKI and M. ISHIWARA (J. Soc. Chem. Ind. Japan, 1933, **36**, 221B).—Microscopical examination of the swollen fibre and *X*-ray analysis show that the fibrils form right and left spirals at approx. 90° in the direction of the principal axis, whilst the micelles lie with their main axes perpendicular to the fibril axis.

A. A. L.

***X*-Ray investigation of proteins. II. Gelatin.** K. Hess and C. Trogus (Biochem. Z., 1933, 262, 131—136; cf. this vol., 731).—The fibres of unstretched sheet gelatin (I) have a high degree of orientation, the axis of the fibres being perpendicular to the plane of the sheet. (I) resembles cellophane and like products. An explanation of the change which occurs on stretching is given, and the *X*-ray diagram of (I) is compared with those of animal products (untwisted gut, isinglass, leather). The result of purification of the materials is considered.

W. McC.

***X*-Ray spectrum of fibrin.** J. R. Katz and A. de Rooy (Rec. trav. chim., 1933, 52, 742—746).—Fibrin is shown to have a cryst. structure. In the stretched material the polypeptide chains lie in the direction of the fibre. E. S. H.

Electrical properties of thin platinum films obtained by cathodic sputtering. A. Féry (Ann. Physique, 1933, [x], 19, 421—507).—Pt-black was deposited by a discharge in air freed from H_2O vapour, and the variation of resistivity as a function of thickness, determined optically and gravimetrically, was investigated between 10 and 1320 mμ. A crit. thickness is indicated at 240 mμ; beyond 285 mμ the resistivity passes to that of ordinary catalytic Pt. Divergent vals. in previous data appear to be due to heating of the Pt in the course of deposition.

N. M. B.

Electrical properties of thin platinum films obtained by cathodic sputtering in elementary gases. A. Féry (J. Phys. Radium, 1933, [vii], 4, 301—315; cf. preceding abstract).—For a discharge in He, O_2, N_2, and H_2, as opposed to air, the Pt films showed no uniform resistivity, and absorbed gas during their formation. On warming to any fixed temp., their resistance diminished isothermally; for higher temp. the surfaces are blistered by the emission of the absorbed gas. N. M. B.

Absence of a permeability anomaly for iron from the wave-length region between 84 and 1300 m. G. R. Wait (Z. Physik, 1933, 83, 786—788).—Polemical against Malov (A., 1932, 449), and reasserting the absence of this anomaly.

A. B. D. C.

Magnetic quadrupole field and energy in cubic and hexagonal crystals. L. W. McKeehan (Physical Rev., 1933, [ii], 44, 38—42; cf. this vol., 766, 767).—Mathematical. N. M. B.

Superconductivity and the Hall effect. E. H. Hall (Proc. Nat. Acad. Sci., 1933, 19, 619—623).—Evidence pointing to the non-existence of the Hall effect in the superconductive state of metals is critically reviewed. N. M. B.

Elastic constants of Rochelle salt by a dynamical method. R. M. Davies (Phil. Mag., 1933, [vii], 16, 97—124).—The elastic limit is a linear function of temp. from 0° to 20°, but there are discontinuities at about 23° and — 40°, corresponding with similar discontinuities observed with other physical properties. The results indicate that the substance is unsuitable for piezo-electric resonators in accurate work, but may be used where only moderate accuracy is required. A. J. M.

Effect of mechanical stress on the disruptive strength of dielectrics. A. Gemant and T. Akahira (Nature, 1933, 132, 99—100).—The increase of disruptive strength by compression and the decrease by dilatation obtained with various substances are described. L. S. T.

Plasticity of quartz. K. Zinserling and A. Schubnikov (Z. Krist., 1933, 75, 454—461; cf. A., 1932, 1080).—The twinning produced by pressure on various faces of a quartz crystal is described and deduced from the crystal structure. The elastic limit of quartz at 573° is about 1/15th that at room temp., but the twinning produced is similar. There are three varieties of plasticity characteristic of rock-salt, calcite, and quartz produced, respectively, by translation, twin-gliding, and with no visible displacement of the crystal particles. C. A. S.

Temperature dependence of Young's modulus for nickel. J. Zacharias (Physical Rev., 1933, [ii], 44, 116—122).—A new method of measurement between 30° and 400° is described, and applied to single crystals and hard-drawn, polycryst. commercial Ni. For annealed specimens up to 200° the decrease is 13%, followed by an increase of approx. 6% to the Curie point, and thence a linear decrease. For hard-drawn specimens and those quenched at 1100°, the min. is absent, the decrease being continuous to the Curie point, where the temp. coeff. changes abruptly. N. M. B.

Determination of mol. wt. of compounds dissolved in liquid ammonia at room temperature. A. I. Schattenstein and A. M. Monossohn (Z. physikal. Chem., 1933, 165, 147—153).—By means of a new type of differential manometer for the determination of v.p. of solutions in liquefied gases the mol. wts. of $CO(NH_2)_2$, fructose, quinhydrone, NH_4Cl, and NH_4NO_3 in liquid NH_3 at 10° have been determined with an estimated precision of 3%.

R. C.

Theory of anomalous magnetic and thermoelectric effects in metals. D. Blochinzev and L. Nordheim (Z. Physik, 1933, 84, 168—194).

Electrical resistance of palladium wires charged with hydrogen. II. Up to 470° and 140 kg. per sq. cm. H. Hagen and A. Sieverts (Z. physikal. Chem., 1933, 165, 1—10).—Results previously reported (this vol., 467) have been confirmed and amplified. With increase of the H_2 pressure at a given temp. Q passes through a max., Q', then through a very flat min., Q''. The pressures corresponding with both of these rise with the temp., and Q' and Q'' could not be located, with the pressures used, above 362° and 212°, respectively. Below 270° Q'' possibly corresponds with the upper concn. limit of the β-phase. R. C.

Thermal and electrical conductivities of several metals between —183° and 100°. W. G. Kannulink (Proc. Roy. Soc., 1933, A, 141, 159—168).—The electrical method previously used (cf. *ibid.*, 1931, A, **131**, 320) to determine the thermal and electrical conductivities of a metal wire has been extended to include observations between −183° and 100°. The wires studied were pure W (in monocrystal form), Mo, Ag, and Fe. L. L. B.

Determinations with the aid of liquid helium. XXII. Resistance of metals, alloys, and compounds. W. Meissner, H. Franz, and H. Westerhoff (Ann. Physik, 1933, [v], **17**, 593—619).—Pure Nb becomes superconducting (I) at 9·2° abs., a temp. $>$ that at which any other pure metal reaches that state. Pb–As alloys existing as heterogeneous mixtures become (I) at the temp. at which Pb does, if there is a continuous Pb path through the sample. Mo–C alloys with 42—58 at.-% C have the same transition point (8·5° abs.). A large no. of compounds with uniform cryst. structure (ε and γ structure), and selenides and tellurides are not (I) above 1·3° abs. A no. of arsenides and W bronzes are not (I). The superconductivity of NbO and SnO is probably due to a small amount of Nb and Sn, respectively. Some other oxides were not (I). CuS is the only sulphide which is (I). A. J. M.

Absorption coefficients of liquids for ultrasonic waves. P. Biquard (Compt. rend., 1933, **197**, 309—311; cf. A., 1932, 900).—An improved method of determining the coeff. of absorption of ultrasonic waves is described. Applied to 8 org. liquids, it gives results from 6 to $<$ 100 times experimental. The coeff. seems to vary as the square of the frequency. C. A. S.

Velocity of sound in gases in tubes. G. W. C. Kaye and G. G. Sherratt (Proc. Roy. Soc., 1933, A, **141**, 123—143).—The velocity of sound at 18° and 100° has been measured by the resonating tube method, using air, H_2, CO_2, SO_2, NH_3, and EtCl contained in glass, Cu, and C tubes of various diameters. Frequencies from 500 to 27,000 cycles per sec. were provided from a valve-oscillator circuit. For all the gases, the Helmholtz–Kirchhoff formula is quantitatively correct as regards the variation of tube velocity with radius and frequency. The formula does not, however, take account of the influence of the wall surface. In smooth tubes there is a reduction of about 10% in the theoretical val. of c, and in rough-walled tubes an increase of about 30%. L. L. B.

Thermal expansion of boron. E. Dupuy and L. Hackspill (Compt. rend., 1933, **197**, 229—230).—The coeff. of linear expansion of cryst. B (99·5% pure) between 20° and 750° is $8{\cdot}3 \times 10^{-6}$, without any anomalies. C. A. S.

Thermal expansion of zinc by the *X*-ray method. E. A. Owen and J. Iball (Phil. Mag., 1933, [vii], **16**, 479—488).—The mean coeff. of linear expansion parallel and perpendicular to the hexagonal axis was measured between 20° and 400°. In this temp. range Zn is hexagonal, no allotropic modifications existing. H. J. E.

F.p. of iridium. F. Henning and H. T. Wensel (Bur. Stand. J. Res., 1933, **10**, 809—821).—Direct and indirect measurements of the ratio of brightness for red light of a black body immersed in freezing Ir to that of a similar black body in freezing Au led to the val. 2454° for the f.p. of Ir. N. M. B.

Method of measuring the specific heats of poor conductors. W. G. Marley (Proc. Physical Soc., 1933, **45**, 591—601).—An improved form of the method of cooling is described and results for various substances are given. N. M. B.

Empirical molecular heat equations from spectroscopic data. W. D. M. Bryant (Ind. Eng. Chem., 1933, **25**, 820—823).—The mol. heats of 18 gases and vapours, calc. from spectroscopic vibration frequencies, agree closely with experimental vals. A group of 16 empirical second-power equations has been derived to fit the theoretical mol. heat curves from 300° to 2000° abs. The deviation is generally $<$ 3%. E. S. H.

Rotational specific heat of a polyatomic molecule for high temperatures. (Miss) E. Viney (Proc. Camb. Phil. Soc., 1933, **29**, 407).—A correction (cf. this vol., 206). N. M. B.

Some properties of pure H^2H^2O. G. N. Lewis and R. T. Macdonald (J. Amer. Chem. Soc., 1933, **55**, 3057—3059).—H_2O containing 99·99% of H^2H^2O, m.p. 3·8°, b.p. 101·42°/760 mm., d^{25} 1·1056, has been prepared. The temp. of max. d is 11·6° (approx.). V.-p. data are recorded. J. G. A. G.

Isopycnals of liquid helium. W. H. Keesom and (Miss) A. P. Keesom (Proc. K. Akad. Wetensch. Amsterdam, 1933, **36**, 482—487).—Isopycnals of liquid He have been measured between the saturated v.p. and 25 atm. and between 1·15° and 4·2° abs. The isopycnals comprise two branches which correspond with He II and He I, respectively, and which meet the λ-curve acutely, *i.e.*, $(\partial p/\partial T)_v$ is discontinuous at this point. As $(\partial p/\partial T)_v$ for liquid He II is negative over the whole region investigated, isentropic as well as isenthalpic expansion is associated with a rise of temp. The phenomenon of the existence of a temp. of max. density is more evident the higher is the pressure. J. W. S.

Comparison of the densities of carbon monoxide and oxygen and the at. wt. of carbon. M. Woodhead and R. Whytlaw-Gray (J.C.S., 1933, 846—854).—The relative densities of O_2 and CO have been measured by the buoyancy balance method (A., 1931, 890). It is concluded that 12·011 is a close approximation to the at. wt. of C on the chemical scale, vals. accepted hitherto being too low. This indicates that the proportion of C^{13} is 1%. These results are in accord with recent observations. J. W. S.

Vapour pressures of fumigants. V. αβ-Propylene dichloride. O. A. Nelson and H. D. Young (J. Amer. Chem. Soc., 1933, **55**, 2429—2431).—The v.p. in the range 15—100° is given by $\log P_{\text{mm.}} = 7{\cdot}7086 - 1782{\cdot}8/T$ (b.p. 96·4°/760 mm., and d^{20} 1·1545). J. G. A. G.

Thermal properties of halides. VII. Formation of polymerised molecules by halide vapours. W. Fischer. **VIII. Gas densities of BF_3, SiF_4, and GeF_4 at room temperature and near the b.p.** W. Fischer and W. Weidemann (Z. anorg. Chem., 1933, **213**, 97—105, 106—114; cf. this vol., 560).—VII. Polymerised mol. formation is correlated with mol. structure, the valency and electron structure of the cation, and with the lattice type of the solid halide.

VIII. Vals. at 20°, at $-34°$ (for GeF_4), and at $-75°$ (for BF_3 and SiF_4) are recorded. Double mol. formation was not observed. The densities of liquid BF_3 and GeF_4 were measured. H. J. E.

Vapour–liquid equilibria of hydrocarbons at high pressures. W. K. Lewis and C. D. Luke (Ind. Eng. Chem., 1933, **25**, 725—727).—Curves for the correction factor, μ, to the gas laws, applicable to hydrocarbons above C_3, are modified in minor details, and corresponding corrections have been made on the fugacity chart. A method of determining the volatility of high-b.p. hydrocarbons at high pressures is based on the volatility of C_6H_6 in N_2 at similar pressures. The correction factor for the internal energy of hydrocarbon vapours at low vapour vols. has been determined by graphical integration from the isometrics of those hydrocarbons for which data are available. The resulting corrections are relatively independent of the temp. C. E. M.

Entropy in intermediate phases. A. Ölander (Z. physikal. Chem., 1933, **165**, 65—78).—Theoretical. By comparison of the val. of the partial molal entropy of constituents of an intermediate phase, derived theoretically, with the val. deduced from data for temp. coeff. of e.m.f. it is possible to decide whether the lattice structure of the phase is ordered or not, and if it is ordered to determine the no. of "misplaced" atoms. Existing data are analysed in this way. R. C.

Van der Waals equation. H. M. Martin (Engineering, 1933, **136**, 1—2).—A criticism. The mol. forces are not gravitational, but are due to residual affinity. C. W. G.

Calculation of the second virial coefficient of gases. T. S. Wheeler (Indian J. Physics, 1933, 7, 595—601).—Mathematical. J. W. S.

Hydrodynamics and kinetic theory of gases: theory of surface tension. Y. Rocard (Compt. rend., 1933, **197**, 122—124; cf. this vol., 113, 503).—The formula deduced is $H=7{\cdot}32\sqrt{\lambda\sigma}(\rho_1-\rho_2)P_c(T_c-1{\cdot}03T)/\rho_cT_c$, where H is the surface tension, λ a numerical factor but little >1, σ the diam. of the mol., ρ_1, ρ_2 the density of the liquid and gas, T_c, ρ_c the critical temp. and density, respectively, and T a temp. not far removed from T_c. It applies accurately to substances with at most a weak dipole and approx. spherical mols., *e.g.*, Hg, O_2, Cl_2, C_6H_6, but shows differences up to 40% for elongated mols., or such as have a strong permanent dipole, *e.g.*, H_2O, alcohols. C. A. S.

Ellipsoidal viscosity distribution. W. S. Kimball (Phil. Mag., 1933, [vii], **16**, 1—49).—Mathematical. A. J. M.

Measurement of the viscosity of a molten metal by means of an oscillating disc. V. H. Stott (Proc. Physical Soc., 1933, **45**, 530—544).—The theory, corrections, and application to molten Sn of the method using a disc of Al_2O_3 are described. N. M. B.

Structure viscosity of dilute amalgams. R. Köhler (Kolloid-Z., 1933, 64, 200—205).—Structure viscosity has been observed in 0·3% Cu amalgam and in 0·5 and 1% Ag amalgams; the viscosity of the latter decreases with time. The results support the view that dil. amalgams are colloidally disperse systems. E. S. H.

***X*-Ray investigations of the gold–rhodium and silver–rhodium alloys.** R. W. Drier and H. L. Walker (Phil. Mag., 1933, [vii], **16**, 294—298).—The Au–Rh system shows two series of solutions. The contraction of the Au lattice and the expansion of the Rh lattice correspond with a solubility of Rh in Au of 4·1—8·9 at.-%, and a solubility of Au in Rh of 1·1—2·5 at.-%. Solubility of Ag in Rh, or vice versa, could not be detected, but theory suggests that they should be slightly sol. in one another. J. W. S.

***X*-Ray study on electrolytic nickel–iron alloys.** K. Iwasé and N. Nasu (Sci. Rep. Tôhoku, 1933, **22**, 328—337).—Fe–Ni alloys deposited from acid solutions of the mixed sulphates consist of solid solutions —pure α with up to 14% Ni, $\alpha+\gamma$ with 14—58% Ni, and pure γ with $>58\%$ Ni in the deposit. A. R. P.

Hall effect and other physical constants of alloys. I. Lead–bismuth alloys. W. R. Thomas and E. J. Evans (Phil. Mag., 1933, [vii], **16**, 329—353; cf. A., 1932, 330).—The electrical resistivities, temp. coeffs. of resistance, thermoelectric powers, densities, and Hall coeffs. have been measured, and the variation of these properties with composition is discussed. H. J. E.

Alloys of platinum with cobalt. V. A. Nemilov (Z. anorg. Chem., 1933, **213**, 283—291).—The system forms a continuous series of solid solutions with a minimum in the liquidus at 1468° and 25 at.-% Pt. The Brinell hardness curve of annealed alloys has maxima at 11·61 at.-% Pt (149) and 50·65 at.-% Pt (195) and a min. at 20·55 at.-% Pt (105); the hardness of alloys quenched from 1200° rises linearly from 111 with 5·15 at.-% Pt to 148 with 40·9 at.-% Pt. These differences are ascribed to a transformation in the nature of the solid solution and are accompanied by changes in the microstructure, the large polygonal grains of the high-temp. solid solution breaking up into smaller crystals on annealing at 900°. A. R. P.

Magnetostriction of nickel–cobalt alloys. Y. Masiyama (Sci. Rep. Tôhoku, 1933, **22**, 338—353). —Alloys with 0—30% Co undergo a longitudinal contraction in a magnetic field which reaches a max. at about 200 gauss and is the less the higher is the Co content. Alloys with $>30\%$ Co contract in low-strength fields and then expand in stronger fields, the initial contraction being smaller and the secondary expansion greater the higher is the Co content; with 40—70% Co the secondary expansion exceeds the initial contraction in fields of >400 gauss. The transverse effect of magnetostriction is the converse of the longitudinal effect, and the vol. effect is the difference of these two effects, being an expansion in alloys with $<75\%$ Co and a contraction in alloys with $>75\%$ Co. A. R. P.

Ferrosilicons. H. Delomenie (Compt. rend., 1933, **197**, 249—252).—Comparison of Si–Fe alloys prepared from pure materials in a ZrO_2 crucible (I) with the industrial product (II) shows that SiFe in (I) occurs in dendrites or granulations, but in (II) in large cryst. masses, due to slower cooling. As the % of Si increases, SiFe disappears and the alloy becomes eutectiform, resembling pearlite. At 50·14—53·5% Si the structure is that of a pure compound ($FeSi_2$) or a solid solution of Si therein, crystals of Si appearing above 54·5% Si. Alloys (I) containing 50% Si do not, as the same alloys (II), crumble in moist air, nor do they do so with small additions of either P or Al, but do so rapidly with evolution of PH_3 if both (0·03—0·04% P and 2—3° Al) are present. C. A. S.

Transformation of solid metallic phases. V. Calculation of kinetic curves for the system Au–Cu. U. Dehlinger (Z. Physik, 1933, **83**, 832—842).—The kinetic differential equation previously deduced (cf. A., 1932, 454) is integrated for the case of transition from disordered to ordered AuCu and $AuCu_3$. A. B. D. C.

M.p. of some binary and ternary copper-rich alloys containing phosphorus. W. E. Lindlief (Met. and Alloys, 1933, **4**, 85—88).—In the Cu–P system the eutectic occurs at 8·38% P and 714° and the liquidus of hypoeutectic alloys falls in a smooth curve very slightly concave to the composition axis. The eutectic temp. is raised by addition of 1% Si to 725°. In the Cu–Zn–P system a ternary eutectic is formed at 690° and 32·5% Zn and consists of α-solid solution, Cu_3P, and a Zn-rich phosphide of unknown composition. Tables and diagrams of the m.p. in the Cu–Zn–P and Cu–Si–P system are included. A. R. P.

Equilibrium diagram of copper–tin–phosphorus alloys. J. Verö (Z. anorg. Chem., 1933, **213**, 257—272).—The ternary system has been examined by thermal methods up to 20% Sn and 8·5% P; diagrams are given for const. P contents of 1, 2, and 3% and for const. Sn contents of 5, 10, 15, and 20%. With up to 5% Sn and 7% P the system is eutectiferous, the α-Cu_3P eutectic at 5% Sn containing about 6·5% P and melting at about 690°. With higher Sn contents a secondary peritectic reaction $\alpha+\text{liq.}\rightleftharpoons\beta$ is followed by the four-phase reaction $\alpha+\text{liq.}\rightleftharpoons\beta+Cu_3P$ at 637°; no evidence of the formation of a ternary eutectic has been found. The solid alloys contain, besides the usual Cu–Sn phases, only the Cu_3P phase, and the various transformation temp. in the Cu–Sn system remain unchanged on addition of P. On annealing eutectiferous alloys just below the eutectic temp., the Cu_3P constituent of the eutectic segregates as spheroidal particles evenly disseminated in the α-matrix. A. R. P.

Carbides of low tungsten and molybdenum steels. F. R. Morral, G. Phragmén, and A. Westgren (Nature, 1933, **132**, 61—62).—*X*-Ray analysis of residues obtained from W magnet steels confirms the presence of WC and Fe_3W_3C (A., 1930, 1503) and reveals that of a third *carbide* (I), probably Fe_4C (with a small amount of Fe replaced by W), lattice parameter 10·51 Å. (I) is also present in small amounts in high-speed steels, whilst in Fe–W–C alloys (II) low in W (2%) it appears to be the only carbide present. In (II) containing 1·5% W, (I) is mixed with cementite. It also occurs in low-Mo steels. A more correct formula is probably $(Fe,W)_4C$ or $(Fe,Mo)_4C$. L. S. T.

***X*-Ray studies of very complex mixtures of long-chain compounds.** E. Ott and D. A. Wilson (Science, 1933, **78**, 16—17; cf. this vol., 342).—In general, long-chain compounds of varied length and type form solid solutions. This is the case with mixtures of the normal C_{10}—C_{18}, the C_{13}—C_{18} alcohols, and the normal paraffins C_{19}, C_{24}, C_{32}, and C_{36} and other substances. L. S. T.

Ternary azeotropic mixtures. II. The heteroazeotrope: acetone–water–carbon disulphide. W. Swientosławski and L. Wajcenblit (Rocz. Chem., 1933, **13**, 318—321).—The heteroazeotrope, b.p. 38·042°, contains CS_2 75·21, $COMe_2$ 23·98, and H_2O 0·81%. R. T.

Curve passing through azeo- and heteroazeotropic points. T. Bylewski (Rocz. Chem., 1933, **13**, 322—333).—The composition of two-phase binary liquid mixtures can be determined with a mean error of $\ngtr 0·01\%$ by Swientosławski's ebullioscopic method. The composition of the vapour phase of the system $Bu^{\beta}OH$–H_2O at the b.p. under various pressures has been determined. The curve connecting azeo- and heteroazeo-tropic points of this system has a break at the point of intersection with the miscibility curve. R. T.

Variations in composition of binary azeotropic mixtures with change in temperature. I. Rabcewicz-Zubkowski (Rocz. Chem., 1933, **13**, 334—339).—In the case of binary azeotropic mixtures of an associated (I) and unassociated liquid, the content of (I) increases with rise of temp., whilst where both are associated the content of the more associated one increases. This rule does not apply to mixtures of H_2O and alcohols. R. T.

Coefficient of volatility of hydrogen chloride in ether. T. Mounajed (Compt. rend., 1933, **197**, 324; cf. this vol., 784).—The coeff. of volatility (cf. this vol., 16) of HCl in Et_2O has been determined for concn. 0·32—7·07M; it increases at first slowly, then rapidly, and then again slowly, which seems to support the theory of complex formation. C. A. S.

Vapour pressure of low-boiling paraffin hydrocarbons in absorber oil. G. L. Matheson and L. W. T. Cummings (Ind. Eng. Chem., 1933, **25**, 723—725).—A modified Calingaert–Hitchcock apparatus (A., 1927, 417) for determining vapour–liquid equilibria is described. All the low-boiling paraffins show a positive deviation from Raoult's law. The pressure deviations of the normal paraffins are found to be approx. the same at a given molal concn. and temp. C. E. M.

High-pressure rectification. II. *n*-Pentane–*n*-heptane system. L. W. T. Cummings, F. W. Stones, and M. A. Volante (Ind. Eng. Chem., 1933, **25**, 728—732).—V.-p. data for the mixtures are recorded and their application to high-pressure rectification is pointed out. C. E. M.

Vapour–liquid equilibria for *n*-hexane–benzene mixtures. C. O. Tongberg and F. Johnston (Ind. Eng. Chem., 1933, **25**, 733—735; cf. B., 1932, 826).—Pure n-C_6H_{14} has been obtained from petroleum by distillation and removal of C_6H_6 by nitration or by distillation with $Bu^{\gamma}OH$. The two hydrocarbons do not form a const.-boiling mixture; enrichment of the vapour practically ceases at concns. $< 3·5$ mols.-% C_6H_6. C. E. M.

Streaming double refraction of critical liquid mixtures. Wo. Ostwald and H. Erbring (Kolloid-Z., 1933, **64**, 229—232).—Streaming double refraction has been observed in crit. liquid mixtures of (*a*) hexane–MeOH, (*b*) CS_2–MeOH, and (*c*) $PhNO_2$–hexane. The effect is traced to deformation during the flow of drops which have low interfacial tension. E. S. H.

Miscibility of aromatic halogen compounds in solid state. L. Klemm, W. Klemm, and G. Schiemann (Z. physikal. Chem., 1933, **165**, 379—390).—Thermal diagrams for binary mixtures of hydrocarbons and their mono-chloro-, -bromo-, and -fluoro-compounds in several aromatic series have been determined in order to obtain information relative to the miscibilities in the solid state. Whilst in some cases the substitution products are all completely miscible with each other and with the parent hydrocarbon, the miscibility is sometimes only partial, and is markedly affected by the position of the halogen. According to the miscibility relations, there is less similarity between the hydrocarbon and its F-compound, and between the F- and Cl-compounds, than between the Cl- and Br-compounds, but the F-compounds appear to be typical halogen compounds in the series. R. C.

Solubility of lime in water and specific conductivities of its saturated solutions. A. D. Grieve, G. W. Gurd, and O. Maass (Canad. J. Res., 1933, **8**, 577—582).—Conductivity data (0—130°) and solubility data (determined conductimetrically) (0—25°) are recorded. The dissociation const. at various temp. is deduced. D. R. D.

Ammonium sulphite. I. Solubility and transition point. II. Equilibrium in the system ammonium sulphite–ammonium sulphate–water. F. Ishikawa and T. Murooka. **III. Equilibrium in the system SO_2–NH_3–H_2O.** F. Ishikawa and H. Hagisawa. **IV. Heat of dissolution of ammonium sulphite and hydrogen sulphite.** F. Ishikawa and T. Murooka (Sci. Rep. Tôhoku, 1933, **22**, 201—219, 220—234, 235—243, 244—248).—I. The solubility of $(NH_4)_2SO_3$ rises from 38·21 g. per 100 c.c. of solution at 0° to 74·88 g. at the transition point (80·8°±0·2); below this the monohydrate is stable and above, the anhyd. salt. The cryohydric point is −12·96° (28·85 g. per 100 c.c.).

II. The solubility of $(NH_4)_2SO_4$ is $41·22+0·09t$ g. per 100 c.c. at t°; the salt forms no double salt or solid solution with $(NH_4)_2SO_3$. The composition of solutions in the univariant system $(NH_4)_2SO_4$–$(NH_4)_2SO_3$–H_2O has been determined between −21·5° (cryohydric point) and 100°.

III. The solubility of $(NH_4)_2SO_3$ in aq. NH_3 at 25° is given by $C_1=39·45-1·346C_2$, where C_1 and C_2 represent g. $(NH_4)_2SO_3$ and NH_3 per 100 c.c. In solutions containing an excess of SO_2 the solid phase is $(NH_4)_2S_2O_5$ and not NH_4HSO_3.

IV. The heat of dissolution of $(NH_4)_2SO_3,H_2O$ is 4·66 and of $(NH_4)_2S_2O_5$ 5·84 kg.-cal. per mol. A. R. P.

Hydrates of cerium sulphate and the inverse fusion points. N. H. J. M. Voogd (Rec. trav. chim., 1933, **52**, 768—793).—The solubilities in H_2O of $Ce_2(SO_4)_3,8H_2O$ and $Ce_2(SO_4)_3,9H_2O$ between 0° and 45° have been determined. Koppel's observation (A., 1904, ii, 819), that the range of stability of the octahydrate is lower than that of the nonahydrate, is confirmed. E. S. H.

Solubilities of weak acids in salts of weak acids at very high concentrations. S. S. Doosaj and W. V. Bhagwat (J. Indian Chem. Soc., 1933, **10**, 225—232).—The solubilities of benzoic, salicylic, cinnamic, and succinic acids in Na formate, acetate, salicylate, citrate, benzoate, and chloride have been determined over a wide range of concn. The solubility of the acid generally increases with its strength, but is influenced also by the basicity. E. S. H.

Solubility of calcium oxalate in salt solutions. K. L. Maljarov and A. J. Gluschakov (Z. anal. Chem., 1933, **93**, 265—268).—Data for 0·3%—10% NH_4Cl, $(NH_4)_2SO_4$, NH_4NO_3, NaCl, $MgCl_2$, and $MgSO_4$ solutions are recorded. H. J. E.

Solubility of thiocarbamide in water, methyl alcohol, and ethyl alcohol. L. Shnidman (J. Physical Chem., 1933, **37**, 693—700).—Vals. are given for the interval 15—80° (H_2O) and 20—70° (MeOH and EtOH). F. L. U.

Hydrotropy. S. Forssman (Biochem. Z., 1933, **263**, 135—143; cf. von Brücke, A., 1932, 1288).—The solubilities (at 16—18° and 100°) of *iso*amyl and octyl alcohols, citronellol (I), *cyclo*hexanol, PhMe, $CH_2Ph·OH$, $PhNO_2$, NH_2Ph, $NHPh·NH_2$, cinnamaldehyde, quinoline, borneol (II), *dl*-fenchyl alcohol, cholesterol, caseinogen, quinine, cinchonine, brucine, gelatin, and human blood-serum in aq. solutions of K Ph_2 and K di-*o*-, *m*-, and *p*-tolyl phosphate have been examined. As regards dissolving power the isomerides form the series $o>m>p$. With (I) but not with (II) changes in $[\alpha]$ indicate the formation of loose additive compounds. W. McC.

Crystallisation. A. Schweizer (Rec. trav. chim., 1933, **52**, 678—700).—Supersaturated solutions of sucrose or tartaric acid cannot be made to crystallise except by inoculating with crystals or crystal nuclei. *d*-Mannitol, pyrogallol, quinol, resorcinol, and pyrocatechol form unstable supersaturated solutions, which crystallise with time. The viscosity of the solution has a considerable influence. Crystallisation nuclei are considered as dissolved mol. complexes, arranged according to the crystal lattice. E. S. H.

Coprecipitation. VI. Internal structural changes on ageing of freshly prepared precipitates. I. M. Kolthoff and E. B. Sandell (J. Physical Chem., 1933, **37**, 723—733; cf. this vol., 564).—Crystals of $KClO_4$ immersed in a saturated solution of $KClO_4$ in $0·1N$-$KMnO_4$ become coloured internally owing to penetration of $KMnO_4$ into submicroscopic cracks and faults in the crystals. Crystals of freshly pptd. CaC_2O_4 or $BaSO_4$ exhibit similar imperfections, in consequence of which the former has been shown to take up KIO_3 and the latter $KMnO_4$. Impurities thus occluded tend to escape by effusion on ageing, but are frequently retained by external blocking of the faults by lattice material. Impure crystals blocked in this way can be purified only by slow recrystallisation by way of the solution. Cryst. ppts. prepared at 100° are more homogeneous than those prepared at room temp. F. L. U.

Theory of Liesegang precipitates. H. BAUER (Kolloid-Z., 1933, 64, 181—184).—A mathematical treatment of the supersaturation theory. E. S. H.

Periodic Liesegang precipitation in non-colloidal media. R. FRICKE, J. LÜKE, and K. MEYRING (Z. Elektrochem., 1933, 39, 629—641).—By diffusion of HNO_3 into aq. $Ba(NO_3)_2$ in a capillary a periodic pptn. of $Ba(NO_3)_2$ was obtained. The capillary was then cut into sections 0·6—0·9 cm. long, and micro-determinations of Ba and HNO_3 were made for each. Beyond the last $Ba(NO_3)_2$ ppt. the liquid was supersaturated with respect to $Ba(NO_3)_2$, a new crystal zone forming when a max. supersaturation was exceeded. The effect of ageing on the concn. distribution was studied. Results are discussed in terms of the diffusion of $Ba^{\cdot\cdot}$ and HNO_3. H. J. E.

Distribution of methylamine between water and chloroform and existence of methylamine complexes of the metal-ammine type. W. A. FELSING and S. E. BUCKLEY (J. Physical Chem., 1933, 37, 779—786).—The distribution ratio of NH_2Me between H_2O and $CHCl_3$ decreases with increasing concn., but is const. for very dil. solutions. A complex of the ammine type is formed with $Cu^{\cdot\cdot}$, the ratio $NH_2Me/Cu^{\cdot\cdot}$ approaching 6 as a max. F. L. U.

Experimental evidence for activated adsorption of hydrogen by charcoal. R. BURSTEIN, A. FRUMKIN, and N. FEDOTOV (J. Amer. Chem. Soc., 1933, 55, 3052—3053).—H_2 adsorbed at 20—100° by activated C does not exchange with $Na^{\cdot}$, whereas H adsorbed in the temp. region of activated adsorption (300—800°) is readily replaced by $Na^{\cdot}$ from NaOH at room temp. In the latter case, if the quantity of adsorbed H is small, the whole is quantitatively exchanged, whereas only part is exchanged if the quantities are larger. Thus, the H adsorbed at high temp. remains on the C surface (probably in an at. form) and does not diffuse into the interior of the solid. J. G. A. G.

Activated adsorption. L. J. BURRAGE (Trans. Faraday Soc., 1933, 29, 677—678).—The experimental basis of the theory is not upheld by recent work. J. S. A.

Adsorption of nitrogen by carbon at high pressures. A. VON ANTROPOFF [with F. STEINBERG] (Z. Elektrochem., 1933, 39, 616).—The adsorption isotherms have been studied from −160° to 150° and up to pressures of 200 kg. per sq. cm. At the higher pressures and lower temp. approx. saturation was observed. Results are represented by the Langmuir formula. H. J. E.

Adsorption. II. Comparison of the isothermals of carbon tetrachloride and carbon disulphide on charcoal. L. J. BURRAGE (Trans. Faraday Soc., 1933, 29, 673—676).—The isotherms for CS_2 and CCl_4 vapours at 25° have been compared with special reference to the displacement of tenaciously held O_2. Contrary to previous results (this vol., 457), CS_2 appears to be less effective than CCl_4 in breaking up the C_xO_y complex. CS_2 appears, like CO_2, to be attached quasichemically to the C_xO_y complex. J. S. A.

Chemisorption on charcoal. I. Acid constituent of charcoal. A. KING (J.C.S., 1933, 842—846).—When pure charcoal is exposed to air or O_2 and then extracted with H_2O, traces of $H_2C_2O_4$ are found in solution. When the O_2 is removed by heating in vac. at 850° and is replaced by N_2, CO_2, or N_2O no $H_2C_2O_4$ is formed, but when replaced by NO a trace is produced. When C exposed to air is shaken with dil. H_2SO_4 and the filtrate added to starch–KI solution a blue colour is produced. The results are interpreted on the supposition that a "peroxide" is formed on the surface of the C (cf. A., 1931, 316) which decomposes on heating into CO_2 and CO, under the action of H_2O into $H_2C_2O_4$, and on treatment with H_2SO_4 producing H_2O_2. J. W. S.

Adsorption and reduction processes on active charcoal. H. LENNIG (Kolloid-Z., 1933, 64, 143—153).—Experiments with Hg^{II} salts, Fe^{III} salts, $Na_2Cr_2O_7$, and $K_2Cr_2O_7$ are described. Adsorption and reduction are parallel. Increase in the concn. of the salt increases the amount of reduced metal after adsorption is complete. The abs. increase of metal adsorbed by the C diminishes the amount of reduced metal in the solution. Max. reduction is obtained at a definite adsorption val., which is sp. for the metal and independent of the nature of the anion. De-gassed C adsorbs salts of $Hg^{\cdot\cdot}$ and $Fe^{\cdot\cdot\cdot}$ more strongly than does ordinary C; no difference is observed with NaOH, but de-gassed C adsorbs HCl less strongly. E. S. H.

Specific heat of sorbed matter. J. L. PORTER and R. C. SWAIN (J. Amer. Chem. Soc., 1933, 55, 2792—2794).—The sp. heat of H_2O adsorbed by highly activated sugar C is nearly unity and therefore the H_2O is essentially in the ordinary liquid state (cf. this vol., 773). On the other hand, the heat capacities of H_2 and A adsorbed on C at $<$ 90° abs. are considerably $<$ those of H_2 and A in the free state. The distinction between the physical adsorption of the gases and the persorption of the H_2O is emphasised. J. G. A. G.

Evolution of gas from worked metals. O. WERNER (Z. Elektrochem., 1933, 39, 611—616).—The emanation from Ba–Zn alloys containing Th-*X* was removed by a CO_2 stream and measured electroscopically. Changes in the alloy on heat treatment, working, and recrystallisation were correlated with changes in the rate of escape of emanation. H. J. E.

Detection of adsorbed gas films on heated filaments. G. VAN PRAAGH (J.C.S., 1933, 798—800).—The presence of an adsorbed monat. film of I does not affect the emissivity of a Pt filament, but increases the accommodation coeff. This method has been used to show that when Pt is heated in I vapour at 0·027 mm. an adsorbed film is formed below 1565° abs., but not above 1635° abs. This result is in agreement with kinetic measurements. J. W. S.

Adsorption of gases at virgin salt surfaces. F. DURAU and A. HORN (Naturwiss., 1933, **21**, 528).—A virgin salt surface can be prepared by evaporating a solution of the salt in vac., melting the product, and powdering it. A virgin surface of $CdCl_2$ has been used in the study of the adsorption of N_2. A. J. M.

Sorption of water vapour by mineral salts. K. V. FLEROV and O. I. GRÜNBERG (Proc. Leningrad Dept. Inst. Fert., 1933, **17**, 183—190).—A classification of mineral salts, based on the nature of the process of H_2O absorption, is suggested. A. M.

Adsorption of iodine by potassium iodide. B. WHIPP (Proc. Roy. Soc., 1933, **A**, **141**, 217—232).—Evidence is presented for the existence of a bimol. layer of I on KI crystals at saturation pressure. An isotherm is suggested which fits the experimental results over the whole pressure range. This expression contains only the two consts. of Langmuir involving the extent of the adsorbing surface and the rate of evaporation of the mols. in the adsorbed phase. The surface mols. in the bimol. film have properties similar to those in the surface of crystals of pure I. The existence of KI_3 as a separate phase has been disproved. L. L. B.

Adsorption of oxides of nitrogen on silica gel. V. N. SCHULTZ, E. M. SCHTEIFON, and A. M. KUBAREVA [with J. V. KORZINKINA] (J. Chem. Ind. Russ., 1933, No. 3, 10—14).—The velocity of adsorption of NO_2 increases with rise of temp. Desorption of NO_2 is practically complete at 150°. Gel saturated with NO_2 can adsorb considerable quantities of H_2O. R. T.

Adsorption of thorium-*B* and -*C* from solution. I. J. F. KING and A. ROMER (J. Physical Chem., 1933, **37**, 663—673).—Technique of the measurements is described. Glass selectively adsorbs Th-*C* to an extent depending on the acidity. F. L. U.

Photographic method of study of phenomena of adsorption of radioactive elements. H. HERSZFINKIEL and M. BIRENBAUM (Rocz. Chem., 1933, **13**, 306—317).—A drop of AgCl, AgBr, $BaSO_4$, or SiO_2 hydrosol is placed on a cover-glass, and exposed to a Pt wire activated in radon. After the colloid has coagulated, the drop is covered with a thin sheet of mica, without displacing the centrally situated coagulate, and a photographic plate is exposed to the action of the system through the mica. The photographs obtained after 15 min. exposure indicate that Ra-*B* and -*C* are partly in solution and partly in adsorption; both mol. dispersion and aggregate formation are observed in each phase. After 45 min. the solution no longer exhibits activity, which is distributed uniformly in the coagulate. R. T.

Adsorption by charcoal of phenols and polyalcohols from aqueous solution. R. AMIOT (Compt. rend., 1933, **197**, 325—327).—Data for glycerol, erythritol, mannitol, sucrose, PhOH, *o*-, *m*-, and *p*-$C_6H_4Me{\cdot}OH$, guaiacol, pyrocatechol, resorcinol, and orcinol are reproduced by an equation of the form $y=ax^n/(1+bx^n)$. C. A. S.

Adsorbent properties and specific surface of lead sulphate. I. M. KOLTHOFF and C. ROSENBLUM (J. Amer. Chem. Soc., 1933, **55**, 2656—2664; cf. this vol., 346).—The solubility and sp. surface of $PbSO_4$ in H_2O, dil. $Pb(NO_3)_2$, and dil. Na_2SO_4 have been determined. The data indicate that if any adsorption of $Pb^{\cdot\cdot}$ and SO_4'' occurs, it is limited to the corners and edges of the crystals. J. G. A. G.

Adsorption of ponceau-4R (new-coccine) and methylene-blue by lead sulphate and the influence of adsorbed ponceau on the speed of kinetic exchange. I. M. KOLTHOFF and C. ROSENBLUM (J. Amer. Chem. Soc., 1933, **55**, 2664—2672; cf. this vol., 346).—The adsorption of methylene-blue by a suspension of $PbSO_4$ is much < that of ponceau-4R, of which approx. 1 ponceau ion is adsorbed from a saturated solution per 6 mols. of $PbSO_4$ at the crystal surface. The adsorption of ponceau increases in the presence of excess of $Pb(NO_3)_2$ and decreases with excess of SO_4'' in the solution. These and other results are interpreted on the basis of a reversible exchange adsorption between ponceau ions and SO_4'' at the surface of the crystal lattice. Adsorbed ponceau ions retard the kinetic exchange of Th-*B* at the H_2O–$PbSO_4$ interface. J. G. A. G.

Adsorptive properties of Armenian volcanic rocks. S. M. VELLER and A. C. ARUTUNIAN (J. Appl. Chem. Russ., 1933, **6**, 571—573).—The decolorising properties of Armenian kieselguhrs and pumices have been determined. R. T.

Quantitative relationships in the phenomena of exchange adsorption. A. I. RABINERSON (Proc. Leningrad Dept. Inst. Fert., 1933, **17**, 151—182).—The data for Na- and H-kaolins, a solonetz, and a permutite show that the adsorption of Ca and Ba can be expressed by $x=km^{1/n}$, where x=quantity of ions adsorbed, m=wt. of adsorbent, and k and n are consts.; the equation is valid over a wide range. The anomalous rise in the curve x/m against m shown by the adsorption of $BaCl_2$ in the Na-kaolin is not observed with H-kaolin. The relation between adsorption and dilution is expressed by $x=kv^{1/n}$, where v=vol. A. M.

Photo-effect and adsorption at the water–air boundary. H. CASSEL (Z. Elektrochem., 1933, **39**, 571—572; cf. Zimmermann, A., 1926, 886).—The surface tension and photo-effect for aq. Et_2 dihydrocollidinedicarboxylate and for a film of NPh_3 on H_2O have been measured. The photo-effect is not due to the formation of a solid surface film. H. J. E.

Adsorption of sodium linoleate in preference to that of sodium oleate on the surface of nickel and copper. B. S. SRIKANTAU (J. Indian Chem. Soc., 1933, **10**, 233—235).—Preliminary results show that at concns. >0·2% Na linoleate is adsorbed preferentially, suggesting that the adsorbed mols. lie horizontally, attached by the double linking. E. S. H.

Surface tension of mercury and water in contact with saturated vapours of organic liquids [at 25°]. F. E. BARTELL, L. O. CASE, and H. BROWN

(J. Amer. Chem. Soc., 1933, **55**, 2769—2776; cf. this vol., 775).—The surface tension (drop wt.) of Hg in contact with the saturated vapours of eleven org. liquids, the interfacial tension (capillary rise) of H_2O in contact with six org. liquids, and the surface tension of H_2O saturated with the org. liquids in contact with the saturated vapours have been determined. The deviations from previously accepted vals. are discussed. The data show that, contrary to the conclusions of others, when a film is spontaneously formed on the surface of a liquid (*e.g.*, Hg, H_2O) the sum of the interfacial tension of the liquid against the film liquid plus the surface tension of the film liquid is equal to the surface tension of the liquid supporting the film at saturation v.p. J. G. A. G.

Action of light on the surface tension of soap solutions. L. D. Mahajan (Nature, 1933, **132**, 67).—Light decreases the surface tension of soap solutions by an amount which varies with the type of soap and with concn. The effect is not confined to Boys' soap solutions. L. S. T.

Solvation of molecules and equation of state of adsorption film. S. E. Bresler, J. B. Chariton, B. A. Talmud, and D. L. Talmud (Z. physikal. Chem., 1933, **165**, 195—208).—Compression curves for films of cetyl alcohol and oleic acid on aq. solutions of glucose and Na and K salts have been obtained. All these solutes increase the surface pressure, and the order of effectiveness of either anions or cations is a lyotropic series. The effect of the sol. substance thus depends on its dehydrating action, which presumably influences the electrostatic interaction between polar groups in the surface film (cf. this vol., 674). A theoretical investigation of the effect of the dehydration of polar mols. on the equation of state of a surface film supports this interpretation. R. C.

Comparison of equation of state of unimolecular films with experiment. J. Guastalla (Compt. rend., 1933, **197**, 307—308).—The proposed equation of state (cf. this vol., 668) shows fair agreement with that obtained experimentally for oleic acid on 0·01N-HCl. The coeffs. seem to depend on the electric moment. C. A. S.

Strength of emulsifier films at liquid–liquid interfaces. J. A. Serrallach, G. Jones, and R. J. Owen (Ind. Eng. Chem., 1933, **25**, 816—819; cf. A., 1931, 1229).—A modified du Noüy tensiometer has been adapted to determine the strength of coherent films at the interface between emulsifier solutions and various oils. Data are given for olive oil, cod-liver oil, castor oil, and mineral oil with several emulsifiers. The strength of the film varies with time in a way which is sp. for each system. The efficiency of an emulsifier does not appear to depend primarily on the strength of the films which are formed; the main factors are probably the preliminary lowering of interfacial tension and the rapidity of film formation. E. S. H.

Hydroxyl group and soap film structure. W. J. Green (Nature, 1933, **131**, 872).—NH_4 oleate (9%) is quickly changed to a thick but clear gel by small amounts of glycol, *cyclo*hexanol, propenol, and EtOH; further quantities of these alcohols produce a limpid, clear liquid. The resulting solutions, especially on dilution, give lasting films which thin to the "black" state through several grades. The reaction suggests that soap mol. aggregates are formed by means of OH groups rather than as ordinary hydrates, and indicates a mechanism by which layers of mols. are rooted in a H_2O surface, or linked in a stable soap film. L. S. T.

Wettability of insoluble substances and power of attraction at interface of immiscible liquids. H. Devaux (Compt. rend., 1933, **197**, 105—108).—For most insol. substances, and especially elementary substances, wettability is imperfect; hence such substances tend to accumulate at the surface of separation of two immiscible liquids, this being a region of specially powerful attraction. It may be exerted on a substance dissolved in one of the liquids, in which case the phenomenon is a special case of adsorption (cf. A., 1932, 1085). C. A. S.

Interaction between soot films and oil. S. C. Blacktin (Nature, 1933, **131**, 873—874).—Attention is directed to the difference in results obtained due to impact (this vol., 672) and those due to interaction (A., 1932, 464). L. S. T.

"Molecular solders" and their applications. D. L. Talmud (Kolloid-Z., 1933, **64**, 227—229).—Theoretical. "Mol. solders" are adsorption layers between the surfaces of two solid phases. E. S. H.

Electrosmosis and anomalous osmosis. D. R. Briggs (Proc. Nat. Acad. Sci., 1933, **19**, 704—710).—The electrokinetic potential in the case of gum arabic is a function of the degree of ionisation of the primary salt valencies of the colloid and of the degree of oriented adsorption of foreign salt. C. W. G.

Stationary, checked, and other states of osmotic systems. I. F. A. H. Schreinemakers (Proc. K. Akad. Wetensch. Amsterdam, 1933, **36**, 516—523).—Theoretical. J. W. S.

Nature of alleged molecular sieve membranes. R. Beutner, M. Caplan, and W. M. Loehr (J. Biol. Chem., 1933, **101**, 391—400).—The contact of collodion (I) with dil. aq. KCl, NaCl, LiCl, or $CaCl_2$ is followed by a chemical surface reaction, whereby base is removed by (I) and liberated HCl is detectable by titration or measurement of p_H. The reaction can be correlated with the surface boundary potentials of the systems if consideration is given to the effect of the liberated HCl (A., 1926, 120). The theory that p.d. following variation in concn. at surfaces of (I) are due to differential ionic mobilities in the pores (A., 1929, 87) is refuted. F. O. H.

Production of Merget's phenomenon by arsonvalisation with short waves. H. Bordier (Compt. rend., 1933, **196**, 255—257).—Merget's phenomenon of thermodiffusion (cf. A., 1874, 380, 759) has been examined in a new way. A porous vessel filled with powdered brick and provided with a tube penetrating to the centre is closely encased with cardboard and heated. If the porous block is dry, no air escapes through the tube, but if it is moist, air escapes in increasing quantity and for a longer period the more moisture there is present. Similar results are obtained if the block is moistened with MeOH, $COMe_2$, or Et_2O, the amount of air expelled increasing with the volatility of the liquid. C. A. S.

Continuity of Merget's phenomenon [thermodiffusion]. H. Bordier (Compt. rend., 1933, **196**, 819—820; cf. preceding abstract).—Thermodiffusion takes place with Et_2O or EtCl as moistening liquid without heating, and continues until all the liquid has evaporated, the temp. of the porous block falling by 1—2°. C. A. S.

Merget's phenomenon may be produced by vaporisation of solids. H. Bordier (Compt. rend., 1933, **196**, 1142—1144; cf. preceding abstracts).—A porous block is impregnated with an Et_2O solution of camphor or I. Evaporation of the Et_2O causes Merget's phenomenon. After complete removal of Et_2O, rise of temp. reproduces the effect when the enclosed solid volatilises. A. C.

Empirical equation for calculating osmotic pressures. (Earl of) Berkeley (Phil. Mag., 1933, [vii], **16**, 298—310).—An empirical equation is shown to fit closely the results obtained with a series of sugar-like compounds. The modifications required to render the equation applicable to salt solutions are also discussed. J. W. S.

Alkoxides and their molecular compounds. I. H. Ulich and W. Nespital (Z. physikal. Chem., 1933, **165**, 294—310).—F.-p. measurements with C_6H_6 solutions of Al ethoxide, *iso*propoxide, and benzyloxide show these solutes to be highly polymerised. The dipole moments are very small, indicating that the polymerised alkoxide mols. have such a structure that the individual group moments cancel themselves out almost completely. The most probable structure is a ring formed from three or four $Al(OR)_3$ mols., each Al atom being surrounded tetrahedrally by four OR groups. These alkoxides have no tendency to form co-ordinated compounds with org. mols. In C_6H_6 solution $Al(OEt)_3,AlCl_3$ is present largely as double mols., which, according to the dipole moment, have a ring structure. $Al(OPr^{\beta})_3$ and $AlCl_3$ react in C_6H_6 forming the *compound* $Al_3Cl_5(OPr^{\beta})_4$, apparently having a ring structure. R. C.

Compressibility of solutions. I. Apparent molal compressibility of strong electrolytes. F. T. Gucker, jun. (J. Amer. Chem. Soc., 1933, **55**, 2709—2718).—With the exception of H_2SO_4 solutions at 18°, the apparent molal compressibility of electrolytes, $\phi(K_2)=\beta V-\beta_1 V_1$, is almost independent of temp. and is a linear function of the square root of the vol. concn. for all cases for which data are available, where β and β_1 are compressibility coeffs. for the solution and H_2O, respectively. The higher is the valency type of the salt, the more negative become the vals. of ϕ, but for all electrolytes, the vals. of ϕ become less negative as the concn. is increased. Vals. of ϕ at infinite dilution are additive properties of the ions. β is related to concn. by the equation $\beta=\beta_1+Ac+Bc^{3/2}$, where A and B are sp. consts. J. G. A. G.

Dielectric constants of dilute solutions of strong electrolytes. M. Jezewski and J. Kamecki (Physikal. Z., 1933, **34**, 561—565).—The dielectric consts. of dil. solutions of HCl, NaCl, KCl, $MgSO_4$, and $CuSO_4$ have been determined by the resonance method. The results for bi-bivalent electrolytes are in agreement with the Debye–Falkenhagen theory, but for uni-univalent electrolytes there are large deviations. A. J. M.

Mechanical subdivision to colloidal dimensions. E. Podszus (Kolloid-Z., 1933, **64**, 129—143).—A review of milling processes. E. S. H.

Influence of convection on Brownian motion. K. Sitte (Z. Physik, 1933, **83**, 266—269).—Polemical, against Satô (this vol., 460). A. B. D. C.

Influence of convection on Brownian motion. II. M. Satô (Z. Physik, 1933, **83**, 412—416).—Convection increases Brownian motion due to condensation and re-evaporation of gas mols. A. B. D. C.

Mechanical properties of disperse systems. I. Deformation of subsoils by pressure. G. I. Pokrowski and V. G. Bulytschev (Kolloid-Z., 1933, **64**, 175—178).—Mathematical. E. S. H.

Thermal conductivity of colloid systems. S. Bresler (Kolloid-Z., 1933, **64**, 178—181).—Theoretical. E. S. H.

Viscosimetry of colloids, especially solutions of cellulose esters. R. Eisenschitz (Kolloid-Z., 1933, **64**, 184—194).—Mainly theoretical. Some experiments on the viscosity of cellite solutions are described, which lead to the view that these solutions are elastic and relaxing. E. S. H.

Influence of particle form and specific volume on the viscosity of lyophilic colloids. I. Sakurada (Kolloid-Z., 1933, **64**, 195—200).—The viscosity formula of Fikentscher and Mark (A., 1929, 1379) is valid for squalene, polystyrene, and cellulose nitrate and acetate solutions. Methods of determining the consts. are worked out. E. S. H.

Viscosity of disperse systems of different plasticity. D. Derjaguin and M. Volarovitsch (Kolloid-Z., 1933, **64**, 233—234).—Polemical (cf. this vol., 460). E. S. H.

Ultra-filtration of soap solutions. J. W. McBain, Y. Kawakami, and H. P. Lucas (J. Amer. Chem. Soc., 1933, **55**, 2762—2769).—By ultra-filtration with cellophane membranes, the degree of hydration of colloidal particles in sols is measured in terms of an added indifferent reference substance of which the concn. in the filtrate is > in the original or the residue. Using KCl, the hydration of K laurate is 12 mols. of H_2O per equiv. of soap, but when the total ionic concn. is small, the effect of the Donnan equilibrium (cf. this vol., 567) is superimposed and higher vals. are obtained. Na palmitate, salted out by the NaCl, has 2 mols. of H_2O per equiv. of soap. J. G. A. G.

Phase equilibria of acid soaps. I. Anhydrous acid potassium laurate. J. W. McBain and M. C. Field (J. Physical Chem., 1933, **37**, 675—684; cf. B., 1927, 18).—The equilibrium diagram for K laurate–lauric acid (KL–HL) is given. The acid salt KL,HL is not miscible in the solid state with either component. It is decomposed above 91·3° and forms a eutectic (40·0°) with HL. F. L. U.

Influence of hydrophilic colloids or adsorbent compounds on the solubility of sparingly soluble substances. I. Influence of gelatin on solubility. H. Brintzinger and H. G. Beier (Kolloid-Z., 1933, **64**, 160—172).—Gelatin increases the solubility of the following substances in H_2O : BzOH, *o*- and *m*-$OH{\cdot}C_6H_4{\cdot}CO_2H$, anisic acid, *o*-, *m*-, and *p*-$NO_2{\cdot}C_6H_4{\cdot}CO_2H$, *o*-, *m*-, and *p*-$C_6H_4Br{\cdot}CO_2H$, cinnamic, sulphanilic, anthranilic, hippuric, and camphoric acid, strychnine, *o*-, *m*-, and *p*-$NO_2{\cdot}C_6H_4{\cdot}NH_2$. The solubility of $NHPh_2$ is not affected by gelatin. Causes are discussed. E. S. H.

Dependence of the stability of carbon suspensions on the gas charge and composition of the solution. II. N. Bach (Kolloid-Z., 1933, **64**, 153—160; cf. A., 1928, 1321).—According to the behaviour in adsorption experiments, the stability of suspensions of platinised C charged with O_2 or H_2 is increased when the conditions favour the adsorption of ions, *i.e.*, the O_2-charged (I) particles are more stable in acid and the H_2-charged (II) particles in alkaline solutions. (I) behaves as a positive colloid, being sensitive to multivalent anions, whilst (II) behaves as a negative colloid. The sign of charge of (II) can be reversed by adding $ThCl_4$, but on further addition the positive particles are coagulated. C which has been oxidised superficially with O_3 has a min. stability in pure H_2O and is stabilised by multivalent anions and cations. Suspensions of platinised C containing H_2 show a min. stability when ion adsorption is least. E. S. H.

Protective action of colloids. I. Ionic adsorption in the coagulation of protected sols. II. S. S. Joshi and A. J. Rao (J. Indian Chem. Soc., 1933, **10**, 237—246, 247—255).—I. Experiments with As_2S_3 sols, protected by gelatin, Na oleate, or starch, using aq. $FeCl_3$, $BaCl_2$, or HCl as coagulating agents, show that generally the adsorption of the coagulator increases when the amount of protective agent is increased. Certain exceptions are discussed.

II. The exceptional behaviour mentioned above is observed also in the viscosity, but not in the turbidity. E. S. H.

Kinetics of coagulation of titanium dioxide sol. S. M. Mehta and (Miss) O. Joseph (J. Indian Chem. Soc., 1933, **10**, 177—188).—In the coagulation of TiO_2 sol by aq. NaCl or $MgCl_2$, Smoluchowski's equation is applicable only to a limited range of concn. of the electrolyte. The velocity curves are S-shaped for sols dialysed up to 18 days, but lose this form after more prolonged dialysis. E. S. H.

Highly polymerised compounds. LXXXIII. Streaming double refraction of dilute solutions of molecule colloids. R. Signer and H. Gross (Z. physikal. Chem., 1933, **165**, 161—187).—Measurements have been made with a new apparatus capable of measuring the streaming double refraction, S, of very dil. solutions of highly polymerised substances. For the hemicolloidal polystyrenes in *cyclo*hexanone solution and the hemi- and eu-colloidal cellulose nitrates in BuOAc solution, S at a given concn. is proportional to the streaming gradient, G, and $S/G\eta c$=const., where c is the concn. and η the viscosity This equation is valid for Et oleate solutions at all concns. up to 100% of ester, whilst for the lower polystyrenes it holds only up to a certain limiting concn., which decreases with increasing mol. wt. and apparently represents the transition from sol to gel solutions. For eucolloidal polystyrenes S is not a linear function of G. These results for the cellulose nitrates and the lower polystyrenes agree with Boeder's theory (A., 1932, 571), showing that the dissolved mols. are straight threads. The vals. of the rotation diffusion consts. calc. by this theory are proportional to the reciprocals of the mol. wts. deduced from viscosity data. Kuhn's theory that the S of solutions of mol. colloids is due to extension of isotropic elongated structures (*ibid.*, 1201) is untenable. R. C.

Reversibility of equilibria in cellulose reactions. C. Trogus (Z. physikal. Chem., 1933, **B**, **22**, 134—144).—In view of the micellar character of the reactions the final states do not represent reversible equilibria. In the reaction between cellulose and aq. N_2H_4 the N_2H_4 concn. necessary for the reaction within the micelles in the formation of hydrazino-cellulose is about 20% > the concn. required to prevent the decomp. of the intramicellar system. This suggests that migration of the reagent in or out of the fibre is opposed by some kind of resistance. The apparent equilibrium encountered in the formation of Na cellulose I and Na cellulose II from hydrocellulose is due to the inadequate precision of the analytical methods; *X*-ray examination shows the absence of true equilibria. R. C.

Size of the micelle and colloidal particle of cellulose nitrate. K. Atsuki and M. Ishiwara (J. Soc. Chem. Ind. Japan, 1933, **36**, 220—221B).—The size is deduced from the no. of particles visible in the ultramicroscope when dil. $COMe_2$ solutions of known concn. are treated with H_2O. The result agrees with that calc. from the rate of diffusion of cellulose nitrate solutions in $COMe_2$. A. A. L.

Mechanical material constants of colloids. R. Eisenschitz and W. Philippoff (Naturwiss., 1933, **21**, 527—528).—Regarding solutions of the cellulose esters as elastic, relaxing bodies, an equation is given connecting amplitude of damped oscillations with the amount of damping and frictional resistance. The equation has been tested experimentally and qual. agreement found. A. J. M.

Lyotropic series in swelling and its extension to organic and non-ionising substances. IX. Influence of aliphatic and alicyclic compounds with two or more hydrophile groups on the swelling of potato starch. J. R. Katz, A. Wedinger, and F. J. F. Muschter (Biochem. Z., 1933, **262**, 355—363).—The power of a series of aliphatic compounds having two hydrophile groups (OH, CO_2H, SO_3Na) to increase the swelling of starch is much < that of related compounds with one such group, due to a corresponding feebler adsorption. With the series of hydroxy-propionates and -butyrates the weakening effect is the greater the greater is the distance between OH and CO_2H. P. W. C.

Mechanism of deformation of thread-like substances. I. O. Kratky (Kolloid-Z., 1933, **64**, 213—222).—A theoretical paper, discussing the relation between degree of stretching and orientation, and the calculation of double refraction. E. S. H.

Colloidal aluminium oxide–cupric chloride systems, prepared by the action of alcoholic cupric chloride solution on aluminium. A. Kutzelnigg and W. Wagner (Kolloid-Z., 1933, 64, 209—211).—When $CuCl_2$ in EtOH acts on Al foil in presence of a little H_2O, green jellies are formed, which dry to brown or green xerogels (I), containing $Al(OH)_3$, $CuCl_2$, and $AlCl_3$. The green (I) are less rich in Cu. Colourless gels, free from Cu, are obtained when displacement of $Cu^{\cdot\cdot}$ proceeds to completion. The (I) decrepitate on adding H_2O, then swell, and dissolve in part colloidally. E. S. H.

Formation of thixotropic ferric oxide gels. A. Kutzelnigg and W. Wagner (Kolloid-Z., 1933, 64, 212).—Thixotropic gels of $Fe(OH)_3$ (containing considerable amounts of $FeCl_3$ and $CuCl_2$) are obtained by acting on Cu with $FeCl_3$ in EtOH. E. S. H.

Paradoxical solubility phenomenon with gelatin. C. E. Larson and D. M. Greenberg (J. Amer. Chem. Soc., 1933, 55, 2798—2799).—Gelatin and AcOH are completely miscible above a certain temp. which decreases with increasing gelatin : AcOH ratio and varies with the sample of gelatin. Dilution of such a homogeneous mixture with AcOH causes pptn. of gelatin. J. G. A. G.

Complex coacervation. XVIII. Experiments on arabates in connexion with the origin of capillary-electrical charge. H. G. B. de Jong and P. van der Linde (Biochem. Z., 1933, 262, 161—174).—The electrochemical equiv. wt. of the arabate ion is approx. 1200, when determined analytically. The change of charge brought about by hexol nitrate, however, indicates an apparent equiv. wt. of about 700. This effect varies with dilution and the consequent shift of p_H. At p_H 3 it gives practically the electrochemical val., whilst at p_H 4·3 it approximates to the val. which is characteristic for neutral arabates. It is suggested that this is in part due to the adsorption of OH′ at neutral positions on the particles. H. W. D.

Complex coacervation. XIX. (*a*) Autocomplex coacervation with negative and positive hydrophile sols. (*b*) Correlation between the reciprocal hexol number and the tendency of negative hydrophile sols to form autocomplex coacervates. H. G. B. de Jong and P. van der Linde (Biochem. Z., 1933, 262, 390—405).—New examples of autocomplex coacervation (I) both in pure aq. medium (Ba chondroitin sulphate, Na thymus-nucleate, agar, etc.) and with the help of desolvation substances, *e.g.*, $COMe_2$, EtOH (sol. starch, glycogen) are described and the reciprocal hexol no. (II) has been determined. The lower is the valency of the cations bringing about (I) in pure aq. medium the less is (II). P. W. C.

Complex coacervation. XX. Correlations. Systems with two co-existing complex or autocomplex coacervates. H. G. B. de Jong and A. de Haan (Biochem. Z., 1933, 263, 33—49).—The origin of the capillary electric charge is considered, and the no. of ionogenic centres is found to be related to the no. of centres of negative capillary electric charge arising from simple contact with H_2O. The phenomena of mutual contacts of two co-existing complex or autocomplex coacervates are examined. Frequently the droplets of the one coacervate are completely enveloped by those of the other. H. W. D.

Union of biocolloids. XIX. Polyosoproteins (polysaccharoproteins). S. J. von Przylecki, E. Mystkowski, and B. Niklewski. **XX. Proteins and crystalloids.** M. D. Grynberg (Biochem. Z., 1933, 262, 260—271, 272—279).—XIX. The rotations of mixtures of proteins (ovalbumin, gelatin) and polysaccharides (dextrin, glycogen) do not correspond with the arithmetical sum of the rotations of the constituents, the deviations varying with the p_H. The turbidities of these substances and mixtures of them in H_2O also vary with the p_H. Union between these two groups of substances has now been detected by a variety of methods and occurs in all cases over a wide range of p_H.

XX. The union of proteins (caseinogen, gelatin, globulin, and albumin) with org. anions and its dependence on p_H and the ratio of the CO_2H/NH_2 groups of the protein are investigated, using H_3PO_4, guanidine, creatine, and creatinine. P. W. C.

Physical chemistry of starch and bread-making. XII. Transformation of starch preparations with the potato-starch (*B*) spectrum into preparations with the wheat-starch (*A*) spectrum and the reverse. J. R. Katz and J. C. Derksen (Z. physikal. Chem., 1933, 165, 228—233; cf. this vol., 464).—On evaporation of an aq. solution of sol. starch at or above 60° a residue with an *A* spectrum results, whilst the product of evaporation at room temp. has a *B* spectrum. Either substance may be partly transformed into a substance having the other spectrum by keeping in contact with H_2O at an appropriate temp. R. C.

Solvo-systems of chemical compounds. L. F. Audrieth (Z. physikal. Chem., 1933, 165, 323—330).—The chemical relations of NH_3 and N_2H_4 to their allied compounds are set out so as to exhibit a parallelism with the relations of H_2O to acids, salts, and bases. R. C.

Relation between kinetics and chemical equilibrium. I. Isomerisation of the *iso*butyl bromides. II. Reversible transformation of Δ^{β}-hexachloro*cyclo*pentenone into Δ^{γ}-hexachloro*cyclo*pentenone. A. Berthoud and D. Porret (J. Chim. phys., 1933, 30, 396—413).—I. The authors' data support Brunel's views (A., 1917, i, 625).

II. Küster's val. (A., 1896, ii, 158) for the equilibrium const. is confirmed, but the observed velocity of transformation is much lower, especially if the materials used are very pure. The conversion of the Δ^{γ}- into the Δ^{β}-compound is accelerated by the formation of a catalyst during the reaction. Deviations from theory observed with these compounds and with $Bu^{\beta}Br$ are attributed to catalytic effects. D. R. D.

Ebullioscopic method for determining the equilibrium constant of esterification. W.

Swientoslawski (J. Physical Chem., 1933, **37**, 701—707; cf. A., 1929, 396).—Improved apparatus is described. The b.p. of equilibrium mixtures for different proportions of AcOH and EtOH are given. F. L. U.

Polyhalides. II. Formation and dissociation of chlorodibromides and tribromides of sodium, potassium, strontium, and barium. S. K. Ray (J. Indian Chem. Soc., 1933, **10**, 213—224; cf. A., 1932, 996).—For dil. solutions (0·5—0·06*N*) and moderate concns. of halogens, the formation of the compounds $NaClBr_2$, $KClBr_2$, $SrCl_2Br_4$, $BaCl_2Br_4$, $NaBr_3$, KBr_3, $SrBr_6$, and $BaBr_6$ has been established by the f.-p. method. Dissociation consts. and heats of formation are recorded. E. S. H.

Dissociation of water in strontium chloride solutions at 25°. J. E. Vance (J. Amer. Chem. Soc., 1933, **55**, 2729—2733).—From the e.m.f. of the cells $H_2|0·013M\text{-}Sr(OH)_2+0·02—2·5M\text{-}SrCl_2|AgCl|Ag$ and $H_2|0·01M\text{-}HCl+0—0·5M\text{-}SrCl_2|AgCl|Ag$ at 25°, the activity coeff. of 0·01*M*-HCl and the dissociation of H_2O in aq. $SrCl_2$ have been computed (cf. A., 1932, 997). J. G. A. G.

Ionisation of *dl*-alanine from 20° to 45°. L. F. Nims and P. K. Smith (J. Biol. Chem., 1933, **101**, 401—412).—The method of determining ionisation consts. of weak bases and acids from e.m.f. measurements of suitable cells without liquid junction (A., 1932, 695) has been modified. Vals. are given for $-\log K_{a_1}$, $-\log K_{a_2}$, and the heats of ionisation of *dl*-alanine at 20—45°. F. O. H.

Acidity of organic acids in methyl and ethyl alcohols. W. L. Bright and H. T. Briscoe (J. Physical Chem., 1933, **37**, 787—796).—Vals. of K_A (in Brönsted's equation) have been determined for aq. MeOH and aq. EtOH solutions of BzOH, its Me, NH_2-, OH-, Cl-, and NO_2-derivatives, and fatty acids C_3—C_6. The results are discussed in reference to the influence of the character and position of substituents and of the nature of the solvent. F. L. U.

Affinity constant of aniline in acetone–water mixtures. A. N. Campbell and E. M. Brown (Trans. Electrochem. Soc., 1933, **63**, 291—295).—The compositions of the two liquid layers formed by NH_2Ph–$COMe_2$–H_2O mixtures over the whole range of two-phase systems at 30° have been determined, and, using vals. of Pring (A., 1924, ii, 596) for K_w in $COMe_2$–H_2O mixtures, vals. of the affinity const. of NH_2Ph in such mixtures are calc. Extrapolation gives 2×10^{-10} as the val. for pure aq. solution (cf. A., 1930, 122). H. J. T. E.

Electrolytes in mixed solvents. V. Free energy of lithium chloride in water–alcohol mixtures and the salting-out of alcohol. J. A. V. Butler and D. W. Thomson (Proc. Roy. Soc., 1933, **A**, **141**, 86—94).—Earlier measurements of the partial v.p. of solutions of LiCl in H_2O–EtOH mixtures (A., 1931, 680) have been extended to solutions containing 2—4 mol.-% EtOH and in each case 0·5, 1·0, and 4·0*M*-LiCl. In a discussion of the thermodynamics of salting out it is shown that extent of the salting out is properly measured, not by the change of the activity of the non-electrolyte, but by the difference between the observed and normal effects. The free energies of transfer of LiCl from H_2O to EtOH solutions have been calc. from the partial pressures. L. L. B.

Amphoteric oxide hydrates, their aqueous solutions and crystalline compounds. XVIII. Comparison of hydrolytic phenomena and aggregation processes in aqueous solutions of beryllium, magnesium, and aluminium salts. W. Heukeshoven and A. Winkel (Z. anorg. Chem., 1933, **213**, 1—11; cf. this vol., 580).—Diffusion coeffs. of $Be^{\cdot\cdot}$ and $Mg^{\cdot\cdot}$ were measured between p_H 0 and 5·8—6·6. The val. for $Mg^{\cdot\cdot}$ is const.; for $Be^{\cdot\cdot}$ it diminishes between p_H 2 and 6 from 0·45 to 0·35 and for $Al^{\cdot\cdot\cdot}$ the decrease is even greater. This is due to hydrolysis, aggregates of lower mobility being formed. The conductometric titration of $Be(ClO_4)_2+HClO_4$ with 2*N*-NaOH is described. H. J. E.

Amphoteric behaviour of metal hydroxides. R. Scholder (Angew. Chem., 1933, **46**, 509—512).—A lecture. E. S. H.

Displacement of equilibrium by variation of mass. R. Étienne (Compt. rend., 1933, **197**, 149—151; cf. this vol., 783).—A graphical method of arriving at the result previously demonstrated. C. A. S.

Chemical law of mass action for concentrated non-ideal solutions. F. Sauerwald (Naturwiss., 1933, **21**, 547).—The validity of the law of mass action in certain conc. non-ideal solutions may be due to special relations between the activity and the concn. A. J. M.

Thermodynamics of very dilute gases and solutions. W. Nernst (Sitzungsber. Preuss. Akad. Wiss. Berlin, 1933, Reprint, 4 pp.).—Attention is directed to the difference between the formula $A=RT\log v/v_0$ in its application to a gas and the formula $EF=RT\log c/c_0$ as applied to a concn. cell. The mechanical work A cannot be actually realised when the gaseous system is very dil., although this is readily accomplished in the case of the electrical work EF even in the case of extremely dil. solutions. A. J. M.

Activity coefficients of the nitrobenzoic acids [at 50°]. P. H. Sykes and P. W. Robertson (J. Amer. Chem. Soc., 1933, **55**, 2621—2625).—The activity coeffs. have been computed from the solubilities of the nitrobenzoic acids in *iso*amyl alcohol, xylene, H_2O, 1—5*N* aq. NaCl and $MgSO_4$, and from distribution ratios. $o\text{-}NO_2\cdot C_6H_4\cdot CO_2H$ is much more highly polar than the other isomerides and has a very high activity coeff. in xylene. J. G. A. G.

Changes of chemical potential of concentrated solutions of certain salts. R. E. Gibson and L. H. Adams (J. Amer. Chem. Soc., 1933, **55**, 2679—2695).—The relative lowering of the v.p. of conc. aq. solutions of LiCl, NH_4NO_3, KCNS, and Na_2SO_4 has been determined in the range 20—27·5° by a modified static method. The data are reproduced by empirical equations by means of which differences in the chemical potential of either component may be calc. J. G. A. G.

Thermodynamic ionisation constants of carbonic acid [at 25°]. D. A. MacInnes and D.

Belcher (J. Amer. Chem. Soc., 1933, 55, 2630—2646).—From the e.m.f. of the cell Ag,AgCl|$XHCO_3(m)+XCl(m)+CO_2$ (dissolved, 1 atm.)|glass|AcO′ buffer+KCl|AgCl,Ag, where X=Na or K, it is shown that the fugacity of 0·54—99·6 mol.-% of CO_2 in N_2 mixtures at 1 atm. total pressure is proportional to the mol. fraction, and the first ionisation const. of H_2CO_3 is computed to be $4{\cdot}54\times10^{-7}$, which, although it is much > previously accepted vals. (A., 1916, ii, 512), is in close accord with a redetermination by a conductivity method. From the e.m.f. of the cell Ag,AgCl|0·0011—0·04*M*-K_2CO_3+0·0025—0·047*M*-$KHCO_3$+0·0025—0·04*M*-KCl|H_2, the second ionisation const. of H_2CO_3 is computed to be $5{\cdot}61\times10^{-11}$, which is consistent with existing vals.
J. G. A. G.

Application of Nernst's approximate formula to cases of complex heterogeneous equilibrium in organic chemistry. Z. E. Zinkov (Anilinokras. Prom., 1933, 3, 144—153).—A thermodynamic consideration of the system NaOPh–CO_2 leads to the conclusion that Davies' "ester salts I and II" (A., 1928, 1329) are respectively $PhNaCO_3$ and Na salicylate, which in Davies' experiments were in false equilibrium with the other phases of the system. Nernst's approx. formula is applicable to the above case of heterogeneous equilibrium. R. T.

Ionic activity at extremely high concentrations. F. Tödt (Z. Elektrochem., 1933, 39, 521—526).—The $H^{\cdot}$ activity in H_2SO_4 up to 37·4*N* has been measured with a H electrode. p_H vals. of 11·86 were observed. Similarly high vals. were obtained for conc. HNO_3 by the inversion of sucrose. H. J. E.

Thermodynamic treatment of stationary systems. B. Bružs (Z. Elektrochem., 1933, 39, 642—645).—Theoretical. H. J. E.

Individual thermodynamic behaviour of tetra-alkylammonium halides in very dilute solution. J. Lange (Z. Elektrochem., 1933, 39, 545—549; cf. A., 1930, 1251).—The osmotic coeff. for NMe_4Cl, NPr_4Cl, NMe_4I, and NPr_4I, calc. from f.-p. measurements at concn. 0·1—0·001*M*, are compared with vals. calc. from electrostatic theory. For the chlorides changes in the hydration outweigh changes in the size of the cation. For the iodides partial association of the ions must be assumed. The conductivity data at 0° are discussed in relation to the Debye–Hückel–Onsager theory and the cryoscopic measurements. H. J. E.

Thermodynamic studies of mercurous bromide. F. Ishikawa and Y. Ueda (Sci. Rep. Tôhoku, 1933, 22, 249—262).—The e.m.f. at 25° of reversible cells containing HgBr lead to: standard free energy of formation −21,350 g.-cal., heat of formation −24,470 g.-cal., entropy change −10·5 g.-cal. per 1°, and entropy of the salt 27·2 g.-cal. per 1°.
A. R. P.

Thermodynamic studies of cadmium bromide. F. Ishikawa and Y. Ueda (Sci. Rep. Tôhoku, 1933, 22, 262—287).—The % of $CdBr_2$ in a saturated solution at 20—35° is $52{\cdot}88+0{\cdot}653(t-25°)+0{\cdot}00243(t-25°)$. Below 36° $CdBr_2,4H_2O$ is the stable solid phase and above 36° $CdBr_2$; there are no intermediate hydrates. The heat of dissolution of $CdBr_2,4H_2O$ is −7340 g.-cal., the heat of formation of $CdBr_2$ from α-Cd 74·471 kg.-cal., and the entropy of $CdBr_2$ 36·8 g.-cal. per 1°. A. R. P.

Heats of combustion of carbon monoxide in oxygen and of nitrous oxide in carbon monoxide at constant pressure. J. H. Awbery and E. Griffiths (Proc. Roy. Soc., 1933, A, 141, 1—16).—The heats of combustion of N_2O and of O_2 in CO, determined by a continuous-flame method involving combustion at const. pressure, are found to be 364,340 and 282,730 international joules per mol., respectively. The reaction was brought about by continuously burning one of the reacting gases in an excess of the other, using an adiabatic calorimeter to measure the heat evolved. From these two vals. the calc. heat of formation of N_2O at 20°/1 atm. is $19{\cdot}5_0$ kg.-cal.^{15} L. L. B.

Bomb calorimeter determination of the heats of formation of nitrous oxide and carbon dioxide. R. W. Fenning and F. T. Colton (Proc. Roy. Soc., 1933, A, 141, 17—28).—From measurements of the heats of reaction of O_2 and N_2O in CO and H_2, the heats of formation of N_2O and CO_2 at a const. pressure of 1 atm. and at 20° were found to be $-19{\cdot}74\pm0{\cdot}07$ kg.-cal.^{15}, and $67{\cdot}65_5\pm0{\cdot}03_5$ kg.-cal.^{15}, respectively. L. L. B.

Perchlorates. II. Heats of dissociation and hydration. C. Smeets (Natuurwetensch. Tijds., 1933, 15, 105—124).—Data are given for the alkali and alkaline-earth perchlorates. For each group the heats of hydration diminish with increase of the at. vol. of the cation, and, correspondingly, the hydrated perchlorates of metals having very small at. vol. (Fe, Mn, Co, etc.) decompose at temp. < those at which they lose H_2O of crystallisation. H. F. G.

Heat of reaction of $2Fe(ClO_4)_3+2Hg=2Fe(ClO_4)_2+Hg_2(ClO_4)_2$ from equilibrium data. V. B. Fleharty (J. Amer. Chem. Soc., 1933, 55, 2646—2649; cf. A., 1931, 802).—The effect of varying the concn. of $HClO_4$ and salts on the reaction $2Fe^{\cdot\cdot\cdot}+2Hg\rightleftharpoons2Fe^{\cdot\cdot}+Hg_2^{\cdot\cdot}$ has been determined at 35°. The true equilibrium const. is 0·0539, and the heat of reaction 20,000 g.-cal. J. G. A. G.

Thermal data on organic compounds. XI. Heat capacities, entropies, and free energies of ten compounds containing oxygen and nitrogen. G. S. Parks, H. M. Huffman, and M. Barmore (J. Amer. Chem. Soc., 1933, 55, 2733—2740).—From sp. heat determinations between 91° and 300° abs., the following entropies per mol., S_{298}, have been computed: $CO(NH_2)_2$ 25·2, glycine 26·1, EtOAc 62·0, *n*-amyl alcohol 60·9, *tert.*-amyl alcohol (I) 54·8, $Pr^{\beta}{}_2O$ 70·4, PhOH 34·1, NH_2Ph 45·8, BzOH 40·8, and sucrose 86·1 g.-cal. per 1°. (I) has a transition point at 146·0° abs. Latent heats of fusion have been determined, and mol.-free energies have been calc. The val. of the latter for $CO(NH_2)_2$ agrees with the val. derived from independent equilibrium data, thus affording further evidence of the validity of the third law of thermodynamics. J. G. A. G.

Dissociation pressure of calcium carbonate. I. Differential thermocouple method. M. Matsui, K. Bito, S. Murayama, and M. Kadono. **II.**

Differential manometer method. M. Matsui, K. Bito, and M. Kadono (J. Soc. Chem. Ind. Japan, 1933, **36**, 155—157b, 157—158b).—I. Results are given by $\log p = -37{,}251/4{\cdot}576T + 9{\cdot}9333$.

II. Observations are given by $\log p = -37{,}502/4{\cdot}576T + 10{\cdot}0092$. H. F. G.

Thermal dissociation of calcium carbonate in a carbon dioxide atmosphere. III. Primary and secondary dissociation points. K. Bito, K. Aoyama, and M. Matsui. **IV. Thermal change of precipitated calcium carbonate.** K. Bito and M. Matsui (J. Soc. Chem. Ind. Japan, 1933, **36**, 152—153b, 154—155b). III. Heating and cooling curves for Iceland spar are recorded.

IV. Corresponding curves for pptd. $CaCO_3$ are given. H. F. G.

Composition and dissociation of thallium peroxide. M. Centnerszwer and T. Trębaczkiewicz (Z. physikal. Chem., 1933, **165**, 367—371).—Tl peroxide, formed at a Pt anode on electrolysis of Tl_2SO_4 solution, has the empirical formula TlO_2, the mol. formula probably being Tl_2O_4. In O_2 (1 atm.) it loses O_2 reversibly above 573°, forming Tl_2O_3. The dissociation pressure, p, between 350° and 573° can be represented by $\log p = -27055/(4{\cdot}571T) + 1{\cdot}751 \log T + 0{\cdot}0052T/4{\cdot}571 + 2{\cdot}8$. The heat of dissociation is 27,055 g.-cal. per mol. of O_2 lost. R. C.

System $BiCl_3$–$ZnCl_2$. E. Jänecke (Z. anorg. Chem., 1933, **213**, 149—154).—A simple eutectic is shown at 215°. Reported abnormalities (Herrmann, A., 1911, ii, 801) are due to BiOCl, formed by H_2O or by exposure to atm. O_2 at 300°. H. J. E.

Affinity of metals for sulphur. IV. Dissociation of zinc and manganese sulphides. E. V. Britzke, A. F. Kapustinski, and B. K. Vesselovski. **V. General conclusions.** E. V. Britzke and A. F. Kapustinski (Z. anorg. Chem., 1933, **213**, 65—70, 71—76).—IV. From static measurements of the equilibrium between ZnS or MnS and gaseous HCl between 300° and 1100°, the dissociation pressures of ZnS and MnS and the affinity of Zn and Mn for S were calc. The heat of formation of MnS=44,600 g.-cal.

V. Dissociation pressures and heats of dissociation of metal sulphides and the order of affinity of metals for S are summarised. The more dissociated a metal sulphide is in solution, the less is its thermal dissociation. H. J. E.

M.-p. diagram of the system phenol–benzoic acid. N. F. Moerman (Rec. trav. chim., 1933, **52**, 601—606).—The system exhibits a eutectic at 31·5°. Liquid PhOH and BzOH have no measurable heat of mixing; their dipole moments are probably approx. equal. E. S. H.

Binary systems. III. Systems with ethane as volatile component. F. E. C. Scheffer and J. Smittenberg (Rec. trav. chim., 1933, **52**, 607—614; cf. A., 1932, 1204).—Data for *as*-*o*-xylidine, *p*-toluidine, *o*- and *m*-$C_6H_4Cl{\cdot}NO_2$, *o*-nitrophenol, and *p*-$C_6H_4Cl{\cdot}NH_2$ afford no evidence of compound formation. E. S. H.

Thermal analysis of certain organic compounds. F. Adamanis (Rocz. Chem., 1933, **13**, 351—359).—The fusion diagrams for 19 binary systems, comprising all possible combinations of quinine, carbamide (I), phenacetin (II), antipyrine, ethylurethane, menthol, and salol, have been determined. Compound formation is in no case indicated. The systems (I)–salol, –menthol, or –quinine yield two immiscible liquid phases, whilst the system (I)–(II) exhibits immiscibility between 3·7 and 65·8 mol.-% of (II). R. T.

System bismuth–tellurium–sulphur. Oruetite. J. Garrido (Anal. Fís. Quím., 1933, **31**, 99—102).—Although the analysis of oruetite conforms closely to the formula Bi_8TeS_4, *X*-ray analysis shows the mineral to consist of a eutectic mixture of various compounds interspersed with Bi. H. F. G.

Equilibria in the system $Ba(NO_3)_2$–HNO_3–H_2O at 18°. R. Fricke and F. Brümmer (Z. anorg. Chem., 1933, **213**, 319—320).—The solubility of $Ba(NO_3)_2$ in H_2O at 18° decreases almost hyperbolically with addition of HNO_3 from 0·6 g.-equiv. per 1000 g. of solution to 0·0256 g.-equiv. with 3·4372 g.-equiv. of HNO_3. A. R. P.

Thermodynamical study of systems of the type $PbCl_2$–RCl–H_2O at 25°. II. A. J. Allmand and L. J. Burrage (Trans. Faraday Soc., 1933, **29**, 679—689; cf. A., 1927, 1030).—Electrometric measurements have been made on the system $PbCl_2$–KCl–H_2O, and the activities of the three components evaluated. J. S. A.

Ternary system $K_4Fe(CN)_6$–K_2SO_4–H_2O. E. Bovalini and E. Fabris (Gazzetta, 1933, **63**, 338—344).—The equilibrium relations at 0°, 30°, 40°, 65°, 74°, 85°, and 90° have been examined. O. J. W.

Heterogeneous equilibrium of system CdI_2–KI–H_2O. H. Hering (Compt. rend., 1933, **197**, 243—245; cf. A., 1932, 574).—CdI_2 crystallises with $4H_2O$ at −2·9°; CdI_2,KI,H_2O exists up to 100°; $CdI_2,2KI$ crystallises with 1 or $2H_2O$ above or below −15·3°, and above 76° with $0{\cdot}5H_2O$. $2CdI_2,3KI,4H_2O$ is formed between 10·3° and −27·6° from solutions containing 0·511—0·536KI per mol. of CdI_2. C. A. S.

System zinc oxalate, potassium oxalate, water. I. At 25°. V. Metler and W. C. Vosburgh (J. Amer. Chem. Soc., 1933, **55**, 2625—2629).—The solubilities in aq. $K_2C_2O_4$ have been determined of ZnC_2O_4 and the complex *salt* $K_2Zn(C_2O_4)_2,7H_2O$ (I) which coexists with the more conc. solutions. (I) is metastable above 34°. J. G. A. G.

Preparation of ammonium phosphates. II. L. E. Berlin and B. M. Mantzev (J. Appl. Chem. Russ., 1933, **6**, 385—389).—The 25° isotherm for the system H_2O–NH_3–P_2O_5–SO_3 has been determined. R. T.

Reciprocal salt pair $CoSO_4 + K_2Cl_2 \rightleftharpoons CoCl_2 + K_2SO_4$. D. Längauer (Z. anorg. Chem., 1933, **213**, 180—182).—Equilibrium data for 25° are recorded. H. J. E.

Lowering of eutectic point of system H_2O–KNO_3–NH_4Cl. H. Muller (Compt. rend., 1933, **197**, 241—243; cf. this vol., 566).—The mol. lowering for the eutectic (H_2O 100, KNO_3 11·9, NH_4Cl 25·1; −18·09°) is 13·1°. C. A. S.

Equilibria of the quaternary system Na_2SO_4–$(NH_4)_2SO_4$–NH_3–H_2O. A. P. Belopolski and N. P. Alexandrov (J. Appl. Chem. Russ., 1933, **6**, 390—415).—The solid phases at 0° and 15° are mirabilite (I), Na_2SO_4 (II), $Na_2SO_4,(NH_4)_2SO_4,4H_2O$ (III), and $(NH_4)_2SO_4$ (IV). (III) is unstable in solutions containing $>$ 65·25 g. of NH_3 per 100 g. H_2O at 0°; the necessary NH_3 concn. rises with temp. A process is described for the prep. of almost pure (IV) from the mother-liquor (V) remaining after crystallisation of Na_2CO_3, prepared from (I) by the Solvay process. Most of (II) in (V) is removed by freezing at −10°, and (IV) is fractionally salted out by addition of NH_3. R. T.

Influence of small amounts of dissolved silicates on the conductance of conductivity water and very dilute solutions of electrolytes. T. I. Taylor (J. Physical Chem., 1933, **37**, 765—777).—The effect of the addition of small amounts of Na silicate on the conductance of conductivity H_2O collected and stored in vessels of pyrex or soft glass has been determined. If the H_2O contains CO_2 there is an initial decrease of conductance due to its reaction with the silicate. On storage CO_2 disappears at a rate depending on the nature and pre-treatment of the storage vessel, owing to reaction with silicates dissolved from it. Very dil. solutions of HCl, NaOH, and KCl have been similarly examined. The "solvent" correction to be applied in conductivity measurements is discussed. F. L. U.

Equivalent conductance of aqueous barium hydroxide solutions [at 28°]. H. G. Leopold and J. M. Luck (J. Amer. Chem. Soc., 1933, **55**, 2655—2656).—The data refer to 0·016—0·21M-$Ba(OH)_2$. J. G. A. G.

Conductivity of alkylammonium picrates in aqueous solution at 0°, 25°, and 90°. III. Hydrolysis of the salts examined. P. Ekwall (Z. physikal. Chem., 1933, **165**, 331—337).—From data for the degree of hydrolysis mobility data (this vol., 467) are revised, without, however, altering the conclusions as to the validity of Stokes' law originally reached. R. C.

Electrical conductivity of solutions of uni-univalent salts in ethyl alcohol. M. Barak and (Sir) H. Hartley (Z. physikal. Chem., 1933, **165**, 272—293).—The conductivities of alkali and NEt_4 salts, NaOEt, and $NaEtCO_3$ have been measured at 25° at concns. of 0·0001—0·0013N. For all these $\Lambda_c = \Lambda_0 - xc^{\frac{1}{2}}$, where c is the concn., but for most x deviates considerably from the Debye–Hückel–Onsager val. The relation of the deviation to the ionic size as deduced from mobility data agrees with the theoretical connexion between the latter and the formation of ion pairs making no contribution to the conductivity. The mobilities of univalent ions in EtOH show that except for some Li salts all uni-univalent salts are somewhat associated even in dil. solution. In a group of analogous alkali salts the degree of association increases with the at. no. of the metal. The mobilities of the alkali ions increase from $Li^{\cdot}$ to $Cs^{\cdot}$, and their effective sizes are greater in EtOH than in H_2O. The effect of the addition of small amounts of H_2O on the conductivity of the EtOH solutions has been examined. R. C.

Anomalous electrolytes. II. Electrical conductivity of solutions of iodine and iodine compounds in ketones. E. J. Birr (Z. physikal. Chem., 1933, **165**, 311—322; cf. this vol., 354).—The nature of these solutions has been investigated by measurements of their conductivity and its change on keeping. I dissolved in $COPh_2$ is simply dissociated into $I^{\cdot}$ and I', whilst in *cyclo*hexanone solution a solvate is formed, which ionises largely. In $COMe_2$, COMeEt, and COPhMe solution the I adds itself to the enol form of the solvent, and the resulting iodohydrin, a pseudo-electrolyte, is more slowly transformed into a non-electrolyte, so that ultimately the conductivity falls to zero. ICN in COMeEt behaves similarly, but ICl_3 follows a more complicated scheme of reaction. R. C.

Conductivity and state of electrolytes dissolved in metal alkyls. F. Hein and H. Pauling (Z. physikal. Chem., 1933, **165**, 338—366, and Z. Elektrochem., 1933, **39**, 537—538).—The mol. conductivity, μ, of solutions of tetra-alkylammonium halides in $ZnEt_2$, $CdEt_2$, and $AlEt_3$ has been determined. The μ–concn. curve for tetra*iso*amylammonium iodide (I) in $ZnEt_2$ solution exhibits a max. This, however, disappears if μ is corr. for viscosity by multiplication with η_v/η_∞, and the curve can then be represented by $\mu_{\text{corr.}}v^n$=const., where v is the dilution and n a const. For a given cation μ increases with the at. wt. of the anion, and for a given anion with the mol. wt. of the cation. Owing to solvation the solutions exhibit high osmotic effects, *e.g.*, in $ZnEt_2$ (I) has the association factor 2. Solvent and dissociating powers decrease in the order $ZnMe_2$, $ZnEt_2$, $CdEt_2$, $AlEt_3$, $HgEt_2$, primarily because the solvating power decreases in the same order. The metal alkyls are to be regarded as insulators comparable with C_6H_6 and $CHCl_3$, although the osmotic effects of insulators are very small. In $ZnEt_2$ or $CHCl_3$ solution C_5H_5NEtI is gradually partly converted into an isomeride. The *compound* $2NEt_4I,ZnEt_2$ has been isolated. R. C.

Electrolytic solutions. V. Conductance of amido-salts in liquid ammonia. C. A. Kraus and W. W. Hawes (J. Amer. Chem. Soc., 1933, **55**, 2776—2785).—From conductivity measurements in liquid NH_3 at −33°, the limiting conductance and dissociation consts., K, of NHNaPh, $NNaPh_2$, $NH_2Na{\cdot}BPh_3$, $NKPh_2$, and $NH_2K{\cdot}BPh_3$ have been calc. Vals. of K increase with increasing size of the negative ions, but bear no relation to their electron affinity. The results are consistent with the theory which attributes the process of ion association to Coulomb forces (this vol., 464). J. G. A. G.

Anhydrous hydrazine as an ionising medium for electrolytes and non-electrolytes. I. Behaviour of typical electrolytes and half electrolytes. P. Walden and H. Hilgert (Z. physikal. Chem., 1933, **165**, 241—271).—Conductivities of solutions of org. and inorg. salts and org. acids at dilutions up to 2500—5000 litres have been measured at 0° and 25°. For all the solutes $\lambda_\infty = \lambda_c + a\sqrt{c}$ at dilutions $\nless (272/\varepsilon)^3$, ε being the dielectric const. of N_2H_4. The vals. of $Kn_1n_2/\varepsilon\eta$, where n_1 and n_2 are the valencies of the ions and η is the viscosity of N_2H_4, usually agree with the observed vals. of a (A., 1924, ii, 387), whilst some of the Debye–Hückel vals. are too small. N_2H_4 is a highly ionising medium, differences in strength between dissolved electrolytes being obscured. Already at a dilution of 375 litres all the solutes have the same degree of ionisation (0·935). The val. of $\lambda_\infty\eta$ is about the same for all the salts, but far exceeds the val. for other non-aq. media. Solutions of N_2H_4 salts have no detectable Grotthus conductivity. Mono-, di-, and tri-alkylammonium chlorides are solvolysed. The principle of independent migration of the ions is valid. In solvents of the N_2H_4 type the val. of $\varepsilon v^{\frac{1}{3}}$, where v is the dilution corresponding with a given degree of ionisation, is at high dilutions the same for all binary salts and is independent of the solvent. Many solutions of salts in differentiating solvents deviate widely from this relation. R. C.

Transport of matter and the passage of current in liquid alloys. K. Schwarz (Z. Elektrochem., 1933, 39, 550—554; cf. A., 1931, 1236).—The transport nos. of Na and K in their amalgams at 26° agree with the vals. calc. from the diffusion potentials. In such liquids the metal is practically completely dissociated into electrons and metal ions of the lowest valency stage. In the electrolysis of binary liquid alloys the ion with the greater charge density moves to the cathode. H. J. E.

Electrical conductivity of solutions of electrolytes in strong fields and at high frequencies. P. Debye (Z. Elektrochem., 1933, 39, 478—482).—A survey of recent developments. H. J. E.

Molecular conductivity of the hydrogen halide acids and nitric acid at high concentrations. E. Wilke (Z. Elektrochem., 1933, 39, 526).—Between 0·1 and 10N the mol. conductivity of the four acids at the same concn. is equal. The conductivity is proportional to concn.$^{1/3}$ H. J. E.

Peculiarities in the conductivity relations of non-aqueous solutions. H. Ulich (Z. Elektrochem., 1933, 39, 483—489).—Electrolytes are divided into (i) those in which the ions are already formed (*e.g.*, NaCl), and (ii) those in which the ions are formed in a reaction (*e.g.*, $NH_3+HX=NH_4^++X^-$; $HCl+Y=Cl^-+HY^+$). (ii) is subdivided into cases where transfer of a proton occurs, those in which an electron transition takes place, and those in which a halogen ion is transferred. This classification is illustrated for various electrolytes and solvents. H. J. E.

Conductivity in solvents of very low dielectric constant. R. M. Fuoss (Z. Elektrochem., 1933, 39, 513—516; cf. this vol., 464).—The conductivity curves for tetra*iso*amylammonium nitrate in mixtures of dioxan (dielectric const. 2·2) and H_2O (78) show min. vals. at concns. which fall as the dielectric const. of the medium decreases. The increased tendency to form pairs and groups of ions due to the lower dielectric const. is discussed. H. J. E.

Electrical conductivity of some fused salt mixtures. E. Ryschkewitsch (Z. Elektrochem., 1933, 39, 531—537).—The sp. conductivity of NaCl, KCl, Na_2CO_3, LiCl, LiF, NaCN, $CaCl_2$, and of NaCl–KCl, NaCl–$CaCl_2$, NaCl–KCl–$CaCl_2$, NaCl–KF, and NaCl–Na_2CO_3 mixtures has been measured between approx. 600° and 1000°. H. J. E.

Electrical conductivity of capillary and colloidal systems. J. J. Bikerman (Z. Elektrochem., 1933, 39, 526—531).—Theoretical. The Debye theory is applied to colloidal particles, for which interionic forces are much stronger than in true solutions, and in which the colloid ion has a correspondingly lower mobility. H. J. E.

Electrostatic theory of the dependence of ionic mobility and dielectric constant on the frequency in mixed solutions of strong electrolytes. H. Falkenhagen and W. Fischer (Z. Elektrochem., 1933, 39, 517—520; cf. this vol., 8).—Theoretical. Expressions are derived for the conductivity and change of dielectric const. for mixed electrolytes in a high-frequency field. These are applied to Spaght's experiments on aq. KCl+aq. $Ca_2Fe(CN)_6$ (A., 1932, 998). H. J. E.

Demonstration of the high-frequency effect in electrolytes. P. Debye and H. Sack (Z. Elektrochem., 1933, 39, 512—513).—The conductivity cell is made to serve as a thermometer bulb (50 c.c.), by an attached capillary. Differences in conductivity using high frequency are demonstrated by a change in the rate of heating of the electrolyte as shown by the liquid rise in the capillary. H. J. E.

Electrostatic theory of dependence of ionic mobility on frequency and dielectric constants in mixed solutions of strong electrolytes. II. Generalisation of the Bennewitz–Wagner–Kühler calculation for the non-stationary state. H. Falkenhagen and W. Fischer (Physikal. Z., 1933, 34, 593—602).—Theoretical. The general solution of the problem of dispersion of conductivity and dielectric consts. of mixed electrolytes is developed, and an explanation of Spaght's dispersion curve given. A. J. M.

Time factor in the conductivity and dielectric capacity of electrolytes in solvents of various viscosities. O. Dobenecker (Ann. Physik, 1933, [v], 17, 699—715).—The time factor has been examined for wave-lengths of 13·5, 9·0, and 4·5 m. in solvents of high viscosity. The viscosity of the solvent was varied by adding sucrose. Sucrose solution shows a large anomalous dipole absorption, and a small dielectric dispersion for short waves, and the magnitudes of both these effects were determined by comparison with a $COMe_2$–H_2O mixture of the same dielectric const. and conductivity. The time factor was determined for NaCl, K_2SO_4, $MgSO_4$, and $Ba_3[Fe(CN)_6]_2$ in sucrose solutions of various concns., and for $K_4Fe(CN)_6$ in 67% sucrose solution. In accordance with theory, the time factor in the case of conductivity increases with the valency and with the frequency, but the effect is $>$ that indicated by theory. The time factor in the case of dielectric capacity is $<$ the theoretical. A. J. M.

Thermo-electric force and Ludwig–Soret effect in solid salts and mixed crystals, and their relation to electrolytic conductivity. H. Reinhold (Z. Elektrochem., 1933, 39, 555—561; cf. this vol., 677).—Theoretical. Systems of the type CuBr–AgBr and Ag_2S–Cu_2S are discussed. H. J. E.

Thermodynamic consideration of the system perfect electrode–dilute solution. K. Gumiński (Rocz. Chem., 1933, 13, 301—305).—Theoretical. R. T.

Potential difference between copper and its amalgam and the reproducibility of the copper electrode. M. Oku (Sci. Rep. Tôhoku, 1933, 22, 288—300).—A standard Cu electrode can be prepared by electrolysis of aq. $CuSO_4$ acidified with H_2SO_4 using a Pt anode and a high c.d. The e.m.f. of the cell Cu|aq. $CuSO_4$|Cu(Hg) is 0·00512 at 25° and $dE/dT=0{\cdot}0000737$ volt per 1° between 0° and 35°. The standard free energy of formation of Cu amalgam is −236 g.-cal. and the heat of formation −1250 g.-cal. A. R. P.

Electrophoretic null point for mercury in aqueous solutions. S. R. Craxford (Phil. Mag., 1933, [vii], 16, 268—274). The potential of the electrophoretic null point for a Hg drop in a series of solutions has been found to be identical, within experimental error, with the electrolytic null point given by the potential of the electrocapillary max., even when the salt from the solution is strongly adsorbed at the surface of the Hg drop. J. W. S.

Effect of sugars on the p_H of sodium molybdate solutions. P. Thomas and (Mlle.) C. Kalman (Compt. rend., 1933, 197, 330—331).—Addition of mannose, fructose, xylose, or galactose increases the acidity or alkalinity of solutions of Na tungstate or molybdate (I), according to whether the solution is initially acid or alkaline. With (I) the effect of the sugars decreases in the order given and the point of inflexion is at p_H 5·7 in all cases. R. S. C.

Hydrolysis and the oxidation–reduction potential of the system $Fe^{\cdot\cdot\cdot}$–$Fe^{\cdot\cdot}$. P. A. Kriukov and G. P. Avsejevitsch (Proc. Leningrad Dept. Inst. Fert., 1933, 17, 135—150).—Glass electrode data for the system are recorded. A. M.

Oxidation–reduction potentials of chlororaphin. B. Elema (Rec. trav. chim., 1933, 52, 569—583).—Oxidation–reduction potentials of phenazine-1-carboxylamide (the oxidation product of chlororaphin; cf. A., 1932, 1043) have shown that in the acid region the reversible reaction occurs in two steps. The results cannot be explained by the formation of a meriquinone, as only one electron is involved in each step; a semiquinone, identical with chlororaphin, is probably formed. The two steps are definite at $p_H < 1$, but in less acid solutions they overlap. At $p_H > 4$ no semiquinone can be detected, and the usual one-step oxidation involving two electrons occurs. E. S. H.

Electrochemistry of photosensitive electrodes with copper salts. R. Audubert (J. Chim. phys., 1933, 30, 389—395).—Cu coated with CuO, Cu_2O, CuI, CuBr, CuCl, or collodion containing an org. dye forms a photosensitive electrode, an illuminated electrode acting in general as anode to an unilluminated one. In contact with $Cu^{\cdot\cdot}$ ions, the latter behaves as a simple Cu electrode. The potential is identical in vac. or in presence of N_2 or H_2, but varies with $[O_2]$, the equilibria $2Cu^{\cdot} \rightleftharpoons Cu^{\cdot\cdot} + Cu$ and $4Cu^{\cdot} + O_2 + 2H_2O \rightleftharpoons 4Cu^{\cdot\cdot} + 4OH'$ being maintained at the electrode. D. R. D.

Boundary conditions for the wave equation. W. H. McCrea and R. A. Newing (Proc. Roy. Soc., 1933, **A**, 141, 216—217).—Mathematical. L. L. B.

Homogeneous reaction between hydrogen and fluorine. H. Eyring and L. S. Kassel (J. Amer. Chem. Soc., 1933, 55, 2796—2797).—There is no appreciable homogeneous reaction between H_2 and F_2 at room temp., but explosions are caused by introduction of extraneous matter. Thermal reaction by way of chains may be expected to begin at 150—250°. J. G. A. G.

Explosions of mixtures of hydrogen and air: specific heats of steam at high temperatures. G. B. Maxwell and R. V. Wheeler (J.C.S., 1933, 882—885).—From time–pressure curves of mixtures of H_2 and air fired centrally in a sphere 19·7 cm. diam., vals. of the sp. heat of steam have been calc. which are > those usually accepted. F. L. U.

Upper pressure limit in the chain reaction between hydrogen and oxygen. G. H. Grant and C. N. Hinshelwood (Proc. Roy. Soc., 1933, **A**, 141, 29—40).—The influence of surface, diameter of vessel, H_2–O_2 ratio, inert gases, and temp. on the upper pressure limit of the low-pressure explosion of H_2 and O_2 has been investigated. The variation of the explosion pressure with H_2–O_2 ratio and with the pressure of the inert gas present can be quantitatively explained on the hypothesis that at the upper limit a branching chain process is balanced by gas phase deactivation in ternary collisions. The theory also explains the very different influences of temp. on the upper and lower limits. L. L. B.

Explosions of methane and air: propagation through a restricted tube. H. Robinson and R. V. Wheeler (J.C.S., 1933, 758—760).—No discontinuity in the combustion within the restricted zone, and no sudden increment in speed of the flame, such as occurs when a detonation wave is initiated, could be detected during the explosion of a mixture containing 10% CH_4 in an open-ended tube 32·3 m. long and 30·5 cm. in diam., provided with eleven rings reducing the diam. to 10·2 cm. (cf. B., 1926, 970). F. L. U.

Influence of temperature on limits of inflammation of combustible vapours. M. Briand, P. Dumanois, and P. Laffitte (Compt. rend., 1933, 197, 322—323).—Temp.–concn. curves for the inflammation of mixtures of air and pure C_6H_6, PhMe, and *cyclo*-hexane and -hexene for temp. 100—300° in a wide pyrex vessel have been determined. They are straight lines slowly falling and rising from the temp. axis, respectively, save as regards the max. concn. of PhMe, which after rising falls slightly, indicating slow preliminary combustion. These results agree with those of White, but not with Berl and Fischer's, due probably to the doubtful purity of their materials and use of too narrow a tube (cf. A., 1925, ii, 553, 413). C. A. S.

Combustion of light hydrocarbons at constant volume. I—III. M. Akita (J. Soc. Chem. Ind. Japan, 1933, **36**, 436—440B).—I. When a mixture of a *n*-paraffin or a *n*-primary alcohol and air or O_2 is heated in a SiO_2 vessel a no. of sudden pressure rises occurs and oxidation is complete at 570—580° (hydrocarbons) or 530—570° (alcohols). The no. of sudden rises is equal to the no. of C atoms in the mol., the temp. at each rise is equal to that of the next following rise for the next higher homologue, and the temp. (except the first) are the same for the alcohols and the hydrocarbons. The following reaction mechanism is suggested: $C_nH_{2n+2}+O\longrightarrow C_nH_{2n+1}\cdot OH\longrightarrow C_{n-1}H_{2n}+CH_2O$; $CH_2O+O\longrightarrow CO(\text{or } CO_2)+H_2O$.

II. The heats of reaction at the three stages are +33·8, −11·9, and +21·9 g.-cal., respectively, independent of the val. of *n*. As *n* increases the flame propagation velocity (I) increases and the combustion velocity (II) diminishes. The initial reaction temp. is the same as the spontaneous ignition temp.

III. Knocking of hydrocarbons diminishes with increasing energy requirement for initiating combustion, with diminishing (I), with increasing (II), and (within a homologous series) with rising reaction temp. Anti-knock agents raise the reaction temp. When the energy required to initiate combustion is low sufficient is supplied by the engine compression and knocking occurs. A. G.

Explosion of carbon disulphide–nitric oxide mixtures. II. J. A. M. van Liempt and J. A. de Vriend (Rec. trav. chim., 1933, **52**, 549—566; cf. this vol., 355).—The degree of association of CS_2 at room temp. and 5—20 mm. is about 3%. The products of reaction differ according to the ratio CS_2 : NO; with increasing amount of NO the amount of S produced decreases. The variation of light energy with composition of the mixture, and the yield for the optimal mixture have been determined. The duration of the flash is shortest when CS_2 : NO= 1 : 3 or 1 : 4, and increases with increasing pressure or vol. For practical purposes (*e.g.*, photography) the duration of the flash may be taken as 0·02 sec.; the light intensity rises relatively slowly at first, then rapidly, to a max., after which it falls rapidly at first and then slowly. E. S. H.

Explosive properties of propylene dichloride–air mixtures. G. W. Jones, W. E. Miller, and H. Seaman (Ind. Eng. Chem., 1933, **25**, 771—773).—The limits of inflammability of $CHMeCl\cdot CH_2Cl$ (I) in dry air at normal pressures and temp. up to 100° are from 3·4 to 14·5 vol.-%. The max. pressure developed in the apparatus used was 67 lb. per sq. in. above atm.; this was given by mixtures containing 5·02% of (I), *i.e.*, slightly > the amount (4·95%) necessary to consume all the O_2 present. (I)–air mixtures developed a max. pressure slightly > that for CH_4 (II)–air mixtures and considerably < that for $COMe_2$ (III), manufactured gas (IV), and HCO_2Me (V). The ignition temp. of (I) were < those for (II), approx.= those for (III) and (IV), and > those for (V). C. E. M.

Thermal decomposition of acetaldehyde and the existence of different activated states. C. J. M. Fletcher and C. N. Hinshelwood (Proc. Roy. Soc., 1933, A, **141**, 41—55).—The rate of decomp. of MeCHO has been measured over a range of initial pressures 0·2—1100 mm. Abrupt changes of slope are shown by the curve connecting reciprocal of time of half decomp. with initial pressure. These results are explained on the assumption that the reaction, even when wholly homogeneous, is kinetically composite, and can be interpreted by the theory that the MeCHO mol. can be activated in a limited no. of ways, and that the different activated states are associated with different transformation probabilities. There are thus several virtually independent quasi-unimol. decomps. for the same chemical reaction. L. L. B.

Thermal decomposition of ethyl azide: homogeneous unimolecular reaction. J. A. Leermakers (J. Amer. Chem. Soc., 1933, **55**, 2719—2729).—The thermal decomp. of 0·08—19·5 cm. of EtN_3 at 199—240° affords N_2, C_2H_4, HN_3, CHMe:NH, C_4H_{10}, and a solid. The reaction is of first order at high pressure, $k_\infty=2\times10^{14}e^{-39,740/RT}$, but k decreases when the pressure is depressed below 2 cm. For the theoretical expressions relating k and pressure to be consistent with the data, a mol. diam. of $6{\cdot}2\times10^{-8}$ cm. and fourteen classical oscillators are required. k is slightly and consistently diminished by increasing the surface : vol. ratio of the reaction vessel. J. G. A. G.

Effect of solvent on the reaction between iodine and hydrogen sulphide. M. R. A. Rao and B. S. Rao (J.C.S., 1933, 836—839).—I and H_2S do not interact in dry CCl_4 solution, but addition of C_5H_5N causes rapid and complete reaction. The reaction is slow and incomplete when small quantities of H_2O or EtOH are present in the solvent. In dry Et_2O the reaction is slow but nearly complete. The progress of the reaction in a given solvent depends on removal of the HI formed; *e.g.*, with C_5H_5N in CCl_4 it is pptd. F. L. U.

Spontaneous change in aqueous solutions of stannic chloride. J. Guéron (Compt. rend., 1933, **197**, 247—249).—The % of Sn not flocculated in aq. solutions containing 2—40 g. of $SnCl_4,5H_2O$ per litre at 20° when plotted against time give similar curves, showing first a period of induction decreasing with decreasing concn. and shorter when tested by ultrafiltration than by centrifuging, followed by a period of flocculation in which most of the Sn is removed by either method, and lastly a period in which the Sn in solution tends to a limit of about 1%. The p_H is always the same as that of the clear liquid, and remains const. as soon as the solution has become opalescent. Only 2±0·5% of the Cl is carried down with the ppt. when formed spontaneously, and this is wholly removed on agitation and centrifuging (cf. J.C.S., 1922, **121**, 441; A., 1929, 29; 1932, 692). C. A. S.

Velocity of bromination of ethyl acetoacetate. I. The water reaction. K. J. Pedersen (J. Physical Chem., 1933, **37**, 751—764).—The velocity has been measured at 18° when the ester is dissolved in H_2O, and in aq. solutions of HCl, NaCl, KCl, and KBr. It is independent of [Br] and is not catalysed by $H^{\cdot}$. The measurements indicate the occurrence of the consecutive reactions (1) $\cdot CO\cdot CH_2\cdot \longrightarrow \cdot C(OH):CH\cdot$, (2) $\cdot C(OH):CH\cdot + Br_2 \longrightarrow \cdot CO\cdot CHBr\cdot + H^{\cdot} + Br'$, (3) $\cdot CO\cdot CHBr\cdot \longrightarrow \cdot C(OH):CBr\cdot$, (4) $\cdot C(OH):CBr\cdot + Br_2 \longrightarrow \cdot CO\cdot CBr_2\cdot + H^{\cdot} + Br'$. The observed velocity is determined by (1) and (3). F. L. U.

Increase in reaction velocity of tertiary acids by the presence of a carbonyl group in the γ-position. H. Appel (Z. physiol. Chem., 1933, **218**, 202—208).—According to the accepted constitution of cholesterol the CO_2H group has a similar position in the acids $C_{24}H_{40}O_3$ (I) and $C_{23}H_{38}O_3$ (II) (A., 1923, i, 1204). The great difference in the saponification velocity of the respective esters is due to the position of the :CO group relative to the CO_2H, since on reduction of the :CO to :CH_2 the esters show a similar saponification velocity, both behaving as esters of *tert.* acids. Evidently the reaction velocity of a *tert.* CO_2H is considerably increased by the presence of :CO in the γ-position. This is further exemplified in the behaviour of camphononic acid (III) and its reduction product. (II) gave the *acid* $C_{23}H_{40}O_2$, m.p. 134—135° [*Me* ester (IV), an oil; *semicarbazone* of (IV), m.p. 182·5°], by Clemmensen reduction. (III) [*semicarbazone* (V), m.p. 225°] formed the *Me* ester, m.p. 29·5—30° (*semicarbazone*, m.p. 220—221°), with CH_2N_2. By Wolff–Kishner reduction at 180°, (V) afforded *camphonanic acid*, m.p. 190—191°, $[\alpha]_D^{15} + 17{\cdot}1°$ in C_6H_6 (*Me* ester, m.p. −6°). J. H. B.

Mechanism of oxidation processes. XXXIV. Anaërobic fermentation of citric acid by yeast. H. Wieland and R. Sonderhoff. **XXXV. Aërobic dehydrogenation of alcohol by yeast.** H. Wieland and F. Wille.—See this vol., 865.

Heterogeneous reactions of the type $A_{solid} + B_{gaseous} \rightleftharpoons C_{solid}$. I. Inconstancy of equilibrium pressure, "apparent equilibria," and their interpretation. II. Kinetics of formation and decomposition of carbonates. J. Zawadzki and S. Bretsznajder (Z. physikal. Chem., 1933, **B**, **22**, 60—78, 79—96; cf. this vol., 474).—I. In such reactions as $CaCO_3 \rightleftharpoons CaO + CO_2$ there may be considerable delay in the establishment of the equilibrium pressure, *p*. Thus if CaO is subjected to a CO_2 pressure much $> p$ and the temp. varied the apparent equilibrium pressures are all too high, whilst if $CaCO_3$ is rapidly decomposed by vac. treatment the pressure–temp. curves are initially too low. Under some conditions the pressure–temp. curves ultimately become normal, but sometimes they fail to do this. A possible partial explanation of these phenomena is that when reaction is rapid a large no. of nuclei of resultant are formed which are so small as to have abnormal dissociation pressures. To arrive at a complete explanation it seems necessary to suppose that the chemosorption of CO_2 prior to the appearance of a second solid phase is not confined to a surface layer, but that between surface compounds in Langmuir's sense and systems of two solid phases there may exist stable intermediate systems with a decomp. tension depending on the composition, particle size, and no. and kind of the active centres.

II. Measurements of the effect of pressure, composition, structure, previous history of the system, and temp. on the rates of the reactions $CaCO_3 \rightleftharpoons CaO + CO_2$ and $CdCO_3 \rightleftharpoons CdO + CO_2$ have given results agreeing with the above theory. R. C.

Autoxidation. VIII. Decomposition of dithionic acid. P. Goldfinger and H. D. Graf von Schweinitz (Z. physikal. Chem., 1933, **B**, **22**, 117—133; cf. this vol., 25).—In acid solution at 85° the rate of decomp. is proportional to $[H^{\cdot}]$ and $[S_2O_6'']$. From the experimental data the heat of activation, Q, is calc. to be 29·8 kg.-cal. for a frequency exponent of 14·2, whilst assuming 10 degrees of freedom to be involved in the decomp. of $H_2S_2O_6$ by H_2O in acid solution the val. of 32·6 kg.-cal. results. In alkaline solution at 120—180° there is decomp. into SO_3'' and SO_4'' at a rate which is proportional to $[S_2O_6'']$ and $[OH']$, unless either of these $> 0{\cdot}32N$, when the velocity coeff. increases with the concn. For this reaction the val. of Q is 25 kg.-cal. In neutral solution decomp. into SO_3'' and SO_4'' occurs at a rate independent of $[H^{\cdot}]$ and $[OH']$. The addition of SO_3'', SO_4'', CrO_4'', and BrO_3' does not influence the rate of decomp. in acid, alkaline, or neutral solutions. It is considered that the process the velocity of which is measured is $S_2O_6'' + H_2O = SO_3'' + SO_4'' + 2H^{\cdot}$, not $H_2S_2O_6 = 2HSO_3$. The absorption of heat in the latter reaction is at least 37 kg.-cal., which also represents a lower limit for the firmness with which the S atoms in $H_2S_2O_6$ are linked. R. C.

Influence of magnetic field on corrosion of iron in solutions of salts of noble metals. H. Forestier and (Mlle.) M. Haury (Compt. rend., 1933, **197**, 54—56; cf. A., 1930, 1002).—The ratio of the amounts of Fe dissolved in presence of a magnetic field to that dissolved in its absence increases with increasing field strength at a decreasing rate tending to a limit, the order of the effect being $HgCl_2 > AuCl_3 > AgF$. When these ratios are plotted against concn. of the other metal there is, except with AgF, first an increase, then a decrease tending to a limit increasing in the order AgF, $AuCl_3$, $HgCl_2$, $CuCl_2$, $CuBr_2$. The effect is attributed to increase in solution pressure of Fe by magnetisation. C. A. S.

Influence of fluid velocity on heterogeneous reactions. I. General theory. S. Uchida (J. Soc. Chem. Ind. Japan, 1933, **36**, 416—420B).—Heterogeneous reactions are dynamically similar to heat transfer processes, the temp. difference, thermal conductivity, and coeff. of heat transfer being replaced by the concn. difference, diffusion const., and reaction const., respectively. A. G.

Kinetics and heat of adsorption of oxygen on platinum. E. B. Maxted and N. J. Hassid (Trans. Faraday Soc., 1933, **29**, 698—702).—The heat of adsorption of O_2 on Pt-black is const. up to the stage where adsorption becomes relatively slow. At advanced stages, the rate of adsorption accords with the expression: adsorbed concn. $= kt^n$, but in the initial stages, the rate is markedly dependent on the pressure. J. S. A.

Catalysis of the hydrogen–sulphur reaction by minute traces of oxygen. E. E. Aynsley, T. G. Pearson, and P. L. Robinson (Nature, 1933, **132**, 101).—The curvature found by Norrish and Rideal (J.C.S., 1923, **123**, 696) in the $(\log d[H_2S]/dt)/(1/T)$

curve is due to traces of O_2 in the H_2–N_2 mixtures. As these traces are more and more completely removed by successive treatments of the H_2–N_2 mixture with alkaline pyrogallol or with $CrCl_2 + Zn$ the rate of H_2S formation approaches that obtained with pure H_2. L. S. T.

Acceleration and retardation by various elements of the oxidation of materials by sulphuric acid. J. Ranedo (Anal. Fís. Quím., 1933, **31**, 195—200).—The influence of compounds of 36 elements on the rate of oxidation of org. matter by hot conc. H_2SO_4, as used in the Kjeldahl method, has been determined. Pt, Pd, Se, Mo, and Hg reduce the time required for complete oxidation from 4·5 hr. to $<$ 1 hr., the three first-named being the most active; B, Al, La, Th, Pb, and Ta increase the time to 8—12 hr. The retarding agents are practically inoperative in presence of, *e.g.*, Pt. When Pt alone is used, the rate of oxidation falls considerably as the quantity of Pt present is reduced, whereas the rate in presence of Se falls but slowly as the Se concn. is reduced. H. F. G.

Inhibitors in reduction of vat dyes. E. Baur (Z. physikal. Chem., 1933, **B**, **22**, 231—239).—The reduction of methylene-blue and phenosafranine with H_2 and the oxidation of the leuco-compounds with O_2 are retarded by various org. and inorg. substances capable of forming reduction–oxidation systems. The retardation varies with the concn. of inhibitor according to the formula previously published (A., 1931, 1250, 1378). R. C.

Relation of hydrogen to nickel with special reference to the catalytic power of the latter. H. N. Huntzicker and L. Kahlenberg (Trans. Electrochem. Soc., 1933, **63**, 335—353).—Ni, free from S, was electrodeposited from $Ni(OAc)_2$ solution. After rubbing with sand, specimens were immersed in aq. solutions of various salts of Cu, Hg, and Ag. No displacement of these metals could be detected, but deposits of Cu_2Cl_2 and Hg_2Cl_2 were obtained from $CuCl_2$ and $HgCl_2$ solutions. From such experiments and from measurements of single potentials of Ni, Cu, Co, Ag, and Au in solutions of salts of Cu, Ag, and Ni, it is concluded that Ni is normally in a passive state which is not dependent on a surface effect. Immediately after cathodic treatment in H_3PO_4 solution Ni readily displaces Cu and Ag from their salt solutions, reduces $KMnO_4$, $FeCl_3$, KNO_3, etc., and, if the treatment has been sufficiently intensive or prolonged, will displace Co, Fe, and even Ni itself from their salt solutions. Raising the temp. of treatment above 35° gives a less active product. Ni charged with H exhibits no change in cryst. form according to the *X*-ray method. The H_2 liberated from Ni cathodes is markedly active even after it has completely left the metal surface; it will reduce S, P, As, Sb, and N_2. H. J. T. E.

Reaction mechanism. V. Active centres of typical hydrogenation catalyst. O. Schmidt (Z. physikal. Chem., 1933, **165**, 133—146; cf. A., 1932, 716).—For the hydrogenation of doubly linked C atoms the catalyst must have a porous fine-structure. Reaction probably takes place, not at active centres on the surface of the crystals, as Taylor supposes, but within the crystals in the cracks or pores visualised by Smekal; *i.e.*, it is not the adsorbed but the absorbed gases which react. The rate of hydrogenation is therefore to a large extent dependent on the closeness of the spacing of the catalyst mols. The active form of H which occurs within elements of the Fe and Pt group consists of positive ions, which could not exist on the surface of the crystals. For these catalysts the activation of the H and the hydrogenation is a reaction in solid solution. The mechanism of such hydrogenations as the above is not, however, necessarily identical with that of other catalysed reductions, such as the reduction of $PhNO_2$ with H_2. R. C.

Catalytic activity and potential of the catalyst. A. R. Miró and N. G. Morales (Anal. Fís. Quím., 1933, **31**, 103—114).—The activity of Pt in catalysing the decomp. of H_2O_2 solutions (0·4—0·5*N*) buffered with phosphate is a max. at p_H 12—13. The diminution of activity which is observed on repeated use of the catalyst is accompanied by an increase of the abs. potential of the Pt. A similar increase occurs in presence of a poison of the catalyst, whilst a reduction occurs during regeneration. When the catalyst is in contact for a prolonged period with strongly alkaline (4*N*-NaOH) solutions, gradual reduction of activity accompanied by slight change of potential is observed. The homogeneous unimol. velocity coeff. of the decomp. of H_2O_2 in $NaHCO_3$ solution passes through a min. at p_H 9·2 and a pronounced max. at p_H 9·7; in solutions buffered with phosphate there is a max. only, at p_H 12—13. H. F. G.

Catalytic activity of chromites for the oxidation of carbon monoxide. E. C. Lory (J. Physical Chem., 1933, **37**, 685—692).—The catalytic activity of Cu, Co, Ni, Fe^{II}, and Mn^{II} chromites in the oxidation of CO has been determined. The first three when heated undergo surface oxidation to chromate, and the last is reduced by CO at the temp. at which the substances are catalytically active. The catalytic action is explained on this basis. F. L. U.

Surface electrons in adsorption and catalysis. H. P. Cady and W. E. White (J. Physical Chem., 1933, **37**, 823—824).—Currents up to 50 milliamp. at 50,000 cycles impressed on a Ni strip used to promote the reaction of H_2 and O_2 did not cause increased catalytic activity, such as would be expected on the theory developed by Nyrop (A., 1931, 1375; 1932, 553). F. L. U.

Influence of the shape and size of the pieces of contact substance on catalytic processes. I. E. Adadurov and D. V. Gernet (J. Appl. Chem. Russ., 1933, **6**, 450—469).—A study of the process of oxidation of SO_2 to SO_3, using a Sn–Ba–V catalyst (I), indicates that % conversion depends not only on the free surface of the individual pieces of (I), but also on the mode of packing of these pieces, and on the resistance offered by them to flow of gas; for these reasons, hemispherical pieces, the sp. surface of which is much $<$ that of rectangular prisms, give somewhat greater % conversion. For each size and shape of pieces of (I) there exist an optimum velocity of flow of gas, $[SO_2]$, and duration of contact. R. T.

Catalysts for ammonia synthesis. D. A. Epstein and J. S. Upolovnikov.—See B., 1933, 668.

Influence of various factors on the synthesis of ammonia. C. Toniolo and G. Giammarco.—See B., 1933, 668.

Thermal reaction between acetaldehyde vapour and oxygen. R. N. Pease (J. Amer. Chem. Soc., 1933, **55**, 2753—2761; cf. A., 1932, 1210).—AcO_2H is the preponderant product of the interaction of 103—482 mm. MeCHO and 104—479 mm. O_2 at 90—150°, except when the reaction vessel is coated with KCl. The reaction is catalysed by broken glass packing and by coating the reaction vessel surface with KCl. H_2O, N_2, H_2, and C_2H_6 have no effect, but EtOH is an inhibitor. The reaction is autocatalytic, and the initial rate is proportional to the square of the MeCHO concn., but is independent of O_2 concn. The oxidation probably proceeds by way of reaction chains starting on the walls and terminating in the gas phase. J. G. A. G.

Reaction mechanism. VI. What elements catalyse hydrogenation? O. Schmidt (Z. physikal. Chem., 1933, **165**, 209—227; cf. this vol., 912).—An extended account of work already noted (this vol., 680). With catalysts of the first class the activation of the H occurs on the surface with the aid of electrons and intermediate formation of H′, $H_2 + 2\ominus + 2Na^{\cdot} = 2NaH$, followed by decomp. of NaH giving H′ and H; the H then reacts with the C_2H_4. With catalysts of the second class activation occurs through the ionisation of the H_2 dissolved in the metal, giving $H_2^{\cdot}$, followed by $H_2^{\cdot} = H^{\cdot} + H$, and the $H^{\cdot}$ reacts with negatively-charged C_2H_4. R. C.

Reduction of sodium sulphate to sulphide. P. Budnikov (Compt. rend., 1933, **197**, 60—63).—When Na_2SO_4 is heated in a SiO_2 flask with sugar C reaction begins at 800°, with pine C at 750°, Acheson graphite at 880°, and lampblack at 750—800°, and proceeds rapidly, being autocatalysed by Na_2S, which lowers the m.p. of Na_2SO_4. With $3Na_2SO_4 : 1C$ the reduction at 850° is complete in 2—3 min., yield 95%; at 1000° in 40 sec., yield 88·6%. It is hence suggested that Na_2S be prepared by injecting powdered Na_2SO_4 into burners for powdered coal. Raising the temp. or prolonging the reaction reduces the yield, probably due to $2Na_2S \longrightarrow Na_2S_2 + 2Na$, and $Na_2SO_4 + Na_2S_2 \longrightarrow 4Na + 2SO_2 + S$ (cf. A., 1913, ii, 405). CO at 850° reduces Na_2SO_4, and at a lower temp. with a catalyst, *e.g.*, C or Ni, but the yield is $\not>$42—45% (cf. B., 1928, 111). H_2 in 45 min. at 800° gave 44% Na_2S, at 900° 68%, at 1000° 60%, and at 1100° 52%; or in presence of Ni 82, 83, 47, and ?, respectively. C. A. S.

Low-pressure hydrogen-oxygen reaction on platinum. E. O. Wiig (J. Amer. Chem. Soc., 1933, **55**, 2673—2679).—Contrary to Tanner and Taylor (A., 1931, 692) H_2 and O_2 at pressures $< 0·1$ mm. react in the ratio 2 : 1 by vol. on a Pt catalyst when every possibility of change in composition of the gaseous mixture due to differential diffusion is eliminated. J. G. A. G.

[Interaction of] platinum oxide and carbon monoxide. P. V. McKinney and E. F. Morfit (J. Amer. Chem. Soc., 1933, **55**, 3050).—Unlike PdO (cf. this vol., 134), PtO is reduced by CO at temp. as low as 0°. The reaction is autocatalytic and has an induction period which is eliminated by the presence of freshly reduced Pt. J. G. A. G.

Electrolytic oxidisability of carbon monoxide. V. Sihvonen and P. Veijola (Suomen Kem., 1933, **B**, **6**, 63—64).—Experiments on the production of CO_2 and CO during electrolysis of aq. H_2SO_4 or NaOH with a graphite anode are described. The depolarising action of CO at a Pt or graphite anode is very slight. F. L. U.

Electrolysis of copper salts of organic acids. G. Kravtzoff (Compt. rend., 1933, **197**, 137—140).—The Cu deposited on electrolysis of solutions of the Cu salts of HCO_2H (I), AcOH (II), $EtCO_2H$ (III), chloro- (IV) and trichloro-acetic acid (V), and $PhSO_3H$ (VI), of concns. 3·65—41·5 g. Cu per litre with c.d. 0·2—0·8 amp. per sq. dm., give brittle deposits of colour varying from normal to bluish-black (II) and green (V). With (III), (IV), and (V) striæ along the lines of force are formed. The ratio of wt. of deposit on the electrode to that of deposit in a coulometer in series is almost always > 1 (1·47—0·96); it diminishes with increased c.d., acidity, dilution, or agitation. *X*-Ray examination of the deposit indicates presence of Cu_2O (cf. A., 1878, 706; 1907, ii, 548). C. A. S.

Electrolytic oxidation. III. Formation of dithionate by electrolytic oxidation of potassium sulphite. S. Glasstone and A. Hickling (J.C.S., 1933, 829—836; cf. this vol., 34).—The amount of S_2O_6'' formed by oxidation of K_2SO_3 at a Pt anode is nearly independent of temp., current strength, and $[SO_3'']$, if the electrode has previously been anodically polarised. If it has not been so treated the yield of S_2O_6'' is less, and still less if it has been polarised cathodically. The yield is a max. at p_H 8. Addition of catalysts for the decomp. of H_2O_2 decreases the yield. Efficiency of anode materials decreases in the order Ni>Pt,Au>platinised Pt>C. The oxidation is not due to a purely electrical process involving discharge of SO_3'', but is effected by H_2O_2. F. L. U.

Use of bimetallic anodes in the electrolytic synthesis of alloys. C. Béchard.—See B., 1933, 673.

Linear velocity of crystallisation of the cathode deposit in the electrolysis of certain lead salts. A. Glazunov and E. Bartuněk (Chem. Listy, 1933, **27**, 172—175).—The linear velocity of crystallisation of Pb at the cathode in the electrolysis of aq. $PbCl_2$ or $Pb(OAc)_2$ is a function of their concn., and of the c.d. R. T.

Stick antimony electrode. [I.] Theory. [II.] Theoretical limitations. L. R. Parks and H. C. Beard (J. Physical Chem., 1933, **37**, 821—822, 822—823; cf. A., 1932, 470).—I. The Sb electrode is of the metal–metal oxide type, in which the oxide is in the form of an adsorbed film and the solution is not saturated with it. The electrode reaction is considered to take place at the interface metal–metal oxide.

II. As a means of determining $[H^{\cdot}]$ the Sb electrode is theoretically correct only in the p_H range 1·60—7·87.
F. L. U.

Prevention of injurious effect of antimony in electrodeposition of zinc and copper. N. Kameyama and H. Iida.—See B., 1933, 631.

Electrodeposition of metals and alloys from formamide solutions. R. D. Blue and F. C. Mathers (Trans. Electrochem. Soc., 1933, **63**, 327—334).—The physical character of Cu, Zn, Bi, Ni, Fe, and Cr electrodeposited from solutions of their anhyd. chlorides in $HCO\cdot NH_2$ was improved by the presence of HCl, but deposits of Sn, Pb, and Cd were unaffected. No deposits of Al or Mg were obtained, but Fe–Al alloys containing up to 17% Al were deposited from a solution of $FeCl_3$ and $AlCl_3$. Alloys of Al with Zn and Mn were obtained, but the Al content was very low. Good deposits of Zn and Ni were obtained from solutions of their thiocyanates in $HCO\cdot NH_2$, and a fair deposit of Cd from $Cd(CNS)_2$ solution.
H. J. T. E.

Electrochemical reduction at the cathode, and its prevention in the electrolysis of barium chloride without a diaphragm. I. S. Katzen (J. Chem. Ind. Russ., 1933, No. 4, 34—41).—In the electrolytic prep. of $Ba(ClO_3)_2$ (I) from $BaCl_2$, part of the (I) formed is reduced at the cathode by H. The addition of $K_2Cr_2O_7$ or of $MgCl_2$, $CaCl_2$, or $SrCl_2$ to the electrolyte and the use of a Cr-plated Fe cathode have very little or no influence on the yield per unit of current used (22—54% of theoretical after 4 hr.), whilst, using graphite electrodes, with 1% of $CaCl_2$ in the electrolyte, 84% yields are obtained. The addition of 0·3% of gum arabic to the electrolyte almost completely inhibits reduction (90% yields, in presence of $CaCl_2$), but leads to the production of large quantities of Cl_2 at the anode. Cathodic reduction is the greater the lower is the temp.; at 70° it is reduced to 3%. 80% yields of (I) are obtained even after 63 hr. under the following optimum conditions: 1% of $CaCl_2$ in the electrolyte, c.d.—anode 0·05 and cathode 0·5 amp. per sq. cm., temp. 50°, using graphite electrodes.
R. T.

Influence of iron salts on the electrolytic reduction of benzophenone. S. Swann, jun. (Trans. Electrochem. Soc., 1933, **63**, 227—228).—Fe salts inhibit the reduction of $COPh_2$ to $[CPh(OH)\cdot]_2$ in aq. $EtOH–H_2SO_4$ when Al cathodes are used.
H. J. T. E.

Formation of organic nitro-compounds by electrolytic action. D. F. Calhane and C. C. Wilson (Trans. Electrochem. Soc., 1933, **63**, 117—127).—In a diaphragm cell with Al cathode and duriron anodes, the anode compartment being furnished with a stirrer and cooling coil, $C_{10}H_8$ suspended in aq. HNO_3 (*d* 1·25—1·29) is anodically nitrated at temp. $< 45°$ using 20 amp. per sq. dm. The HNO_3 concn. in the anode compartment rises, but remains much $<$ that needed for chemical nitration. The action of the current in promoting nitration is attributed to the formation of a film of much more conc. HNO_3 on the anode surface.
H. J. T. E.

Primary process in the oxidation of tartrates in alkaline solution at a high anode potential. V. Sihvonen (Suomen Kem., 1933, **B**, **6**, 64—65).—By causing the electrolyte (alkaline Na tartrate solution) to stream past a Au anode, glyoxylic acid may be obtained with a max. current yield of 45%. If the anode liquid is not rapidly removed the glyoxylic acid is further oxidised to HCO_2H, $H_2C_2O_4$, and CO_2.
F. L. U.

Influence of active nitrogen on oxidation. M. Prettre (Compt. rend., 1933, **197**, 328—330).—A mixture of 40% CO + 12% O_2 + 48% N_2, if the N_2 is activated by passage across a condensed spark and cooled, inflames at 620—655°, 560°, 520°, and 450° if the intervals between the N_2 leaving the spark and becoming mixed with the CO and O_2 are respectively 0·5, 0·2, 0·15, and 0·08 sec. If the active N is luminescent it inflames a mixture of CO and O_2 at room temp. (cf. A., 1927, 1156; this vol., 231).
C. A. S.

Formation of ozone in the alternating-current corona discharge with tubes coated with paraffin, stearic acid, and platinum. H. G. Thode and A. C. Grubb (Trans. Electrochem. Soc., 1933, **63**, 297—314).—The dependence of yield of O_3 on velocity of O_2 through an a.c. corona discharge tube has been investigated at various power inputs. The yield increases when the surface of the glass discharge tube has become sputtered with Pt, whereas coating the tube with paraffin decreases the yield, and coating with stearic acid causes further decrease. The corresponding thermal equilibrium temp., the electron efficiency, and the no. of mols. of O_3 formed per max. no. of ion pairs are calc. The nature of the wall effect is discussed in relation to theories of O_3 formation.
H. J. T. E.

Behaviour of argon and krypton with fluorine in electrical discharges. O. Ruff and W. Menzel (Z. anorg. Chem., 1933, **213**, 206—207; cf. this vol., 578).—No diminution in pressure or compound formation was observed. In presence of O_2, O_2F_2 was isolated.
H. J. E.

Behaviour of argon and krypton with fluorine in electrical discharges. A. von Antropoff (Z. anorg. Chem., 1933, **213**, 208; cf. preceding abstract).—The author used different conditions (condensed discharge and circulating gas) in attempts to prepare rare gas halides.
H. J. E.

Deposition of sputtered films. R. W. Ditchburn (Proc. Roy. Soc., 1933, **A**, **141**, 169—188).—The deposition of sputtered Cd on glass and metal surfaces placed near the cathode has been investigated. There is no indication of a crit. density phenomenon similar to that found for the condensation of vapour. The rate of deposition for insulated surfaces is only slightly influenced by temp. changes from 30° to −150°, but it is affected by the conditions of the discharge and the potential of the target, being faster for surfaces collecting slow positive ions, slower for those collecting fast positive ions, and almost negligible for surfaces collecting electrons. In the last case the rate can be hastened by cooling. The sputtered metal giving these effects is uncharged. Experiments on the thickness and structure of the deposits are described, and a theory is suggested according to which the deposition is assisted by a surface cleaning effect of positive ions.
L. L. B.

Photochemical union of chlorine and hydrogen in presence of oxygen, and relative rates of formation of water and hydrogen chloride in illuminated mixtures of the three gases rich in oxygen. D. L. Chapman and J. S. Watkins (J.C.S., 1933, 743—745; cf. *ibid.*, 1923, **123**, 3062).—When the proportion of Cl_2 is small, illumination of such mixtures may cause a greater no. of H_2O than of HCl mols. to be formed. The theoretical bearing of this result is considered. F. L. U.

Photographic sensitivity of silver sulphide. K. Hickman and W. Weyerts (Nature, 1933, **132**, 134—135).—Colloidal Ag_2S suspended in solutions of $NaAgS_2O_3+Na_2SO_3$ is darkened by light and deposits Ag. The darkening occurs best in solutions of Ag_2SO_3 in excess of alkali sulphite and in $AgNO_2$ in alkali nitrite. The sulphide is slightly sensitive in double Ag tartrates, formates, and NH_3–Ag complexes. The darkening is due to the deposition of Ag on or near the sulphide surface. The reaction appears to concern adsorbed ions and the speed is approx. proportional to $[Ag^{\cdot}]$. The limiting factor is apparently the exclusion of light from the active surface by the reduced Ag. Spectral sensitivity extends from the violet into the infra-red. The reaction is practically independent of p_H between 11 and 5, is depressed by gelatin, and shows a negative temp. coeff. with NO_2' and a positive coeff. with SO_3''. With photographic materials it affords a kind of image building or optical intensification. L. S. T.

Topography of the latent *X*-ray image. Lüppo-Cramer and H. Steps (Z. wiss. Phot., 1933, **32**, 113—128).—Ripening (*i.e.*, production of sensitive nuclei), without increase of grain size, increases the sensitivity of pure AgBr emulsions to *X*-rays. Treatment with CrO_3 or desensitising dyes reduces the sensitivity to some extent (much $<$ the desensitisation to ordinary light). CrO_3, and also AcOH with developing agents, strongly attack a latent *X*-ray image. Pure AgBr emulsion is more sensitive than emulsion containing AgI, but the former is always larger-grained. From these results it is concluded that the primary Ag ("ripening" nuclei) is sensitive to *X*-ray action, and that the latent *X*-ray image cannot lie very deep in the grain of AgBr. J. L.

Schwarzschild effect with colloid-free silver bromide. A. J. Rabinovitsch and C. S. Bagdassarjan (Z. wiss. Phot., 1933, **32**, 110—112).—Reciprocity failure is found to occur with varying exposure of pure AgBr (activated with dil. NaOH) to light, the results being measured by determining the amount of Ag pptd. J. L.

Influence of hydrogen-ion concentration on the light-sensitivity of colloid-free silver bromide. A. J. Rabinovitsch and C. S. Bagdassarjan (Z. wiss. Phot., 1933, **32**, 97—109).—The sensitivity of AgBr suspensions increases with increased particle size (which reaches a max. on keeping). Using buffer solutions, the sensitivity increases rapidly with alkalinity above p_H 7·5. The adsorption of OH' also increases markedly at this point. Presence of a large excess of Br' greatly reduces the effects. The OH' also strongly sensitises AgBr to red light. J. L.

Photo-activity in anodic polarisation at peroxide-forming metals. V. Sihvonen and A. Jussila (Suomen Kem., 1933, **B**, 6, 65—66).—When Pb or Ag in *N*-H_2SO_4 and *N*-NaOH, respectively, are anodically polarised in the dark, illumination causes the anode potential to decrease. If the potential is maintained const., the increase of current caused by illumination $\propto$ the light intensity. The metals are photosensitive only over a limited range of c.d. Pb responds to light extending to the orange, Ag to the red. Cu, Fe, Ni, Pt, and graphite do not show the effect, which is probably related to decomp. of metal peroxide. F. L. U.

Chemical reactions induced by light. V. L. Vecchiotti and C. Piccinini (Gazzetta, 1933, **63**, 319—322; cf. this vol., 602).—The action of sunlight for several months on a mixture of $PhNO_2$ and *m*-$C_6H_4Me{\cdot}NH_2$ gave orange 2′-*hydroxy*-3-*methylazobenzene*, m.p. 105°. O. J. W.

Formation of sugars in mixtures of tartaric acid and aldehydes in tropical sunlight. V. Gore (J. Physical Chem., 1933, **37**, 745—749).—Sugar formation has been detected (by Benedict's solution) in mixtures of aq. tartaric acid with EtOH, BuOH, $C_5H_{11}{\cdot}OH$, CH_2O, and MeCHO, exposed to tropical sunlight. None was found in similarly treated solutions of tartaric acid or CH_2O separately. F. L. U.

Photovoltaic effects in Grignard solutions. III. R. T. Dufford (J. Physical Chem., 1933, **37**, 709—721; cf. A., 1931, 802).—Further experiments are described. The photovoltaic effect can be affected by, but is not caused by, surface films on the electrode. The response to *X*-rays is large compared with that to visible light. The origin of the effect is discussed. F. L. U.

Colloid substrate in photosynthesis. M. Copisarow (Nature, 1933, **132**, 67). L. S. T.

Action of electrons on nitrogen iodide and other explosives. J. J. Trillat and H. Muraour (Bull. Soc. chim., 1933, [iv], **53**, 443—445).—NI_3, picric acid, Pb picrate, trinitrotoluene, glyceryl nitrate, and nitrated cotton do not explode when bombarded by electrons in a Coolidge–Lenard tube. E. S. H.

Effect of electronic bombardment on lead azide and silver acetylide. Thermal decomposition of explosives. H. Muraour (Chim. et Ind., 1933, **30**, 39—40T).—On bombardment with electrons both explosives blacken, the metals being liberated. No explosion was observed with $Pb(N_3)_2$, whilst of three experiments with Ag_2C_2 only one resulted in explosion and that after 3 min. The slow decomp. is analogous to that on heating the compounds. It is concluded that the decomp. of a single mol. is insufficient to initiate decomp. of the whole mass, but that the development of a combustion or detonation wave is dependent on the simultaneous decomp. of a large no. of mols. in the same region. J. W. S.

Chemical action of audible sound. E. W. Flosdorf and L. A. Chambers (J. Amer. Chem. Soc., 1933, **55**, 3051—3052).—Sound of high energy density and of frequency between 1000 and 15,000 causes coagulation of albumins, hydrolysis of carbo-

hydrates and esters, and pptn. of the hydroxides of Cu, Mn, Al, Ni, and Cr from their chlorides. In the presence of O_2, halides afford free halogen and H_2S gives S. Au is pptd. from $AuCl_3$. The reactions may be due to a conversion of sound into heat.
J. G. A. G.

Action of quartz and alkali silicates on alkali carbonates. C. Kröger and E. Fingas (Z. anorg. Chem., 1933, **213**, 12—57).—The dissociation pressures of $LiCO_3$ between 750° and 1100° were measured. Equilibria in the systems $Li_2O-SiO_2-CO_2$, $K_2O-SiO_2-CO_2$, and $Na_2O-SiO_2-CO_2$ were studied between approx. 400° and 1100° by measurement of the equilibrium CO_2 pressure. The conditions of formation of the following silicates were determined: Li_2SiO_3, Li_4SiO_4, Li_6SiO_5 (or Li_8SiO_6), K_2SiO_3, K_2SiO_5, K_4SiO_4, Na_2SiO_3, $Na_2Si_2O_5$, $Na_2Si_3O_7$, Na_4SiO_4. The heats of formation of these silicates were calc. from the temp. dependence of the equilibrium CO_2 pressures.
H. J. E.

Dissolution of salt in metal. T. Peczalski (Compt. rend., 1933, **197**, 227—229).—When a Cu rod was heated for 8 hr. at 700° in $CaCl_2$ the salt became red and the rod lost 3% of its wt. If the rod is wrapped around with steel wire the salt is blackened by dissolved Fe and the wire covered with Cu; the Cu rod is strongly cemented and its $d^{19\cdot4}$ reduced from 8·90 to 8·484. KCl, KF, and $BaCl_2$ behave similarly. When a current of 3 amp. per sq. cm. is passed between two such Cu rods in $CaCl_2$ at 700° for 1 hr., the cathode was much, the anode little, cemented. The positive ions of the salt thus enter the metal; a Debye–Scherrer photograph shows the effect.
C. A. S.

Oxidation of colloidally-dissolved substances. II. S. Vosnessensky and V. Skvorzov (Kolloid-Z., 1933, **64**, 205—209; cf. A., 1932, 1002).—The amount of $0\cdot04N$-HCl reacting with colloidal Ag at 20° is equiv. to the $[Ag^{\cdot}]$ of the intermicellar liquid, but at 100°, using $1N$-HCl, it is equiv. to the amount of $Ag^{\cdot}$ in the micelles. The metallic Ag of the colloidal particle does not in any circumstances react. $FeCl_3$, however, converts colloidal Ag into AgCl. $KMnO_4$ oxidises colloidal Ag to Ag_2O_2.
E. S. H.

Higher valency states of silver. M. S. Ebert, E. L. Rodowskas, and J. C. W. Frazer (J. Amer. Chem. Soc., 1933, **55**, 3056—3057).—By interaction of Ag and F_2 at 300°, an unstable black material which is a powerful oxidising agent and contains $> 75\%$ of AgF_2 has been prepared. Other properties are described.
J. G. A. G.

Hydrates of magnesium perchlorate. E. Moles and C. Roquero (Anal. Fís. Quím., 1933, **31**, 175—184).—The *d* of $Mg(ClO_4)_2$ and of the tri- and hexa-hydrates are 2·208 (lit. 2·600), 2·06, and 1·906, respectively. It is probable, from spatial considerations, that the so-called trihydrate is not a true compound but consists of mixed crystals. The dihydrate is probably a hydroxonium derivative, in which the mol. vol. of the H_2O is 10, whilst in the hexahydrate the mol. vol. of each of the four additional H_2O mols. is 13.
H. F. G.

Calcium silicates. I. Synthesis. S. Kondo and T. Yamauchi (J. Soc. Chem. Ind. Japan, 1933, 36, 167B).—The reactions between 3 : 1, 2 : 1, 3 : 2, and 1 : 1 mixtures of $CaCO_3$ and SiO_2 when heated at temp. between 600° and 1800° have been studied. Four very pure Ca silicates have been prepared.
H. F. G.

Hydrothermal synthesis of calcium silicates under pressure. III. S. Nagai (J. Soc. Chem. Ind. Japan, 1933, 36, 403—407B).—When CaO and SiO_2 in the proportions 1 : 1—5 : 1 are heated in an autoclave with H_2O most of the SiO_2 and a part of the CaO and H_2O combine. The compounds are considered to be $CaO,SiO_2,0\cdot25H_2O$, $3CaO,2SiO_2,8H_2O$, $3CaO,2SiO_2,H_2O$, and $2CaO,SiO_2,H_2O$ or mixtures of these.
A. G.

Synthesis of calcium silicates. VI. S. Nagai and K. Murakami (J. Soc. Chem. Ind. Japan, 1933, 36, 326—330B).—Thermal synthesis of Ca silicates from a mixture of $CaCO_3$ and SiO_2 showed that the reaction is almost completed in 3 hr. at 1450°. $3CaO,SiO_2$ can be produced easily at this temp., one heating giving 99·65% purity. When further heated at 1150° $3CaO,SiO_2$, but not $2CaO,SiO_2$, showed slight decomp., which was accelerated by the presence of CaO, CaF_2, and $CaSO_4$. The dissociation was unaffected by $Ca_3(PO_4)_2$, MgO, or $2CaO,SiO_2$.
C. A. K.

Calcium sulphate hemihydrate and its products of dehydration. P. Gaubert (Compt. rend., 1933, **197**, 72—75).—Crystals of $2CaSO_4,H_2O$ obtained by evaporation of a boiling solution of $CaSO_4$ in HNO_3 are rhombohedral, not rhombic (cf. A., 1916, ii, 450), *d* 2·735, n_ω 1·558, n_ϵ 1·586. When heated in air the crystals are dehydrated at 130° forming van 't Hoff's γ-anhydrite, *d* 2·61, n_ω 1·505, n_ϵ 1·548. At 170° this passes into the β-form, which appears to be rhombic, and seems to be Lacroix's "probably triclinic form," *d* 2·85, n_β 1·595, n_α 1·562. When heated in vaseline $2CaSO_4,H_2O$ loses no H_2O below 170°, and if rapidly heated passes directly into β-anhydrite. The β-form at 650° is transformed into the α-form (cf. A., 1932, 482).
C. A. S.

Properties of tricalcium silicate from basic open-hearth steel slags. O. Andersen and H. C. Lee (J. Washington Acad. Sci., 1933, **23**, 338—351).—Crystals of $3CaO,SiO_2$ isolated from the non-magnetic fraction of basic slags by treatment with a mixture of CH_2I_2 and CCl_4 (*d* 3·24), on which they floated, contained SiO_2 22·77, TiO_2 0·18, P_2O_5 1·72, Al_2O_3 0·20, Fe_2O_3 0·76, FeO 2·01, MnO 1·20, MgO 1·29, and CaO 68·65%. About 12% of the 14% of impurities present was in solid solution. The crystals are trigonal with rhombohedral development, *c/a* 1·773, d_4^{30} 3·224, n_D 1·724, and birefringence $(\omega—\varepsilon) = 0\cdot005$. At 1400° the substance is decomposed into β-$2CaO,SiO_2$ and free CaO.
A. R. P.

Calcium carbide and calcium cyanamide. J. Gelhaar.—See. B., 1933, 668.

Calcium arsenate. G. Fester and F. Bertuzzi (Angew. Chem., 1933, **46**, 477—478).—A suspension of As_2O_3 in H_2O is treated with bleaching powder (containing 7·1% active Cl) with const. stirring at 25—30°. $Ca_3(AsO_4)_2$ is pptd. and is rapidly removed, as it reacts further to form $CaCl_2$.
E. S. H.

Hydrated calcium aluminates. A. Travers and P. Leduc (Compt. rend., 1933, **197**, 252—253).—The transformation of hexagonal into cubic Ca aluminate (cf. this vol., 794) is the more rapid the higher is the p_H, *e.g.*, with $p_H > 12$ in 30 min. at 40—45°, or 24 hr. at room temp., although sometimes it occurs more slowly, or there may be false equilibria. The transformation is reversible (cf. A., 1930, 162, 436, 1262). C. A. S.

Oxidation of zinc dimethyl. H. W. Thompson and N. S. Kelland (J.C.S., 1933, 746—756).—The velocity of oxidation of $ZnMe_2$ vapour by O_2 at low pressures and room temp. is very high but measurable. The product is ZnMe·OMe. At higher pressures the reaction is explosive, the principal products being CO, CH_4, and H_2. Both reactions are preceded by an induction period. The mechanism is discussed. F. L. U.

Oxidation of zinc diethyl. H. W. Thompson and N. S. Kelland (J.C.S., 1933, 756—757; cf. preceding abstract).—The vapour is oxidised by O_2 with measurable rapidity at 50°, giving rise to a peroxide $ZnEt_2O_2$, which does not decompose explosively. F. L. U.

Mechanism of precipitation processes. XIII. Processes in which $HgCl_2$ participates. Z. Karaoglanov and B. Sagortschev (Z. anorg. Chem., 1933, **213**, 155—160; cf. this vol. 564).—The HgS pptd. from excess of aq. $HgCl_2$ by aq. Na_2S contains the *compound* $2HgS,HgCl_2$, which increases in amount on keeping. Formation of this compound is hindered by HCl or NaCl. Aq. $HgCl_2$ and aq. NaOH form the compound $4HgO,HgCl_2$ similarly. HgO and $HgCl_2$ react more readily than do HgS and $HgCl_2$. This is due to the greater solubility of HgO. Undissociated mols. of $HgCl_2$ take part in these reactions. H. J. E.

Action of phosphorus trichloride on boron tribromide. E. Wiberg and K. Schuster (Z. anorg. Chem., 1933, **213**, 94—96).—With excess of either PCl_3 or BBr_3 only the solid white *compound* BBr_3,PCl_3 (m.p. 42°) is formed. It is decomposed by H_2O (cf. Tarible, A., 1901, ii, 153). H. J. E.

Dimethylamino-substituted boron trichlorides. E. Wiberg and K. Schuster (Z. anorg. Chem., 1933, **213**, 77—88; cf. A., 1912, i, 171).—The *compounds* BCl_2NMe_2, $BCl(NMe_2)_2$ and $B(NMe_2)_3$ were isolated from the reaction products of BCl_3 with various proportions of $NHMe_2$. They are colourless liquids with f.p. —46°, —54°, and —40° and b.p. 111·9°, 146·1°, and 147·5°, respectively. The v.p. were measured. They react with H_2O forming H_3BO_3, HCl, and $NHMe_2$. With HCl they form the solid *compounds* $BCl_2{\cdot}NMe_2,HCl$, $BCl(NMe_2,HCl)_2$, and $B(NMe_2)_3,5HCl$, respectively. H. J. E.

Different chemical compounds of the formula BCl_2,NMe_2. E. Wiberg and K. Schuster (Z. anorg. Chem., 1933, **213**, 89—93; cf. preceding abstract).—Liquid $BCl_2{\cdot}NMe_2$ deposits on keeping or warming white monoclinic crystals of the same composition (a 6·47, b 6·63, c 6·47 Å.; 2 mols. in unit cell). The crystals are unattacked by H_2O or gaseous HCl. The mol. wt. in C_6H_6 show a double mol. The mol. of the liquid is single in C_6H_6. The constitution of the solid is discussed. H. J. E.

Action of boric acid on alkaline-earth chlorides and nitrates. Peng Chung-Ming (Compt. rend., 1933, **197**, 153—155).—By heating in steam at 150—300° mixtures of H_3BO_3 and MCl_2 or $M(NO_3)_2$ (M=Ca, Sr or Ba) in ratios 1 : 10 to 6 : 1, HCl is rapidly, H_3BO_3 slowly evolved. In all cases $MO,4B_2O_3$ is formed (cf. A., 1927, 325), but (especially for M=Ca) is gradually destroyed on continued heating. Formation of $3CaO,B_2O_3,CaCl_2$ was not confirmed (cf. A., 1884, 1261). C. A. S.

Amorphous aluminium carbide. L. Wöhler and K. Hofer (Z. anorg. Chem.. 1933, **213**, 249—254).—Electric furnace preps. of Al_4C_3 consist of a mixture of yellow crystals (I) and a chrome-yellow amorphous powder (II), of the same composition. (I) remains undecomposed when heated at 1000°, whereas (II) decomposes slowly into Al and C at >700°. (II) reacts readily with conc. HCl, (I) only slowly, and with H_2O at 50° (II) evolves twice the vol. of CH_4 evolved by (I) in the same time. The difference in behaviour is ascribed to the larger surface of (II). A. R. P.

New phosphors from the hydrated sulphates of aluminium and other metals with organic luminous substances. M. Travniček (Ann. Physik, 1933, [v], **17**, 654—678).—A new class of phosphors can be prepared from $Al_2(SO_4)_3,18H_2O$ and similar sulphates with org. mols. like fluorescein and uranin. For the successful prep. of phosphors the org. mol. must be molecularly dispersed in the ground material. A certain amount of H_2O in the mol. of the ground material is necessary. The effect of concn. of fluorescein and temp. on the phosphorescence of the $Al_2(SO_4)_3,18H_2O$–fluorescein phosphors was investigated. In these phosphors the Al can be replaced by Be, Zr, or Th, whilst the SO_4 may be replaced by SeO_4. A. J. M.

Chemistry of indium. A. W. Downes and L. Kahlenberg (Trans. Electrochem. Soc., 1933, **63**, 163—166).—Determinations of replacing power and electrode potential indicate that In is slightly less noble than Sn. The electrode potential is scarcely affected by gases. Passage of H_2 over molten In gives a brown coating of *hydride* which decomposes at 330°. H. J. T. E.

Indium sulphate. R. P. Seward (J. Amer. Chem. Soc., 1933, **55**, 2740—2744).—At room temp. in presence of excess of H_2SO_4, $In_2(SO_4)_3,H_2SO_4,7H_2O$ crystallises, but in the absence of excess of acid $In_2(SO_4)_3,9H_2O$ crystallises, whilst EtOH ppts. $In_2O(SO_4)_2,6H_2O$. $In_2(SO_4)_3,6H_2O$ and $In_2(SO_4)_3,3H_2O$ exist. The decomp. pressure of anhyd. $In_2(SO_4)_3$ is 1 atm. at 810°. The salt is hydrolysed in aq. solution. J. G. A. G.

Stability of methane, ethane, and carbon monoxide at low temperature. F. E. C. Scheffer (Bull. Soc. chim. Belg., 1933, **42**, 251—268).—A lecture on the reactions (*a*) $xNi+CH_4 \rightleftharpoons Ni_xC+2H_2$, (*b*) $xNi+2CO=Ni_xC+CO_2+49{\cdot}5$ kg.-cal., (*c*) $xNi+2C_2H_6=Ni_xC+3CH_4$. Ni_xC is an exothermal compound, stable below 420°, but decomposing at 420° according to $Ni_xC=xNi+C-7{\cdot}4$ kg.-cal. E. S. H.

Influence of combined oxygen on determination of vapour isothermals on porous solids. II. L. J. Burrage (J. Physical Chem., 1933, 37, 735—744; cf. this vol., 563).—CCl_4 vapour used to flush out adsorbed H_2O from SiO_2 gel reacts with the former at 100° to give $COCl_2$ and HCl. Part of the structural H_2O is also removed, thereby diminishing the capacity of the gel. C_6H_6 is less effective than CCl_4 for removing H_2O, but at 100° it produces a definite cleansing effect, resulting in increased capacity. At 230°, however, the gel structure is affected and the capacity diminished. Further experiments with C as adsorbent have shown that rapid equilibrium and a stepped isothermal can be obtained by flushing at 110° as well as at 800°. It is considered that in all previous work isothermals on C relate to surfaces poisoned by CO_2. F. L. U.

Zirconium sulphides. Picon (Compt. rend., 1933, **196**, 2003—2006).—By the action of H_2S on ZrO_2 at 1100—1700° three sulphides, ZrS_2, Zr_2S_3, and Zr_3S_5, d'' 3·87, 4·10, and 4·62, respectively, have been obtained. In H_2 (in a graphite boat) S is lost and a carbide (5% C) is formed; in N_2 at 2000° a nitride (volatile) and carbide are formed. C. A. S.

Properties of zirconium sulphides. Picon (Compt. rend., 1933, **197**, 151—153; cf. preceding abstract).—The sulphides are referred to in the order ZrS_2, Zr_3S_5, Zr_2S_3. Dry Cl_2 reacts at 250°, 235°, 250°; HCl at 165°, 210°, 280°; O_2 forms SO_2, basic sulphate, and oxide from 180°, 225°, 350°; SO_2 oxidises from 140°, 170°, 175°; Br reacts at room temp., more rapidly if moist; S with H_2 at 1000° converts all into ZrS_2; H_2O at 200° slowly forms sulphate and oxide; aq. HCl acts slowly on ZrS_2 and Zr_3S_5, not on Zr_2S_3; 10% aq. H_2SO_4 attacks all slowly; NH_3 at 1000° forms a nitride to the extent of 25%; aq. NH_3 attacks only ZrS_2; conc. HNO_3 attacks all violently, dil. does not attack ZrS_2; CO_2 at 500° gives CO, S, and ZrO_2; Mg (in H_2) removes S at 1000°; aq. NaOH attacks ZrS_2 rapidly, Zr_3S_5 slowly, Zr_2S_3 not at all; no compound is formed with PtS or Sb_2S_3 (in H_2) at 1000°; H_2O_2 attacks all with decreasing rapidity; aq. $KMnO_4$ attacks all slowly; aq. $K_3Fe(CN)_6$ more slowly. C. A. S.

Stannous oxide. M. Straumanis and C. Strenk (Z. anorg. Chem., 1933, **213**, 301—309).—Pure SnO is obtained as a bluish-black cryst. powder by dehydration of $Sn(OH)_2$ at 50° in the presence of small quantities of NaOH, Na_2CO_3, or HCl; it has a tetragonal structure, a 5·364±0·003, c 4·833±0·003 Å., c/a 0·901; $d_{calc.}$ 6·393. With larger amounts of acid or alkali grey to brown hydrated oxides of indefinite composition are formed. On heating a thick paste of hydroxide with a few crystals of $SnCl_2$ at 100° a yellowish-red hydroxide $2SnO,H_2O$ is formed; the air-dried hydroxide (white) has the composition $3SnO,2H_2O$. A. R. P.

Intensive drying. II. Reaction between ammonia and phosphorus pentoxide. E. Moles and J. Sancho (Anal. Fís. Quím., 1933, 31, 172—174).—Pure and intensively dried NH_3 (gas) reacts instantaneously when brought into contact with sublimed P_2O_5; the product is vitreous on the surface and apparently unchanged in the interior. The ratio $NH_3 : P_2O_5$ varies between 0·58 and 1·40 according to the conditions of the experiment. H. F. G.

Preparation of phosphorus oxychloride. N. A. Elmanovitsch and L. C. Majofis (J. Chem. Ind. Russ., 1933, No. 4, 59—62).—90% yields of $POCl_3$ are obtained by passing Cl_2 through a solution of 1 mol. of P_2O_5 in 3 mols. of PCl_3, with the addition of 0·5 vol. of $POCl_3$; the process is complete in 6·5 hr. at 80°. R. T.

Phosphates. I. Ammonium magnesium phosphate and related compounds. II. Orthophosphates of the type $M_3(PO_4)_2,xH_2O$. III. Complex orthophosphates of sodium and a bivalent metal, and some orthophosphate solid solutions. H. Bassett and W. L. Bedwell (J.C.S., 1933, 854—871, 871—876, 877—882).—I. Salts of the type $NH_4M^{II}PO_4,6H_2O$ show strong incandescence on ignition, in contrast to the corresponding monohydrates, in which it is very faint. When M=Co or Ni the hexahydrates have colours characteristic of the cation, the monohydrates mixed colours indicating that part of the bivalent metal is anionic. The salts are true NH_4 compounds and not ammines, since NH_3 cannot be replaced by C_5H_5N. The hexahydrates are considered to be unimol., and the monohydrates quadrimol. On ignition they yield $M_2P_2O_7$ and $(M_2P_2O_7)_2$, respectively, of which the first is unstable, its heat of transformation into the second causing the observed incandescence. All the compounds $KMPO_4$ and most of the type $MHPO_4,xH_2O$ are probably quadrimol. The following *salts* are described: $KNiPO_4,6H_2O$; $KMPO_4,H_2O$ (M=Mg, Mn, Co, Ni, Cu, Cd); $CoHPO_4,2H_2O$; NH_4CoPO_4; $CuHPO_4,H_2O$.

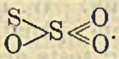
II. Normal orthophosphates of Mg, Co, Ni, and Zn have been prepared and studied. Those of Cu, Mn, and Cd could not be obtained. The *compounds* $Cu_4P_2O_9,1{\cdot}2H_2O$ and $Cu_4P_2O_9,1{\cdot}6H_2O$ are described. The normal salts become incandescent on ignition, the heat evolved during the change being nearly the same as for the pyrophosphate of the same metal. The hydrates have usually 4 or 8 H_2O. Pink $Co_3(PO_4)_2,8H_2O$ has a blue (probably non-ionic) isomeride.

III. Na_2HPO_4, when used to ppt. salts of bivalent metals, may give normal phosphates as described in Part II, or compounds or solid solutions containing Na. The following *salts* are described: $Na_3MgH(PO_4)_2$; solid solutions $xNaMPO_4,yNa_2HPO_4$ (M=Mn, Cu, Cd), and $2CdHPO_4,Cd_3(PO_4)_2,12H_2O+2K_2HPO_4,Cd_3(PO_4)_2,4H_2O$. Structural formulæ are developed for all the compounds described. F. L. U.

Decomposition of arsenites by heat. R. Rat (Compt. rend., 1933, **197**, 59—60).—Na, K, and Ba di-, meta-, pyro-, and ortho-arsenites were heated rapidly to 730°. The diarsenites were undecomposed after several hr. at that temp. With the others conversion into arsenate and As is more rapid as the base is stronger and in greater proportion relatively to As_2O_3, and proceeds until an approx. fixed proportion of As_2O_3 has been so converted, 12·9—14·4% for meta-, 72—74% for pyro-, and 100% for ortho-arsenites. The temp. at which conversion begins is the lower the greater is the proportion of base, and its strength (cf. A., 1932, 810). C. A. S.

Formulæ of antimonic acid and the antimonates. L. PAULING (J. Amer. Chem. Soc., 1933, 55, 3052).—Concerning priority (cf. this vol., 664). J. G. A. G.

Amorphous sulphur. O. VON DEINES (Z. anorg. Chem., 1933, 213, 183—188).—The soft amorphous S obtained by acidifying aq. $Na_2S_2O_3$, aq. thionates, or aq. Na polysulphide, or from aq. SO_2 and aq. H_2S always contains S-rich H_2S_x, and may be made to yield H_2S. The only amorphous form of S is the solid, insol. in CS_2. H. J. E.

Sulphur sesquioxide. L. WÖHLER and O. WEGWITZ (Z. anorg. Chem., 1933, 213, 129—148; cf. A., 1925, ii, 890).—The chemical identity of S_2O_3 has been confirmed. The thermal decomp. of S_2O_3 at 40—80° yields $S+SO_3$ (20%), and $SO+SO_2$ (80%). The SO is not isolated. It decomposes into S and SO_2. No $EtNaSO_2$ or Na_2SO_2 was detected in the reaction of S_2O_3 with NaOEt. The products were S, Na_2SO_4, Na_2SO_3, $Na_2S_2O_3$, $Na_2S_3O_6$, and EtSH (or MeSH when NaOMe was used). The occurrence of these products is correlated with the mechanism of decomp. of S_2O_3. The formula is  $\begin{smallmatrix}S\\O\end{smallmatrix}\!>S\!\ll\!\begin{smallmatrix}O\\O\end{smallmatrix}$. H. J. E.

" Blue acid " of the lead chamber process. II. W. MANCHOT (Z. anorg. Chem., 1933, 213, 255—256; cf. this vol., 240).—A reply to Berl (this vol., 580). The formation of " blue acid " decreases with decreasing $OH\cdot SO_2\cdot NO_2$ content of the H_2SO_4; it can be obtained with oleum and $OH\cdot SO_2\cdot NO_2$ instead of $NaNO_2$. A. R. P.

Action of thiosulphate on dilute acid solutions. F. PRAKKE and E. STIASNY (Rec. trav. chim., 1933, 52, 615—639).—The main reactions are (*a*) $H^{\cdot}+S_2O_3''\rightleftharpoons HSO_3'+S$, and (*b*) $6H^{\cdot}+5S_2O_3''\rightleftharpoons 2S_5O_6''+3H_2O$. The influence of each of the products is examined from the viewpoint of the law of mass action. Reaction (*b*) is very slow; no S_3O_6'' appears to be formed. At p_H 0—0·3 (*a*) occurs to the extent of 92·5%, whilst at $p_H>3$ (*b*) proceeds to the extent of 92%. The p_H at which $Na_2S_2O_3$ begins to react with acids depends on the concns. of the reagents. At room temp. only traces of H_2S are formed. H_2S is not a primary product and its formation is explained on the assumption of two tautomeric forms of $Na_2S_2O_3$. E. S. H.

Action of thiosulphate on dilute chrome alum solutions. E. STIASNY and F. PRAKKE (Rec. trav. chim., 1933, 52, 640—656).—In addition to the reaction products obtained from $Na_2S_2O_3$ and acids (cf. preceding abstract), a sulphito-sulphato-Cr complex is produced to an extent which varies with the proportions in which the reagents are mixed. Determinations have been made of SO_4'' bound with (*a*) the Cr complex, (*b*) $Cr^{\cdot\cdot\cdot}$, (*c*) $Na^{\cdot}$, SO_3'' bound with Cr complex or $Cr^{\cdot\cdot\cdot}$, S_2O_3'' bound with Cr complex or $Cr^{\cdot\cdot\cdot}$, polythionates, $Cr^{\cdot\cdot\cdot}$, $Ba^{\cdot}$, and pptd. S. E. S. H.

Preparation of heavy metal polythionates. O. VON DEINES and E. CHRISTOPH (Z. anorg. Chem., 1933, 213, 209—239).—Heavy metal polythionates can be prepared by double decomp. of the K polythionate with the tartrate, fluosilicate, or, best, perchlorate of the heavy metal. Conc. ice-cold solutions must be used and the filtrate from the insol. K salt must be evaporated rapidly in vac., since the heavy metal polythionates soon decompose in presence of H_2O. The following have been prepared: *pentathionates*, $Cu(xH_2O)$, $Co(6H_2O)$, $Ni(7H_2O)$, $Mn(7H_2O)$, $Zn(6H_2O)$, $ZnH_2(S_5O_6)_2,xH_2O$; *tetrathionates*, $Cu(xH_2O)$, Cu en, $Ni(7H_2O)$, Co, Zn, $ZnH_2(S_4O_6)_2$, $Mn(5H_2O)$, $Bi_2O(S_4O_6)_2$; *trithionates*, Cu en, $(BiO)_2S_3O_6$. Cu, Ni, Co, and Zn trithionates are unstable, decomposing immediately into thiosulphates and sulphates; pure $Cu_2S_2O_3$, NiS_2O_3, CoS_2O_3, and ZnS_2O_3 have been prepared. A. R. P.

Co-ordination compounds of chromic chloride. D. R. CHESTERMAN (J.C.S., 1933, 796—798).—The *compounds* $[CrCl_2,4MeOH]Cl$, $[CrCl_3,3Pr^{\alpha}OH]$, and $[CrCl_3,3Pr^{\beta}OH]$ have been prepared. The last two, with the known $[CrCl_3,3EtOH]$, are differentiated from the first and the hexahydrate in that increasing size of the co-ordinating mol. causes fewer mols. to be co-ordinated. In the prep. of the compounds from metallic Cr chromous products were first formed, but not isolated. Compounds (not purified) were also formed with $COMe_2$ and BuOH. F. L. U.

Decomposition of permanganic acid in the presence of certain acids. J. CHLOUPEK (Chem. Listy, 1933, 27, 217—222, 270—275).—$KMnO_4$ decomposes in the presence of H_2SO_4, AcOH, and H_3PO_4, but not H_3AsO_4, to yield MnO_2 and O_2; the velocity of decomp. increases with concn. of acid. At equiv. concns., the activity of acids increases in the order $H_3PO_4<AcOH<H_2SO_4$. The degree of oxidation of Mn in strongly acid solutions can be determined by potentiometric titration with $Fe^{\cdot\cdot}$ salts. R. T.

Topochemical transformations. VI. Reactions of crystalline ferric sulphate. I. H. W. KOHLSCHÜTTER [with L. SPRENGER and H. SIECKE] (Z. anorg. Chem., 1933, 213, 189—205; cf. A., 1932, 822).—Cryst. $Fe_2(SO_4)_3$ reacts with aq. NaOH, forming pseudomorphic Fe_2O_3,xH_2O (I). Better results are obtained with aq. NH_3. Reaction occurs very near the crystal surface. The dehydration and hydration of (I) resembles that of zeolites, although the substance is not cryst. H. J. E.

Ferrous ferrites. II. Constitution and ferromagnetism of the ferrous ferrites, and the autoxidation of ferrous hydroxide. A. KRAUSE and J. TULECKI (Z. anorg. Chem., 1933, 213, 292—300).—For the prep. of Fe^{II} ferrite from γ-FeO_2H an excess of $Fe(OH)_2$ is required, since part of the latter is oxidised with the simultaneous formation of H_2O_2. The constitutional formula of the ferrite is similar to that of spinel, but not all the cation positions are occupied. The ferromagnetism of the compound is explained by the presence of $\cdot Fe\dot{:}(O_2)\dot{:}Fe\cdot$ groups. The ferrites produced from α-FeO_2H are formed by the substitution of FeO for the co-ordinately combined H_2O. Fe_2O_3 prepared by gentle ignition of γ-FeO_2H

or by strong ignition of α-Fe_2O_3 adsorbs up to 0·5 mol. FeO per mol. of Fe_2O_3. $BaSO_4$ accelerates oxidation of $Fe(OH)_2$ in air probably owing to the formation of a Ba salt of ferrisulphuric acid. A. R. P.

Composition of Prussian blue and Turnbull's blue. Influence of adsorption on the composition. A. K. Bhattacharya and N. R. Dhar (Z. anorg. Chem., 1933, **213**, 240—248).—The compositions of the reaction products of $FeCl_3$ and $K_4Fe(CN)_6$ and of $FeSO_4$ and $K_3Fe(CN)_6$ tend to approach $Fe_2(CN)_5$ on ageing owing to oxidation and reduction reactions between the anion and cation. When an excess of the cyanide is used in the pptn. the "sol. Prussian (or Turnbull's) blue" obtained is a colloid containing adsorbed $K_4Fe(CN)_6$ or $K_3Fe(CN)_6$; adsorption is more marked in the first case. A. R. P.

Contamination of nickel crystals grown in a molybdenum resistance furnace. A. Dingwall, J. Zacharias, and S. L. Siegel (Trans. Electrochem. Soc., 1933, **63**, 395—400).—Specially pure Ni after melting in an alundum crucible in a Mo resistance furnace was found to contain 0·1% Mo homogeneously distributed throughout it. Such contamination was avoided by use of a modified furnace in which the crucible was surrounded with a gas-tight porcelain tube, but some contamination with Si resulted. H. J. T. E.

Compounds of tartaric acid and nickel. J. P. Mathieu (Compt. rend., 1933, **197**, 56—59).—Absorption and rotation determinations of solutions containing Na_2 tartrate and $NiSO_4$ in varying proportions indicate formation of $NiC_4H_4O_6$. On addition of NaOH there are indications of formation of a complex nickelotartrate in which $Ni:Na=1$. The solutions exhibit mutarotation and gradually acquire colloidal properties and are then separable by ultra-filtration into a dextrorotatory filtrate and lævorotatory suspension (cf. A., 1900, i, 587). C. A. S.

Affinity. LIX. Ruthenium sulphides. R. Juza and W. Meyer (Z. anorg. Chem., 1933, **213**, 273—282).—Tensimetric measurements and X-ray examination show that RuS_2 is the only stable Ru sulphide; certainly no lower sulphide exists and no pure higher sulphide can be obtained by dehydration of pptd. sulphides. The heat of formation of RuS_2 at 1170° is 77 kg.-cal. per g.-mol. A. R. P.

New methods in analytical chemistry. G. G. Longinescu (Bul. Chim. Soc. Române, 1933, **34**, 81—96).—An account of the author's researches in analytical chemistry during the past 12 years. A. R. P.

Chemical analysis of things as they are. G. E. F. Lundell (Ind. Eng. Chem. [Anal.], 1933, **5**, 221—225).—A criticism of present-day analytical procedure. E. S. H.

Comparative chemistry. I. General introduction. II. Classifications. I. N. Longinescu (Bul. Chim. Soc. Române, 1933, **34**, 97—100, 100—104). A. R. P.

Quantitative analysis by spectroscopic methods. O. S. Duffendack, R. A. Wolfe, and R. W. Smith (Ind. Eng. Chem. [Anal.], 1933, **5**, 226—229).—Modifications of technique are described. Each plate is calibrated by putting upon it an intensity pattern, and a means of standardising the arc source used in analysing alloys has been devised. Results for Ba–Ni alloys show that the accuracy is approx. equal to that attained by chemical means. E. S. H.

Technique of spectrographic analysis. O. Feussner (Arch. Eisenhüttenw., 1932—1933, **6**, 551—556).—The conditions necessary for obtaining reproducible spectrographs are discussed and modern electrical apparatus for producing standardised spark discharges and optical apparatus for measuring the intensity of the lines are described. A. R. P.

Sedimentation analysis. R. Loebe and R. Köhler (Mitt. Lab. preuss. geol. Landesanst., 1932, No. 17, 13 pp.; Chem. Zentr., 1933, i, 838).—Sedimentation analysis with Köhn's pipette apparatus gives trustworthy vals. for the determination of fine fractions ($< 50\ \mu$). Coarser fractions require elutriation. $Na_2C_2O_4$ in general produces a higher degree of dispersion. L. S. T.

Recommended specifications for analytical reagent chemicals. Benzoic, boric, formic, sulphanilic, and sulphurous acids, aniline, hydrogen peroxide, mercuric bromide, potassium biphthalate, potassium oxalate, sodium sulphite anhydrous. W. D. Collins and collaborators (Ind. Eng. Chem. [Anal.], 1933, **5**, 289—292).—Requirements and tests are specified. Corrections are made to published specifications for H_3PO_4, $(NH_4)_2SO_4$, $CaCl_2,2H_2O$, and $NaBiO_3$. E. S. H.

Sources of error in the use in water analysis of Fairchild's method for determination of fluoride in phosphate rock. M. D. Foster (Ind. Eng. Chem. [Anal.], 1933, **5**, 238).—The method (A., 1930, 725) is accurate only to 0·2—0·4 mg. F. E. S. H.

Determination of hypochlorite. F. K. Revva and V. V. Illarionov (J. Appl. Chem. Russ., 1933, **6**, 568—570).—Equally accurate results are obtained by titrating excess of H_3AsO_3 not oxidised by HOCl with I, $KMnO_4$, or $HBrO_3$. R. T.

Determination of traces of bromine in presence of great excess of chlorine. F. Hahn (Compt. rend., 1933, **197**, 245—247).—To about 1 c.c. of the solution to be examined a drop of 0·0005M-Na fluoresceinate is added with 3 drops of aq. NaOAc of p_H 5·5—5·6 and a drop of 0·1M-$C_6H_4Me{\cdot}SO_2{\cdot}NClNa$ as oxidiser; after 1—2 min. further reaction is stopped by addition of a drop of aq. $Na_2S_2O_3$; the amount of Br is then determined colorimetrically. The method is suitable for determining blood-Br. C. A. S.

Bromo-acidimetric processes. V. L. Rosenthaler (Pharm. Acta Helv., 1932, **7**, 223—226; Chem. Zentr., 1932, ii, 3925).—The following reactions can be utilised: $HCO_2Na + Br_2 = HBr + NaBr + CO_2$, $H_2C_2O_4 + Br_2 = 2HBr + 2CO_2$, $K_2S_2O_5 + 2Br_2 + 3H_2O = 2KHSO_4 + 4HBr$, $NaNO_2 + Br_2 + H_2O = NaNO_3 + 2HBr$. L. S. T.

Potentiometric silver–halogen titration with indifferent electrodes. W. Böttger and B. M. Schall (Z. physikal. Chem., 1933, **165**, 398—410).—

An attempt to find why such indifferent materials as Pt, Au, Hg, and C may serve as indicator electrodes in the above titration has yielded inconclusive results. A possible explanation is the formation of a film of Ag on the indifferent electrode. R. C.

Determination of iodates in presence of hypochlorites, bromates, and chlorates. F. K. REVVA and V. V. ILLARIONOV (Z. anal. Chem., 1933, 93, 344—345).—Two rapid and exact methods depend on the reduction of the salts with $Na_2S_2O_3$ or $Na_2S_2O_4$ in acid solution, and determination of I in the resulting iodide. F. L. U.

Colorimetric determination of fluoride in water using ferric chloride. M. D. FOSTER (Ind. Eng. Chem. [Anal.], 1933, 5, 234—236).—The intensity of the coloration produced by a given amount of $FeCl_3$ in presence of NH_4CNS, the $FeCl_3$ being in excess, decreases in proportion to the amount of F' present. Special precautions are necessary if SO_4'' and Cl' are present. The F' contents of several natural waters have been determined. E. S. H.

Determination of fluorides in Illinois waters. C. S. BORUFF and G. B. ABBOTT (Ind. Eng. Chem. [Anal.], 1933, 5, 236—238).—H_2O containing small amounts of F' can be conc. without loss of F if made alkaline to phenolphthalein. F is distilled as H_2SiF_6, and the distillate is titrated with $0{\cdot}01N$-$Th(NO_3)_4$, using a mixture of $Zr(NO_3)_4$ and alizarin-red in aq. EtOH as indicator. The accuracy is about $\pm 0{\cdot}1$ p.p.m. Results for H_2O from different districts do not show the presence of F' to be characteristic of any one stratum. E. S. H.

Colorimetric determination of nitrites in water. R. UZEL.—See B., 1933, 654.

Determination of ammonia by steam distillation in a vacuum. D. BACH (Bull. Sci. pharmacol., 1932, 39, 607—615; Chem. Zentr., 1933, i, 820).—A method for the determination of NH_3, especially in biological liquids, is described. L. S. T.

Differentiation of the three stages of dissociation of phosphoric acid. J. V. DUBSKÝ and A. LANGER (Z. anal. Chem., 1933, 93, 272—273).—The colour reactions of 13 indicators with $0{\cdot}1N$-aq. Na_3PO_4, Na_2HPO_4, and NaH_2PO_4 are recorded. H. J. E.

Rapid iodometric determination of phosphites and hypophosphites isolated or mixed. D. RAQUET and P. PINTE (J. Pharm. Chim., 1933, [viii], 18, 5—10).—Phosphites (I) are oxidised by I to phosphate in alkaline solution, whilst hypophosphites (II) are oxidised in acid solution. For determination of (I), $0{\cdot}1N$-I and $Na_2B_4O_7$ are added and after 15 min. the solution is acidified with AcOH and the excess of I is titrated with $Na_2S_2O_3$. (II) is determined by the addition of $0{\cdot}1N$-I and HCl, heating at 70—80° for 15 min., and cooling. $Na_2B_4O_7$ is added and after 15 min. the mixture is acidified with AcOH and the excess of I titrated with $Na_2S_2O_3$. When both (I) and (II) are present the first process determines (I), whilst the second determines both (I) and (II). W. O. K.

Rapid determination of arsenates. M. FITZGIBBON (Analyst, 1933, 58, 469—470).—The use of large amounts of acid and KI, the possibility of back reaction, and the lengthy time required to ensure reduction in Williamson's method are avoided by reduction at the b.p. in the presence of H_2SO_4, $0{\cdot}1N$-I, and 0·2 g. of 100-mesh amorphous P, any I formed from the HI being automatically reduced by the P. When colourless (I-free), the solution is filtered, almost neutralised with NaOH, and titrated with $0{\cdot}1N$-I in presence of excess of $NaHCO_3$. J. G.

Distinction between ter- and quinque-valent arsenic by the formation of iodoantipyrine antimonate. P. DUQUÉNOIS (Compt. rend., 1933, 197, 339—341).—Antipyrine and KI in HCl with $Sb^{\cdot\cdot\cdot}$ and $Sb^{\cdot\cdot\cdot\cdot\cdot}$ compounds give golden-yellow and brick-red ppts., respectively. In the latter case $Sb^{\cdot\cdot\cdot\cdot\cdot}$ liberates I from KI, thus forming iodoantipyrine which gives the insol. antimonate (called "antipyrine iodoantimonate"). R. S. C.

Determination of ozone. III. Influence of the alkalinity on the iodometric method. R. RUYSSEN (Natuurwetensch. Tijds., 1933, 15, 125—130).—Concordant results (deviation $\ngtr 0{\cdot}5\%$) are obtained with pure KI solution, N-KI in $0{\cdot}1N$-NaOH, and N-KI buffered (with phosphate or borate) to p_H 7—9. In presence of air or N oxides, however, the use of the unbuffered solutions leads to errors of several %. H. F. G.

Approximate determination of sulphate in drinking water. L. W. WINKLER.—See B., 1933, 654.

Quantitative precipitations in highly concentrated solutions. IV. V. NJEGOVAN and V. MARJANOVIĆ (Z. anal. Chem., 1933, 93, 353—358; cf. A., 1928, 497).—Further details regarding the pptn. of $BaSO_4$ are given. F. L. U.

Nephelometric determination of sulphurous acid and its salts. BYČICHIN and LÁSKA (Chem. Listy, 1933, 27, 269—270).—The SO_3'' content of solutions can be determined by oxidation by means of H_2O_2 to SO_4'', which is determined nephelometrically. R. T.

Volumetric determination of hydrogen peroxide and Caro's acid in the presence of perdisulphuric acid. A. J. BERRY (Analyst, 1933, 58, 464—467).—H_2O_2 is determined by direct titration with $Ce(SO_4)_3$ at 0°, no indicator being necessary. The Caro's acid (I) is then reduced at room temp. by a measured excess of $(VO)_2(SO_4)_3$ which is then titrated with $KMnO_4$ without an indicator, whilst $H_2S_2O_8$ is obtained by repeating this reaction at the b.p.; alternatively (and more conveniently) (I) and $H_2S_2O_8$ are determined together at this stage by the usual $FeSO_4$ and $KMnO_4$ method. J. G.

Simplification of the Treadwell and Mayr method [for the determination of thiocyanate]. Bromometric determination of bismuth. R. MONTEQUI and J. G. CARRERÓ (Anal. Fís. Quím., 1933, 31, 242—254).—The CNS′ solution ($\ngtr$ 75 mg. KCNS) is treated with 0·5 g. of KBr and 15 c.c. of conc. HCl; $0{\cdot}1N$-$KBrO_3$ is added until the colour of Br persists, starch and KI are added, and the solution is titrated with $0{\cdot}1N$-$Na_2S_2O_3$. In the determination of Bi ($\ngtr$25 mg.), the solution, which should be free from halogen and 0·5—1N with respect to free acid, is treated with a freshly prepared solution of $K_3Cr(CNS)_6$; pptn. is facilitated by adding a trace of the solid reagent. PhMe (5—10 drops) is added, and the ppt. is removed, washed, and treated with about 5—10 c.c. of a solution containing 150 g. Na K tartrate, 108 g. NaOH, and 100 g. KBr per litre. The clear solution is heated until its colour changes to green, when it is cooled and treated with 150 c.c. of conc. HCl and sufficient 0·1N-$KBrO_3$ to yield an excess of Br, which is titrated with 0·1N-$Na_2S_2O_3$ after addition of KI and starch. The method requires only 10—15 min. H. F. G.

Detection of traces of carbon monoxide in air. H. R. Ambler and T. C. Sutton.—See B., 1933, 653.

Acidimetric method for the determination of the alkali metals. V. M. Gortikov (Proc. Leningrad Dept. Inst. Fert., 1933, **17**, 211—223).—A modification of Wöhlk's method (A., 1929, 163) is proposed. A. M.

Volumetric cobaltinitrite method for [determining] potassium. I. N. Antipov-Karataiev and A. M. Miasnikova (Proc. Leningrad Dept. Inst. Fert., 1933, **17**, 69—80).—The technique of Druschel's method (A., 1908, ii, 66, 735) as applied to aq. and acid extracts from soils is described. The accuracy is given as ±3%. A. M.

Colorimetric picrate method for [determining] potassium. I. N. Antipov-Karataiev and A. M. Miasnikova (Proc. Leningrad Dept. Inst. Fert., 1933, **17**, 81—88).—The picrate method suggested by Caley (A., 1931, 452) was tested under varying conditions. Pptn. can be carried out at 12—15°; stirring for 10—15 min. after addition of reagent gives larger crystals which are best filtered through a plug of glass wool in an ordinary funnel. $Ca^{\cdot\cdot}$, $Mg^{\cdot\cdot}$, $Al^{\cdot\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, P, and Si do not interefere, but if Na is $>$ twice K the results are poor. A. M.

Potentiometric determination of potassium. B. P. Nikolski and I. N. Lavrov (Proc. Leningrad Dept. Inst. Fert., 1933, **17**, 45—55).—K is pptd. as $K_2CaFe(CN)_6$ and the excess $Ca_2Fe(CN)_6$ is titrated potentiometrically with standard $ZnSO_4$ solution. The solubility of the ppt. is reduced by the addition of EtOH–$CaCl_2$. With a K content between 40 and 130 mg. the error is $\not>$ 0·5 mg. $Na^{\cdot}$, $Mg^{\cdot\cdot}$, $Ca^{\cdot\cdot}$, SO_4'', CO_3'', and SiO_3''' do not interfere. Details of the prep. of $Ca_2Fe(CN)_6$, the method of titration, and calculation of results are given. A. M.

Determination of potassium and sodium as sulphates. H. Remy and R. Siegmund (Z. anal. Chem., 1933, **93**, 321—331).—To expel H_2O completely K_2SO_4 must be heated at 400° and Na_2SO_4 at 900°. K_2SO_4 begins to volatilise appreciably above 800°. Loss by decrepitation, with K_2SO_4, can be avoided by introducing some H_2SO_4 before heating. The last traces of SO_3 are removed by heating at 400—800° after addition of $(NH_4)_2CO_3$. F. L. U.

Application of mercurimetry in the determination of silver. J. V. Dubský and J. Trtílek (Z. anal. Chem., 1933, **93**, 345—348; cf. this vol., 364).—The Ag solution is treated with excess of 0·1N-KCl and the excess is titrated with 0·1N-$Hg(NO_3)_2$, using diphenylcarbazide or diphenylcarbazone as indicator. F. L. U.

Adsorption indicator system silver iodide–starch; modification of the Haen–Low method for the determination of copper. F. Sierra (Anal. Fís. Quím., 1933, **31**, 26—33).—The indicator is prepared by adding 5 c.c. of starch paste and 5 drops of 0·1N-$AgNO_3$ to 20—30 c.c. of 0·2N-KI. It is added to 20—25 c.c. of $Na_2S_2O_3$ solution which has been standardised against $Cu(NO_3)_2$ solution, and the solution under examination is added from a burette until the ppt. becomes blue. The [Cu] should be 0·14—3 g. per litre, and the solution should not contain SO_4''. H. F. G.

Determination of Ca and Mg in presence of NH_4Cl and NaCl. E. N. Nabilkova (Trans. Dokuchaiev Soil Inst., 1933, **8**, No. 8, 43—51).—Ca and Mg may be determined in NH_4Cl and NaCl soil extracts without removal of these salts. A. M.

Effect of the presence of perchloric acid in the proximate analysis of limestone. F. H Fish and F. M. Taylor (J. Chem. Educ., 1933, **10**, 246—247).—The use of $HClO_4$ for dehydrating SiO_2,xH_2O involves one evaporation and no baking. $HClO_4$ in the solution does not affect later determinations. Ch. Abs.

General method of quantitative microchemical analysis. I. Determination of calcium. L. T. Fairhall and R. G. Howard (J. Roy. Microscop. Soc., 1933, [iii], **53**, 129—138).—CaC_2O_4 is pptd. under regulated conditions by the neutralisation of an acid solution by NH_3 evolved from boiling $(NH_4)_2CO_3$ solution. The ppt. is centrifuged into a calibrated capillary with sides ground plane and parallel, and the length occupied is measured with an eyepiece micrometer. 10^{-5} g. may be determined within 5%. J. S. A.

Determination of beryllium. L. Fresenius and M. Frommes (Z. anal. Chem., 1933, **93**, 275—279, 285—307; cf. B., 1932, 429).—A crit. review of the literature. A ppt. of $Be(OH)_2$ may be ignited before it is washed free from NH_4Cl. No loss due to volatilisation of $BeCl_2$ occurs. $BeCl_2$ on ignition is transformed quantitatively into BeO. H. J. E.

Determination of metals by means of 8-hydroxyquinoline. I. Effect of p_H on the precipitation of Mg, Zn, Co, Ni, Cu, and Mo from acetate solutions. H. R. Fleck and A. M. Ward (Analyst, 1933, **58**, 388—395).—Complete pptn. of Mg with 8-hydroxyquinoline, under specified conditions, takes place in the p_H range 9·44—12·66, of Zn, 4·58—13·4, of Co, 4·33—14·5, of Ni, 4·33—14·58, of Cu, 5·33—14·55, of Mo, 3·60—7·33. Of the possible separations, those of Mo from Co, of Ni from Mg, of Mo from Zn, and of Mg from Zn have been successfully carried out. E. C. S.

Microchemical determination of magnesium as magnesium calcium hexamethylenetetramine ferrocyanide. L. Debucquet and L. Velluz (Compt. rend., 1933, **196**, 2006—2007).—To determine approx. 0·1 mg. of Mg the solution is evaporated to dryness and 2·5 c.c. of 2·5% $K_2CaFe(CN)_6,C_6H_{12}N_4,6H_2O$ (cf. A., 1930, 752) in 10% aq. $C_6H_{12}N_4$ are added. On keeping for 1 hr. the Mg is entirely converted into insol. $3CaMgFe(CN)_6,4C_6H_{12}N_4,40H_2O$, which after washing with 20% $C_6H_{12}N_4$ and $COMe_2$ and drying is dissolved in H_2O and determined colorimetrically as $Fe_4[Fe(CN)_6]_3$. C. A. S.

Volumetric determination of lead by the nickel dioxide–arsenite process. R. Lang and J. Zweřina (Z. anal. Chem., 1933, **93**, 248—260; cf. A., 1927, 126).—To 50 c.c. of the neutral aq. Pb solution (up to 0·45 g. Pb) 20—25 c.c. of 2·5*N*-NaOH, 20 c.c. of aq. $Ni(NO_3)_2$ (135 g. per litre), 2 g. of $K_2S_2O_8$, and 60—80 c.c. of 1 : 1 HNO_3 are added. A ppt. of PbO_2 forms. Excess of 0·1*N*-Na_3AsO_3, 10 c.c. of 1 : 1 HCl, and 1 drop of 0·005*M*-KIO_3 are added, and the excess Na_3AsO_3 is determined with 0·1*N*-$KMnO_4$. The potentiometric titration of Pb is described. PbO_2 is first pptd., and converts $Mn^{\cdot\cdot}$ into $Mn^{\cdot\cdot\cdot}$, which is titrated with Na_3AsO_3. Errors up to 1% are due to incomplete pptn. of PbO_2. The method is inapplicable in presence of Co, Bi, Sb, Sn, halides, and phosphates. The determination of Pb and Mn together is described. Sn and Sb may be removed from Pb–Sn–Sb alloys by dissolving in H_2SO_4 and heating with HCl and KBr. H. J. E.

Microchemical determination of heavy metals with dithizone (diphenylthiocarbazone). I. Lead. II. Copper. H. Fischer and G. Leopoldi (Wiss. Veröff. Siemens-Konz., 1933, **12**, No. 1, 44—52, 52—60).—I. The Pb solution is made just ammoniacal (litmus), treated with an excess of KCN, and shaken with a green CCl_4 solution of dithizone (6 mg. per 100 c.c.) until the CCl_4 ceases to turn red. After removal of the aq. layer the red CCl_4 is shaken with very dil. aq. NH_3 to remove excess of dithizone and treated with dil. H_2SO_4 until the colour changes to green, and this colour is compared with that produced by a standard Pb solution treated similarly using a wedge colorimeter. The method can be used for the determination of Pb $>$0·0005% in Zn, Cd, Cu, Hg, Ag, As, Sb, Al, and Be.

II. Prolonged shaking of a dil. acid (H_2SO_4 or HNO_3) solution containing Cu with the CCl_4 dithizone solution results in all the Cu passing into the CCl_4 layer. Excess of reagent is removed and the analysis finished as above. In acid solution large amounts of Pb, Zn, Cd, Ni, Co, Al, As, Sb, and $Sn^{\cdot\cdot\cdot\cdot}$ do not interfere. A. R. P.

Dithizone reactions. H. Fischer (Angew. Chem., 1933, **46**, 517).—A criticism of procedure (cf. this vol., 798). E. S. H.

Separation and determination of traces of lead in the presence of small amounts of bismuth. J. H. Hamence (Analyst, 1933, **58**, 461—464).—Addition of $FeCl_3$ to the sample followed by aq. NH_3 removes Bi and Pb by adsorption (cf. A., 1932, 1223), the ppt. being then dissolved in 25 c.c. of H_2O and 0·5 c.c. of HNO_3, and 2 c.c. of saturated NH_4CNS and 1 c.c. of C_5H_5N are added. The Bi and Fe are then removed by extraction twice in a mixture of Et_2O and $C_5H_{11}\cdot OH$ (1 : 1), and the Pb is determined colorimetrically as PbS in the filtered residual liquid. J. G.

Analytical scheme for the toxicological investigation of metals, including thallium, uranium, and vanadium. L. S. Guisande (Arch. Méd. lég., 1930, **3**, 205—218).—Org. matter is destroyed by repeated heating with HNO_3, and with mixed HNO_3 and H_2SO_4; on dilution Pb, Ba, Sr, Ca are pptd. as MSO_4. After filtration (I) Pb is separated with $[CH(OH)\cdot CO_2NH_4]_2$ and aq. NH_3, the residue fused with Na_2CO_3, Ba separated as $BaCrO_4$, Sr as $SrSO_4$, Ca as $Ca_2Fe(CN)_6$. From (I) Hg, Ag, Bi, Cu, Cd, As, Sb, Sn are pptd. with H_2S (II), and As, Sb, Sn, dissolved out with hot KOH (III). Hg is separated with HNO_3, Ag with HCl, Cu with $K_4Fe(CN)_6$, Bi with aq. NH_3, Cd with KCN and H_2S. As is separated from (III) with HCl, Sb with Pt and Zn, Sn with Fe and $HgCl_2$. From (II) Tl is pptd. with KI, and the other metals with Na_2S. The ppt. is dissolved in 2*N*-HCl (IV); Ni and Co are insol. and are identified with $[CMe{:}N\cdot OH]_2$ and nitroso-β-naphthol, respectively. (IV) is oxidised with HNO_3 and with H_2O_2 in alkaline solution; Fe, Mn, and U are pptd. (V) Zn, Al, Cr, V remain in solution (VI). From (V), U is separated with $NaHCO_3$, Fe identified with $K_4Fe(CN)_6$ or KCNS, Mn with PbO_2 and HNO_3, Zn (if present) with Na_2S; in (VI) Cr is detected with H_2O_2 and Et_2O and separated with $BaCl_2$, V with cupferron, Al with aq. NH_3, Zn with Na_2S. Confirmatory tests are given for all metals. R. N. C.

Separation and determination of copper and nickel by salicylaldoxime. H. L. Riley (J.C.S., 1933, 895; cf. this vol., 478).—Details of procedure are given. The method for Ni compares favourably with that using dimethylglyoxime, the reagent giving slight turbidity in a neutral solution containing 1 part Ni in 10,000,000. Co must be absent. F. L. U.

Analysis of pure synthetic ultramarine. K. Leschewski (Z. anal. Chem., 1933, **93**, 273—274).—1 g. of the sample is treated with Br and HNO_3; SiO_2 is determined, and the filtrate diluted to 1000 c.c. In this solution the total S is determined as $BaSO_4$, Al as Al_2O_3, and alkali as sulphate (after removing Al). H_2S liberated by dil. H_2SO_4 is determined iodometrically. H. J. E.

Analysis of aluminium acetate solution. C. Rohmann.—See B., 1933, 668.

Determination of small amounts of manganese in salt solutions. N. A. Clark (Ind. Eng. Chem. [Anal.], 1933, **5**, 241—243).—The colorimetric method involving oxidation of $Mn^{\cdot\cdot}$ with KIO_4 in H_3PO_4 can detect a difference of 0·001 mg. Mn in 50 c.c. The blue coloration formed by benzidine can be stabilised by addition of small quantities of KNO_3, NH_4Cl, NH_4NO_3, or $MgCl_2$ and is suitable for determining about 0·005 mg. of Mn, but at higher dilutions the colour fades. E. S. H.

Colorimetric determination of manganese by means of persulphate. F. Alten and H. Weiland (Z. Pflanz. Düng., 1933, **30**, A, 193—198).—The use of H_3PO_4 instead of H_2SO_4 in this method permits the oxidation of larger amounts of $Mn^{\cdot\cdot}$ and prevents pptn. of MnO_2. Accuracy is not affected

by the presence of AgCl. The method is applicable to the examination of soil extracts and plant ash.
A. G. P.

Colorimetric determination of iron by the thiocyanate procedure. L. DE BROUCKÈRE and A. E. GILLET (Bull. Soc. chim. Belg., 1933, **42**, 281—293).—The colour produced varies with the prep. and age of the solutions used. A considerable excess of KCNS is advisable. Results are accurate to about 1% when the solution is *N* with respect to NH_4Cl, KCl, KNO_3, $MgCl_2$, $Ca(NO_3)_2$, $BaCl_2$, or $AlCl_3$. Large quantities of Mn produce a positive error. In presence of SO_4'' or PO_4''' the concn. of acid in the solutions used should be about *N*.
E. S. H.

Iodometric determination of $Fe^{\cdot\cdot}$ in the presence of organic matter. N. F. SOLOVËVA (Proc. Leningrad Dept. Inst. Fert., 1933, **17**, 21—28).—$Fe^{\cdot\cdot}$ is oxidised with I solution, and $Fe^{\cdot\cdot\cdot}$ is removed from solution by $NH_4F+K_2C_2O_4$ (5 : 1), 6 g. of the mixture being used for each determination. Methylene-blue is used as indicator. The presence of humus, as in acid extracts, does not affect the determination appreciably. Potentiometric methods may be used. Mohr's iodometric method for the determination of $Fe^{\cdot\cdot\cdot}$ is untrustworthy in the presence of org. matter.
A. M.

Phenanthrolene-ferrous ion: a reversible oxidation-reduction indicator of high potential and its use in oxidimetric titrations. G. H. WALDEN, jun., L. P. HAMMETT, and R. P. CHAPMAN (J. Amer. Chem. Soc., 1933, **55**, 2649—2654; cf. A., 1931, 1385).—The *o*-phenanthrolene-ferrous ion is a completely reversible indicator for the titration of $FeSO_4$ in 0·3—5*M*-H_2SO_4 with $K_2Cr_2O_7$, $Ce(SO_4)_2$, and 0·01*N*-$KMnO_4$. In general, the mean error is $<\pm0{\cdot}7$ part per 1000. The prep. of the indicator is described.
J. G. A. G.

Simultaneous potentiometric determination of ferricyanide and chromate in alkaline solution by means of vanadous sulphate. C. DEL FRESNO and E. MAIRLOT (Anal. Fís. Quím., 1933, **31**, 122—128).—Two well-defined breaks in the potential curve are observed, corresponding with reduction to $Fe(CN)_6''''$ and $Cr^{\cdot\cdot\cdot}$, respectively. The solution should contain 13—18% of free NaOH, the temp. should be 50—70°, and air must be excluded.
H. F. G.

Volumetric determination of cobalt by means of ferrous sulphate and potassium dichromate. L. A. SARVER (Ind. Eng. Chem. [Anal.], 1933, **5**, 275—276).—Dil. H_2SO_4 and $NaBO_3$ are added to the $Co^{\cdot\cdot}$ solution, and $Co(OH)_3$ is pptd. by excess NaOH. Excess of $FeSO_4$ solution is introduced with exclusion of air; the ppt. is dissolved by adding H_2SO_4 and then H_3PO_4. Excess of Fe is titrated with $K_2Cr_2O_7$, using Ba diphenylaminesulphonate as indicator. Nitrates and other oxidising substances must be absent. Ni does not interfere.
E. S. H.

Determination of metals with anthranilic acid. II. Cobalt, nickel, and copper. H. FUNK and M. DITT (Z. anal. Chem., 1933, **93**, 241—247; cf. this vol., 244).—Neutral aq. solutions of Co, Ni, or Cu salts are pptd. at the b.p. with 3% aq. Na anthranilate. The ppts. of metal salts are cryst., readily filtered, and coloured rose-yellow, bluish-green, and green, respectively. The ppt. is washed with EtOH, dried at 105—110°, and weighed. The sensitivities of the reactions are 1 in 8×10^5, 1 in $4{\cdot}45\times10^5$, and 1 in 10^6, respectively. A volumetric method depends on the dissolving of the ppt. of Co, Ni, or Cu anthranilate in acid and determining the org. acid with bromide–bromate solution.
H. J. E.

Potentiometric determinations on nickel and cobalt ferrocyanides. I. A. ATANASIU and A. I. VELCULESCU (Bul. Chim. Soc. Române, 1933, **34**, 71—75).—Potentiometric titrations of $CoSO_4$ and $NiSO_4$ (I) with $K_4Fe(CN)_6$ (II) give curves which show inflexions at a mol. ratio (I) : (II) of 5 : 4, indicating that the ppts. are probably mixtures of $3K_2MFe(CN)_6$ with $1M_2Fe(CN)_6$, where M=Ni or Co. In the presence of NH_4 or alkali salts, mixed ferrocyanides of high absorptive powers are formed; in mixed Ni and Co solutions the two metals behave as one.
A. R. P.

Increased sensitivity of a microchemical reaction for chromium. I. M. KORENMAN (Z. anal. Chem., 1933, **93**, 268—271).—The sensitivity of the reaction for the detection of Cr by oxidation and pptn. as Ag_2CrO_4 is increased from 1 in 80,000 to 1 in 571,000 by co-pptn. with Ag_2SO_4. The ratio Cr : SO_4 should be between 1 : 50 and 1 : 200.
H. J. E.

Rapid macro- and micro-determination of bismuth. G. SPACU and P. SPACU (Z. anal. Chem., 1933, **93**, 260—265).—The Bi solution is made slightly acid with HNO_3, excess of KI is added, and Bi is pptd. at the b.p. with hot conc. aq. $[Co\,en_2(SCN)_2](SCN)(\frac{1}{6})$ (cf. Werner, A., 1900, i, 86). The orange-yellow cryst. ppt. of $[BiI_4][Co\,en_2\,(SCN)_2](\frac{1}{6})$ (20·65% Bi) is washed with EtOH and Et_2O, dried in a vac. desiccator, and weighed. The method is applicable for micro-determinations.
H. J. E.

Determination of bismuth in copper. ANON.—See B., 1933, 631.

Inhibiting action of certain ions on the fluorescence of the uranyl ion and its applications to inorganic chemical analysis. VOLMAR and MATHIS (Bull. Soc. chim., 1933, [iv], **53**, 385—392).—The fluorescence of $UO_2^{\cdot\cdot}$ is destroyed by Cl′, Br′, I′, SCN′, $Fe(CN)_6''''$, $Fe(CN)_6'''$, NO_2', S′, S_2O_3'', CrO_4'', Cr_2O_7'', MnO_4', AsO_3''', and salicylate. The limiting quantity of each ion required has been determined. The concn., temp., and p_H of the $UO_2^{\cdot\cdot}$ solution have practically no influence. Iodides at a concn. of *N*/3000 destroy the fluorescence. The phenomenon may be adapted for methods of analysis. E. S. H.

Application of the micropolychromar to micro-determination of m.p. K. RICHTER and H. DAMM (Naturwiss., 1933, **21**, 517—518).—The micropolychromar can be applied to the micro-determination of m.p. of cryst. substances and particularly of fats.
A. J. M.

Radiation thermopiles for use at liquid air temperatures. C. H. CARTWRIGHT (Rev. Sci. Instr., 1933, [ii], **4**, 382—384).—Bi+11% Sb is the best combination.
C. W. G.

Refrigeration with ammonium thiocyanate. H. Seekamp and W. Pfahler.—See B., 1933, 607.

Ice calorimeter to measure very small thermal effects. W. Swientoslawski, A. Zmaczynski, I. Zlotowski, J. Usakiewicz, and J. Salcowicz (Compt. rend., 1933, **196**, 1970—1973).—The apparatus has a useful space of 500 c.c., and is accurate to ±0·03 g.-cal. per hr., and in the case described was able to detect a heat evolution of $1—3\times10^{-5}$ g.-cal. per g. per hr. C. A. S.

Apparatus for producing a controlled temperature programme. W. B. Warren (Ind. Eng. Chem. [Anal.], 1933, **5**, 285—286).—The apparatus enables the rate of rise of temp. of an electric furnace to be controlled at will, with complete reproducibility. E. S. H.

Air thermostat for solubility determinations. H. G. Beier and H. Brintzinger (Kolloid-Z., 1933, **64**, 173—175).—The electrically-controlled apparatus is const. to 0·1° over the range 20—80° and can be used below room temp. E. S. H.

Thermo-electric temperature scale of Pt|Pt–Rh thermocouple. K. Bitō and M. Matsui (J. Soc. Chem. Ind. Japan, 1933, **36**, 421—424B).—Temp. scales based on the two sets of fixed points Sb, Ag, Au (I) and Zn, Sb, Ag (II) and on the two equations $E=a+bt+ct_2$ (III) and $t=a+bE+cE^2$ were compared, using five Pt|Pt–Rh couples. Using equation (III) and fixed points (I) and (II) the deviations at the m.p. of Zn and Au, respectively, were $\not>$0·5°, but the differences between the two equations were greater. A. G.

Pt|Pt–Rh thermocouple. K. Bitō and M. Matsui (J. Soc. Chem. Ind. Japan, 1933, **36**, 424—426B).—Under-cooling of Ag used for calibrating thermocouples is avoided if the rate of cooling is small. Zn can be used as a secondary fixed point. A. G.

Microphotometer for registering the blackening of a photographic plate. W. Schütz (Physikal. Z., 1933, **34**, 566—569).—The apparatus is described. A. J. M.

Air chamber for studying photosynthesis under natural conditions. A. J. Heinicke (Science, 1933, **77**, 516—517). L. S. T.

Calcium target for *X*-rays. H. Kersten and J. Maas (Rev. Sci. Instr., 1933, [ii], **4**, 381).—The target is made by melting and grinding 5 g. of SiO_2, 5 g. of CaO, and 0·3 g. of clay. C. W. G.

Demountable metal *X*-ray tube. E. P. Miller (Rev. Sci. Instr., 1933, [ii], **4**, 379—380).—The cathode assembly is made completely of Cr-plated brass. Vac.-tightness is obtained by means of rubber gaskets. C. W. G.

Spectroscopic examination of thin metallic films. A. Harvey and E. S. Dreblow (J. Sci. Instr., 1933, **10**, 224—225).—A spark between a Cu electrode and the thin film on glass is examined. C. W. G.

Method of taking *X*-ray photographs of crystalline powders at the temperature of liquid air. J. A. Santos and J. West (J. Sci. Instr., 1933, **10**, 219—221).—A small fountain of liquid air is caused to play over the specimen. C. W. G.

Photo-electric spectrophotometer. A. G. Winn (Trans. Faraday Soc., 1933, **29**, 689—697).—Two photo-electric cells are used, an electrometer triode being employed as null-reading, amplifying voltmeter. Calibration against a rotating variable sector is obviated, and the range of the instrument thereby extended. J. S. A.

Photo-electric comparator for precise and rapid measurement of reflexion and transmission. C. H. Sharp and H. J. Eckweiler (J. Opt. Soc. Amer., 1933, **23**, 246—250). N. M. B.

Constant deviation *X*-ray vacuum monochromator. G. I. Harper (Proc. Camb. Phil. Soc., 1933, **29**, 408—416).—An instrument which provides an accurately monochromatised beam by reflexion at a crystal, and permits the wave-length to be changed without moving either the *X*-ray tube or the measuring apparatus, is described. N. M. B.

Measurement of light absorption. Accuracies of several spectrophotometric methods. R. Fonteyne (Natuurwetensch. Tijds., 1933, **15**, 131—137).—A theoretical discussion is given of the relative degrees of accuracy obtainable by the spectrophotometric, photographic, and photo-electric methods. H. F. G.

Determination of conductivity and dielectric constants of electrolytes for wave-lengths of 1 m. P. Wenk (Ann. Physik, 1933, [v], **17**, 679—698).—An accurate barretter method for carrying out the above determinations simultaneously is described. The results are compared with those derived from the Debye–Falkenhagen dispersion theory. There is good qual. agreement, but deviations increasing with concn., valency, and frequency are found. A. J. M.

Electron-tube potentiometer for the determination of reduction–oxidation potentials. C. H. Werkman, C. A. Johnson, and H. D. Coile (Iowa State Coll. J. Sci., 1933, **7**, 163—175).—Simple apparatus is employed. Ch. Abs.

Use of micro-coulometers in the determination of transport numbers by the moving boundary method. W. O. Reevely and A. R. Gordon (Trans. Electrochem. Soc., 1933, **63**, 261—265).—For the measurement of small quantities of electricity, a Ag coulometer consisting of a Pt crucible containing about 3 c.c. of 10% aq. $AgNO_3$, with a fine linen bag or glass tray to catch anode slimes, gives accurate and reproducible results by using a micro-balance for the weighings. Determinations of the transport no. of $K^{\cdot}$ in 0·1N-KCl by the moving boundary method, using this type of coulometer, give 0·4899±0·0003 at 25°. H. J. T. E.

Apparatus for measuring hydrogen-ion concentration. G. Demortier (Bull. Inst. agron. Gembloux, 1932, **1**, 65—73).—Details of new types of compact standard cell, HgCl electrode, and H_2 electrode are given. Nutr. Abs. (*b*)

Use of the vacuum-tube electrometer with extremely high input resistance. R. E. Burroughs and J. E. Ferguson (Rev. Sci. Instr., 1933,

[ii], 4, 406).—The method is suitable for use with cells of very high internal resistance. C. W. G.

Portable double Geiger counter. R. D. Bennett, J. C. Stearns, and W. P. Overbeck (Rev. Sci. Instr., 1933, [ii], 4, 387—390).—A thermionic valve method is described. C. W. G.

Amplified ballistic method for measurement of glass electrode electromotive force. A. Hemingway and E. L. Arnow (Ind. Eng. Chem. [Anal.], 1933, 5, 278).—A new circuit is described. The bulb of the electrode is filled with HCl–KCl buffer saturated with quinol and contact is made by a bare Pt wire. E. S. H.

Application of compensated valve-voltmeter to measurements of glass electrode potentials. A. S. McFarlane (J. Sci. Instr., 1933, 10, 208—212).—An instrument having a grid-input impedance of 5000 megohms is described. Glass electrode potentials can be measured to 0·05 mv. C. W. G.

Apparatus glass. I, II. F. H. Zschacke (Chem.-Ztg., 1933, 57, 521—523, 542—544).—A review of recent improvements in glass and its application in chemical industry. Compositions of modern glasses are given and their properties (chemical resistance, expansion coeff., softening temp., hardness, and homogeneity) are discussed. E. S. H.

Apparatus for the separation and measurement of steam distillates. W. H. Simmons and C. A. Hills (Analyst, 1933, 58, 396). E. C. S.

[Laboratory] fractional distillation. R. McIntyre (Chem. and Ind., 1933, 578—579).—In the American "single condenser" system of distillation the vapour from the still head is completely condensed and divided, part being run back down the column. This is applied to laboratory fractionation by the use of a vertical Liebig condenser fitted above the column having an expansion at its lower end and a side tube with tap. The latter allows the proportion of distillate removed to be controlled. C. I.

Fractional distillation. R. G. W. Eadie (Chem. and Ind., 1933, 618).—Modifications of McIntyre's apparatus (preceding abstract) are suggested. E. S. H.

Arsenic distillation apparatus without ground-glass connexions. B. S. Evans (Analyst, 1933, 58, 470—471).—A modified Wurtz flask, in which a T-piece is inserted in the neck and the side tube is bent vertically and attached to a Liebig condenser by corks in both cases, is described. During distillation a slow stream of air passed in through one arm of the T-piece prevents the acid from attacking the cork. J. G.

Fractional distillation at reduced pressure. A. G. Banús (Anal. Fís. Quím., 1933, 31, 311—313).—Brühl's apparatus has been modified to render it suitable for use with substances of high m.p. A Hg-in-glass manometer for use in reduced pressure distillation is described. H. F. G.

Glass packing for laboratory fractionating columns. C. D. Wilson, G. T. Parker, and K. C. Laughlin (J. Amer. Chem. Soc., 1933, 55, 2795—2796).—The coils are made by winding softened glass on a metal rod. Single and double turns from such coils afford highly efficient packing for fractionating columns. J. G. A. G.

Efficiency of the standard and some new types of reflux condenser. F. Mach and R. Herrmann (Chem. Fabr., 1933, 6, 199—201, 211—213).—The results of comparative tests on the efficiency of nineteen types of reflux condensers are tabulated and discussed. The standardised German type is among the most efficient; more complicated forms are therefore unnecessary. A. R. P.

Handling of distilled water in aluminium. H. V. Churchill (Ind. Eng. Chem. [Anal.], 1933, 5, 264—266).—A review, favouring the use of Al. E. S. H.

Large-capacity extractor. N. L. Drake and J. R. Spies (Ind. Eng. Chem. [Anal.], 1933, 5, 284).—The apparatus, having a capacity of 12 litres, is designed for use with MeOH, but can be used with few changes for any solvent having b.p. $< 100°$. E. S. H.

Micro-extractor. L Titus and V. W. Meloche (Ind. Eng. Chem. [Anal.], 1933, 5, 286—288).—The apparatus may be used with 5 c.c. of Et_2O. E. S. H.

Divided titration pipette-stirring rod. R. Richardson (J. Amer. Chem. Soc., 1933, 55, 2794—2795).—Part of the liquid to be titrated is sucked through the narrow jet into the hollow barrel of the pipette-stirring rod, which has a tap at the upper end. When a slight excess of reagent has been added rapidly from the burette, the liquid in the pipette is added by opening the tap and the titration completed dropwise. Rapid titrations in a fixed time can be effected in this way. J. G. A. G.

Measurement of the permeability of porous media for homogeneous fluids. R. D. Wyckoff, H. G. Botset, M. Muskat, and D. W. Reed (Rev. Sci. Instr., 1933, [ii], 4, 394—405).—Detailed descriptions of technique, using both gases and liquids, are given for substances such as rocks. C. W. G.

Gas bubbler for very small pressure drops. C. C. Furnas (Ind. Eng. Chem. [Anal.], 1933, 5, 250).—The apparatus is satisfactory for absorbing CO_2 from gases containing 1—90% at velocities up to 50 c.c. per min. E. S. H.

Measurement of viscosities of liquids saturated with gases at high pressures. B. H. Sage (Ind. Eng. Chem. [Anal.], 1933, 5, 261—263).—A viscosimeter suitable for studying the effect of dissolved gas on the viscosity of crude oils is described. The time required for a sphere to roll or slide down an inclined tube filled with the liquid is determined. A wide range of viscosity can be covered by using spheres of different sizes. E. S. H.

Water-motor stirrer. R. E. Dunbar (Ind. Eng. Chem. [Anal.], 1933, 5, 266). E. S. H.

Chain arrangement for rubber stoppers. R. A. Osborn and A. G. Sterling (Ind. Eng. Chem. [Anal.], 1933, 5, 274).—A device for attaching the stopper to the neck of the container. E. S. H.

Simple laboratory tachometer. W. A. Sperry (Ind. Eng. Chem. [Anal.], 1933, 5, 288).—An automobile speedometer may be converted suitably.
E. S. H.

Simple hygrometer. K. Mellanby (Nature, 1933, 132, 68).—A simple method for measuring humidity in small or inaccessible places is described. Humidity at a leaf surface or among vegetation can thus be determined. L. S. T.

Telephonic drop counter. C. F. Graham (Science, 1933, 77, 542—543). L. S. T.

Stop-cock clamp. A. F. Roe (Science, 1933, 77, 566).—A spring clamp suitable for manometers, vac.-pump distributors, etc. is described. L. S. T.

Laboratory measurement of gas currents. C. Padovani and G. Monti (Giorn. Chim. Ind. Appl., 1933, 15, 331—334).—The principles and apparatus involved in measuring gas flow are discussed. Contrary to makers' guarantees, capillary fluxometers of the Riesenfeld type obey the Poiseuille linear law within only very narrow load limits. Experiments on the flow of gas through such porous diaphragms as filter-paper, porous glass, graphite, and refractories show that many of these substances behave absolutely as capillary systems and that the gas flow through them obeys Poiseuille's law over very wide ranges of load. Porous diaphragm fluxometers are thus distinctly advantageous, and may, moreover, be used to measure the flow of gas under high pressure.
T. H. P.

Rotatable wooden burette holder as titration stand. H. Härdtl (Z. anal. Chem., 1933, 93, 332—335). F. L. U.

Phosphoric anhydride as drying agent. W. A. Bone (Chem. and Ind., 1933, 246—247).—The necessity of purifying P_2O_5 before using it as a drying agent in studying gas reactions is emphasised.
A. R. P.

Terpenes, sesquiterpenes, and related compounds. II. Micro-method for mol. wt. determination using camphene as a cryoscopic solvent. S. Uchida and K. Shimoyama (J. Soc. Chem. Ind. Japan, 1933, 36, 388—392B).—Camphene has the advantage of a lower m.p., but has a low solvent power for polar compounds, especially acids. The use of a more accurate method of calculation than van 't Hoff's equation is discussed. A. A. L.

Precision weights. J. J. Manley (Phil. Mag., 1933, [vii], 16, 489—504).—Experiments on the corrosion of wts. by fumes from glue are described. Other sources of error in wts. are discussed.
H. J. E.

Mass spectrometer with directional and velocity focussing. H. Bondy and K. Popper (Ann. Physik, 1933, [v], 17, 425—444).—The spectrometer has been constructed according to the theory of Bartky and Dempster. By combining a radial electric field with a homogeneous transverse magnetic field the directional and velocity focussing can be obtained in one and the same position. W. R. A.

Production of highly concentrated emanation preparations. O. Werner (Z. physikal. Chem., 1933, 165, 391—397).—A simple apparatus for the purification and concn. of Ra emanation, starting from highly emanating dry preps., and an electric oven suitable for the production of glass capillaries with a wall thickness of 10 μ or less, which can be filled with emanation and are permeable to α-particles, are described. R. C.

Nomograph for rapid calculation of sulphate : carbonate ratios. R. T. Sheen (Ind. Eng. Chem. [Anal.], 1933, 5, 276—277). E. S. H.

Geochemistry.

Determination of atmospheric ozone by visual photometry. J. Gauzit (Compt. rend., 1933, 197, 178—180; cf. this vol., 45).—A modification of the method is described. The mean equiv. thicknesses of the O_3 layer at Montpellier during the months Feb. to June 1933 have been 0·29, 0·33, 0·38, 0·37, and 0·32 cm., respectively, or substantially $>$ the corresponding vals. for 1931 (cf. A., 1927, 1164).
C. A. S.

Chloride and sulphate in rain-water. W. D. Collins and K. T. Williams (Ind. Eng. Chem., 1933, 25, 944—945).—Data are reviewed. The average contents of Cl and SO_4 in rain-H_2O on reaching the earth in the U.S.A. are approx. 0·3 and 2 p.p.m., respectively. H. J. E.

Characteristics of the newly discovered lakes to the north of the Volga delta : Deschscheschak, Bekesch-Sor, etc. V. I. Nikolaev and B. I. Stepanov (J. Appl. Chem. Russ., 1933, 6, 436—449).—Analytical data are given for a no. of salt lakes, possessing an unusually high NaCl content, and depositing on evaporation $NaCl,MgSO_4,4$, 5, 6, and $7H_2O$, $KCl,MgCl_2,6H_2O$, $MgCl_2,6H_2O$, and $MgSO_4,Na_2SO_4,4H_2O$. R. T.

Batalpaschinsk (N. Caucasus) salt lake. P. N. Laschtschenko and A. I. Morozova (J. Appl. Chem. Russ., 1933, 6, 416—435).—The composition of the saline varies considerably with the season, and from year to year. During the winter months mirabilite is pptd. and is redissolved during the summer months; the ratios $[\mathrm{Na}^{\cdot}]/[\mathrm{Mg}^{\cdot\cdot}]$ and $[\mathrm{Cl}']/[\mathrm{SO}_4'']$ remain fairly const. The lake is fed by ground-H_2O, the composition of which becomes more nearly that of the lake the closer it is to the latter. Na_2SO_4 originates from interchange of Na and Ca between soil colloids or mud from the lake-bottom and dissolved $CaSO_4$.
R. T.

Lithium in sea-water. B. D. Thomas and T. G. Thompson (Science, 1933, 77, 547—548).—A method for the spectrographic determination of Li is described. Sea-H_2O contains 0·1 mg. Li per litre.
L. S. T.

Boron content of sea-water. E. G. Moberg and M. W. Harding (Science, 1933, 77, 510; cf. this vol., 802).—Sea-H_2O from N. California and Tortugas, Florida, contains 4·30—4·80 mg. per kg. The variation corresponds with the variation in salinity, the average ratio of B to halides being 0·000239.
L. S. T.

Lepidolite system. A. N. Winchell (Amer. Min., 1932, 17, 551—553).—Structural relations are discussed; a diagram shows the variations of optical properties with composition. Ch. Abs.

Serendibite from Warren County, N.Y., and its paragenesis. E. S. Larsen and W. T. Schaller (Amer. Min., 1932, 17, 457—465).—Serendibite, $3Al_2O_3,4MgO,2CaO,B_2O_3,4SiO_2$, of hydrothermal-contact-metamorphic origin, is triclinic, n_α 1·701, n_β 1·703, n_γ 1·706. Polysynthetic twinning is prominent.
Ch. Abs.

Magnesiosussexite. J. W. Gruner (Amer. Min., 1932, 17, 509—513).—Magnesiosussexite, $2(Mg,Mn)O,B_2O_3,H_2O$, found as a veinlet in hæmatite, had hardness 3, d 2·83 approx., n_α 1·595, n_γ 1·660, and contained MgO 29·32, MnO 23·48, R_2O_3 0·34, B_2O_3 36·18, H_2O+ 10·18, H_2O- 0·22, SiO_2 0·43, CaO 0·05, total 100·20%. The mineral is isomorphous with sussexite and camsellite. Ch. Abs.

Refractive indices of bloedite. W. T. Schaller (Amer. Min., 1932, 17, 530—533).—Bloedite has n_α 1·4826, n_β 1·4855, n_γ 1·4868. Ch. Abs.

Castanite from Chuquicamata, Chile. M. C. Bandy (Amer. Min., 1932, 17, 534—537).—Castanite, $Fe_2O_3,2SO_3,8H_2O$, associated with amarantite and other Fe sulphates, has hardness 2·5, n_α 1·550, n_β 1·645, n_γ 1·660. Ch. Abs.

Mellite. T. F. W. Barth and C. J. Ksanda (Amer. Min., 1933, 18, 8—13).—Mellite, $Al_2C_{12}O_{12},18H_2O$, a mellitate, has a 22·0, c 23·3 Å., $d_{calc.}$ 1·65; the unit cell, a tetragonal prism, contains 16 mols. Ch. Abs.

Balkashite. G. L. Stadnikov (Brennstoff-Chem., 1933, 14, 227—229; cf. B., 1931, 4).—A no. of different varieties of balkashite (I), distinguished as ordinary, young, old, and weathered (I), respectively, have been examined. The variation in composition, particularly in O content, is discussed. It is assumed that oxidation proceeded most vigorously during the formation (by polymerisation etc. of the fatty acids) of the (I), the O content, therefore, as well as other characteristics, being determined more by the conditions prevailing during formation than by those to which (I) has subsequently been exposed. Ordinary (I) on carbonisation in the Al assay apparatus yielded: tar 69·4% (d 0·844; bases 0·42%; carboxylic acids 1·86%; phenols and asphaltenes nil); semi-coke 5·5%; gas 16·3%; H_2O of decomp. 8·8%.
A. B. M.

Thorianite from Easton, Pa. R. C. Wells, J. G. Fairchild, and C. S. Ross (Amer. J. Sci., 1933, [v], 26, 45—54).—Analyses are given and the age is calc. to be pre-Cambrian. C. W. G.

Insolation hypothesis of rock weathering. E. Blackwelder (Amer. J. Sci., 1933, [v], 26, 97—113).—A discussion adversely criticising the theory for lack of supporting evidence. C. W. G.

Magnetic properties of certain igneous rocks. A. F. Hallimond [in part with E. F. Herroun] (Proc. Roy. Soc., 1933, A, 141, 302—314).

Thermal expansion of plagioclase. S. Kôzu and J. Ueda (Proc. Imp. Acad. Tokyo, 1933, 9, 262—264).—Vals. for plagioclase from five different sources are given. C. W. G.

Triangular biotitic phlogophite in basalt from Mutsuré-jima and its chemical composition. S. Kôzu and S. Tsurumi (Proc. Imp. Acad. Tokyo, 1933, 9, 269—272).—Analyses are given. There are 4 mols. to the unit cell, which has a_0 5·29, b_0 9·27, $d_{(001)}$ 20·05 Å. C. W. G.

Mica basalt from Mutsuré-jima. S. Kôzu and B. Yoshiki (Proc. Imp. Acad. Tokyo, 1933, 9, 265—268).—Analyses are given. C. W. G.

Geochemistry of boron. V. M. Goldschmidt and C. Peters (Nachr. Ges. Wiss. Göttingen, 1932, 402—407; Chem. Zentr., 1932, ii, 3857).—With a Cu arc 0·0005% B_2O_3 can be detected and the method is quant. Volcanic and sedimentary rocks, meteorites, coal and wood ashes have been examined. A German granite and gabbro contained 0·001% B_2O_3, whilst meteorites showed a somewhat lower B content than volcanic rocks. Argillaceous sedimentary rocks contain larger quantities of B_2O_3 (approx. 0·1%). This high B content must come from the hydrosphere, especially sea-H_2O, and it appears that in phyllite and micaceous schists, the regional metamorphic descendants of such sediments, considerable amounts of freshly-formed tourmaline are widespread. A marked concn. of B occurs in coal ash. L. S. T.

Emery [rocks] of Greece and bauxites. J. de Lapparent (Compt. rend., 1933, 197, 75—77).—The emery rock from Samos, which resembles that from Naxos, was probably originally a metamorphic bauxite. It is pisolitic, and consists essentially of diaspore with particles of anatase and rutile, and some hæmatite, united by a siliceous cement; corundum occurs occasionally in fair-sized crystals with inclusions of anatase and rutile. C. A. S.

Chemical and mineralogical changes in a miocene marl at contact with a granite laccolite. L. Glangeaud and Boutiron (Compt. rend., 1933, 197, 164—166).—In Jebel Al-rujaud, 15 km. W. of Cherchel (Algeria), a laccolite has been intruded into marl, which has been metamorphosed below it. The first change of the marl is into a felspathic and pyroxenic hornfels; nearer the laccolite appears spherulitic prehnite, which is gradually on still nearer approach replaced by diopside, evidently the result of fumarole action. Analyses are given of the marl, hornfels, and the prehnite- and diopside-containing rocks. C. A. S.

Physical properties of colloidal clay. II. C. La Rotonda (Z. Pflanz. Düng., 1933, 30, A, 269—284; cf. A., 1932, 806).—Experimental data confirmatory of earlier work are recorded. Addition of electrolytes in artificial fertilisers to acid soils improves their physical condition by transformation of colloids from sol into gel forms. A. G. P.

X-Ray examination of ceramic raw materials. II. T. Nakai and Y. Fukami (J. Soc. Chem. Ind. Japan, 1933, **36**, 434—435B).—Kaolin begins to lose its cryst. structure at 350—400° and is completely amorphous at 780°. The amorphous Al_2O_3 begins to crystallise at 900—1000°. Quartz is unaffected by temp. up to 1000°. A. G.

Chemical composition of mechanical fractions of podsols and bog soils. A. A. Rode (Trans. Dokuchaiev Soil Inst., 1933, **8**, No. 3, 1—56).—The chemical composition of the fractions (1—0·0025 mm., 0·0025—0·00025 mm., and $<$ 0·00025 mm.) is used to show the successive stages of podsolisation and gley formation. A. M.

Icelandic soil types. F. Weiss (Kong. Vet.-Landb. København, Aarsskr., 1933, 1—18).—These soils are derived from materials of glacial or volcanic origin. Although they contain no free CaO they have a p_H varying from 6 to 7. The fraction sol. in $(NH_4)_2C_2O_4$ is high, as is the total N. The C : N ratio varies from 10 to 18. The ratio hygroscopic H_2O : total absorption complex is fairly const. A. M.

How can the "descriptive" soil map be used in soil valuation. A. Till (Z. Pflanz. Düng., 1933, **30**, **A**, 319—323).—Extension of the uses of the author's method of charting soils (this vol., 369) is described. A. G. P.

Characteristics of the organic matter of soils of the U.S.S.R. I. N : C ratio of the organic matter. N. P. Remezov. **II. Approximate qualitative composition of the organic matter.** N. P. Remezov and (Mme.) M. M. Vlasova (Z. Pflanz. Düng., 1933, **30**, **A**, 285—299, 299—311).—I. The significance of the C : N ratio of soil org. matter is discussed and data for numerous soils of various types are recorded.

II. The methods of Waksman (B., 1930, 633) are applied to the examination of Russian soils. In the grey-soil area, the org. matter contains little cellulose or hemicellulose, and the proportion of "protein" substance exceeds that of the lignin–humus (I) complexes. In chestnut-coloured soils hemicellulose is present and the (I) fraction occurs in greater proportion than "protein" matter. In chernozems the total org. matter content is high, and the (I) fraction averages 2·5—3 times the "protein" fraction. The podsolisation process is associated with a decrease in the (I) fraction. A. G. P.

Soil classification based on the composition of the colloidal clay fraction. III. Terra rossa formation in comparison with limestone weathering under varied climatic conditions. IV. Comparison between the weathering of limestone and basic eruptive rocks in the Mediterranean area. A. Reifenberg and S. Adler (Z. Pflanz. Düng., 1933, **30**, **A**, 345—356, 356—358; cf. B., 1933, 559).—III. Soils derived from limestone may be classified according to the SiO_2 : sesquioxide ratio of their colloid fractions. The importance of the $SiO_2 : Fe_2O_3$ ratio as well as the $SiO_2 : Al_2O_3$ ratio is emphasised. Whilst desert and steppe soils have a particularly wide $SiO_2 : Fe_2O_3$ ratio, the terra rossa have a wide $SiO_2 : Al_2O_3$ and relatively narrow $SiO_2 : Fe_2O_3$ ratios. This results in the accumulation of both SiO_2 and sesquioxide, and with it is associated the protective action of SiO_2 against pptn. of sesquioxides by $Ca^{\cdot\cdot}$ during dry periods. In neighbouring brown-earth soils the apparent enrichment in Fe_2O_3 and Al_2O_3 is due to the removal of SiO_2. In tropical areas this removal of SiO_2 is intensified and the apparent enrichment in Fe_2O_3 and Al_2O_3 still greater. Such soils are, however, sharply differentiated from terra rossa in both origin and properties. Max. apparent accumulation of sesquioxides occurs in tropical laterites, in which sesquioxide sols are flocculated during dry periods and the SiO_2, more stable in low concns. of electrolytes, is leached away. Complete latérisation may not occur over limestone rock owing to partial pptn. of SiO_2 by $Ca^{\cdot\cdot}$.

IV. Soils derived from eruptive rocks (basalt etc.) have a smaller SiO_2 : sesquioxide ratio than those from limestone. Both Fe_2O_3 and Al_2O_3 are equally concerned in this difference. The presence of $Ca^{\cdot\cdot}$ tends to restrict the leaching of SiO_2. A. G. P.

Iodine content of soil in Kentucky. J. S. McHargue and D. W. Young (Soil Sci., 1933, **35**, 425—434).—In the area examined I was highest in soils derived from limestone strata and lowest in those from sandstone. The I content of phosphatic and non-phosphatic profiles varied considerably at different depths, but no correlation between I and PO_4''' contents was apparent. Soils from limestone rock contained much more I than the unaltered rock. A. G. P.

Formation of muscovite in soils, and refinements in specific gravity separations. N. J. Volk (Amer. J. Sci., 1933, [v], **26**, 114—129).—Detailed descriptions of the use of s-$C_2H_2Br_4$ and $PhNO_2$ for the mechanical separation of minerals are given. C. W. G.

Occurrence of sphaerosiderite in a sub-bituminous coal from Hsian coal mine, Liaoning Province. C. Y. Hsieh (Contrib. Sin Yuan Fuel Lab., China Geol. Survey, 1932, No. 7).—Small oolites in Chinese Cretaceous coal contained FeO 51·62, CO_2 30·95, org. matter 2·62, insol. 1·06%. Ch. Abs.

Organic Chemistry.

Origin of petroleum. I. E. Berl and H. Biebesheimer. **II.** E. Berl and W. Dienst (Annalen, 1933, **504**, 38—61, 62—71).—I. The possibility is investigated that vegetable material is the precursor of petroleum and that the transformation of the material is conditioned by the chemical and physical action of inorg. deposits commonly associated with petroleum. Treatment of cotton wool with

N-NaOH at 310—330°/180—200 atm. ($CaCO_3$ or dolomite behave similarly) gives gases, mainly CO_2 and H_2, and a " protoproduct " (I) which gradually passes into a black, asphalt-like mass when exposed to air. (I) is strongly unsaturated, and contains small amounts of acidic material and naphthenes; alcoholic OH is present. Hydrogenation of (I) (Fe reductum and I) at 420—460° gives a liquid resembling petroleum physically and containing aliphatic, olefinic, naphthenic, and aromatic hydrocarbons the distribution of which in the various fractions is similar to that in natural petroleum. The isolation of a hydrocarbon, $C_{24}H_{50}$, m.p. 50·5°, is described. The possibility of the production of H_2 by the following reactions is considered: (1) $Fe(OH)_2+H_2O=Fe(OH)_3+H$; (2) $FeCO_3+H_2O=CO_2+Fe(OH)_2$, and thence as in (1); (3) $FeS+H_2O=FeO+H_2S$ and $FeO+2H_2O=Fe(OH)_3+H$; (4) $H_2S=H_2+S$. Considerable amounts of H_2 are evolved from FeS and H_2O at 420—430°/133 atm.

II. Cracking of (I) at 400°/110 atm. yields liquid hydrocarbons containing traces of oxygenated material. They comprise paraffins, olefines, and aromatics closely resembling those of natural petroleum. In the more volatile fractions paraffins predominate ($C : H \simeq 2$), whereas the less volatile portions consist mainly of aromatics and olefines. Formation of liquid hydrocarbons rich in H_2 during cracking is accompanied by the production of a coke-like residue poor in H or, under milder conditions, probably of an asphalt-like residue. The ratio C : H in (I), cracked product, residue, and natural asphalt is 1 : 1·09, 1 : 2·1—1·08, 1 : 0·7—0·6, and 1 : 0·7—0·8, respectively. H. W.

Thermal decomposition of organic compounds from the viewpoint of free radicals. III. Calculation of the products formed from paraffin hydrocarbons. F. O. Rice (J. Amer. Chem. Soc., 1933, 55, 3035—3040; cf. A., 1932, 1108).—The decomp. products of paraffin hydrocarbons can be calc. by assuming that they decompose by a chain mechanism, that Me and Et are the only stable radicals, and that the relative chances of reaction of primary, *sec.*, and *tert.* H atoms are 1 : 2 : 10, respectively. Results are in accord with experiments. R. S. C.

Two reactions of gaseous methyl and ethyl. J. H. Simons and M. F. Dull (J. Amer. Chem. Soc., 1933, 55, 2696—2701).—Me from $PbMe_4$ forms NaMe with Na and MeI with CI_4. Et from $PbEt_4$ reacts analogously. J. G. A. G.

M.p. of naturally occurring *n*-nonacosane. A correction. K. S. Markley and C. E. Sands (J. Biol. Chem., 1933, 101, 431).—The val. 63·5—63·7° is substituted for 64·7—65·1° previously given (this vol., 104; cf. A., 1923, i, 990; 1932, 203). F. O. H.

Microanalysis of gases. II. Carbon monoxide, ethylene, and acetylene. F. E. Blacet, G. D. MacDonald, and P. A. Leighton (Ind. Eng. Chem. [Anal.], 1933, 5, 272—274).—The apparatus (A., 1931, 1027) has been improved. CO is determined by Ag_2O, C_2H_4 by $H_2S_2O_7$, and C_2H_2 by a mixture of CuCl and KOH. E. S. H.

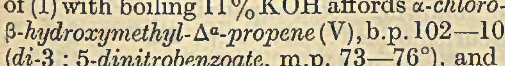
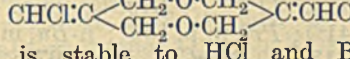
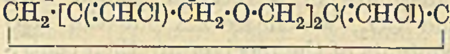
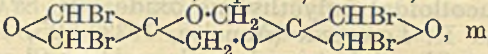
Synthesis of acetylene by pyrolysis of methane. H. H. Storch and P. L. Golden (Ind. Eng. Chem., 1933, 25, 768—771).—Pyrolysis of CH_4, and CH_4 diluted with H_2O or CO_2, using a rapid cooling device, yields a product containing approx. 10% of unsaturated compounds (I), chiefly C_2H_2, with mixtures containing 75—90% of CO_2, in contact with a surface at 1500° for 0·03—0·04 sec. With longer contact the % of H_2 and CO increases, (I) remaining const. There is little C deposition. The use of steam as a diluent causes polymerisation and C formation. A. A. L.

α-Iodo-Δ^{α}-butinene. T. H. Vaughn and J. A. Nieuwland (J.C.S., 1933, 741—743).—Δ^{α}-Butinene in NH_3 at −34° with I gives α-iodo-Δ^{α}-butinene, b.p. 71·5—71·6°/102 mm. (yield 96%; cf. this vol., 694), which undergoes polymerisation and oxidation (retarded by lower temp. and by antioxidants) at room temp. to an inflammable resin sensitive to shock. The change under various conditions is followed by means of the refractive index. Separation of the polymerides from the partly changed products with solvents is described. These polymerides are very sensitive to O_2, to heat, and to shock (less inflammable in the earlier stages of polymerisation). Similar products obtained from material stabilised with antioxidants are difficultly inflammable, and insensitive to shock. A. A. L.

Acetylene polymerides. XV. δ-Halogeno-$\Delta^{\alpha\beta}$-butadienes. Mechanism of 1 : 4-addition and of αγ-rearrangement. XVI. Preparation of orthoprenes by the action of Grignard reagents on δ-chloro-$\Delta^{\alpha\beta}$-butadienes. W. H. Carothers and G. J. Berchet (J. Amer. Chem. Soc., 1933, 55, 2807—2813, 2813—2817; cf. this vol., 694).—XV. Vinylacetylene, when passed into liquid HBr, gives *δ-bromo-$\Delta^{\alpha\beta}$-butadiene* (I) (53·5%), b.p. 64—66°/181 mm., 109—111°/760 mm., and βδ-dibromo-Δ^{β}-butene (II) (36%). δ-Chloro-$\Delta^{\alpha\beta}$-butadiene (III) with NaBr in $COMe_2$–H_2O gives (I) (25% yield) and with NaI in 80% EtOH or $COMe_2$ *δ-iodo-$\Delta^{\alpha\beta}$-butadiene*, b.p. 43—45°/38 mm., which reacts instantly with aq. $AgNO_3$ and is very rapidly polymerised as a result of previous isomerisation to the very unstable *β-iodo-$\Delta^{\alpha\gamma}$-butadiene* (*iodoprene*), b.p. 111—113°, rapidly formed therefrom with much tar at 125—130°. (III) or (I) and aq. Na_2CO_3 at 60—90° give *δ-hydroxy-$\Delta^{\alpha\beta}$-butadiene* (IV) (50% yield), b.p. 68—70°/53 mm., 126—128°/760 mm. (IV) is hydrogenated to $Bu^{\alpha}OH$, is unaffected by NaOEt, 25% H_2SO_4, or 2% HCl, but gives with boiling 18% HCl a 9%, or with PCl_3 and a little C_5H_5N a 62%, yield of (III), and with Ac_2O and a drop of H_2SO_4 (75% yield) or NaOAc in AcOH (59% yield) affords *δ-acetoxy-$\Delta^{\alpha\beta}$-butadiene*, b.p. 85—86°/125 mm., 140—140·5°/780 mm. [also obtained from (I) in 73% yield], hydrogenated to $Bu^{\alpha}OAc$ and hydrolysed to (IV). No rearrangement occurred during the above reactions. (III) with 18% HCl at 70—80° gives a little chloroprene, obtained in 70% yield if $CuCl_2$ is added and to a considerable extent by dry $FeCl_3$. These and the results reported below show that αγ-rearrangements are not a preliminary to 1 : 4-addition and cannot proceed by any mechanism involving free ions. The αγ-change is considered to be brought about by co-ordination of the atom or group attached to the α-C atom with the γ-C atom. If this atom or group is small, co-ordination and consequently the *αγ*-change is assisted by a salt which can form a co-ordination complex. An explanation of the "abnormal" nature of the Grignard reaction is offered.

XVI. β-Substituted $\Delta^{\alpha\gamma}$-butadienes are termed "orthoprenes." δ-Chloro-$\Delta^{\alpha\beta}$-butadiene and MgMeI or MgMeCl in $Bu^{\alpha}{}_2O$ give isoprene. MgBuBr gives β-*butyl*-$\Delta^{\alpha\gamma}$-*butadiene* (not isolated pure), giving with naphthaquinone 2-n-*butyl*-1 : 4 : 4a : 9a-*tetrahydroanthraquinone*, m.p. 63—64°. *n*-C_7H_{15}·MgBr gives tetradecane and β-n-*heptyl*-$\Delta^{\alpha\gamma}$-*butadiene* (*heptoprene*), b.p. 52—54°/5 mm., affording 2-n-*heptyl*-1 : 4 : 4a : 9a-*tetrahydroanthraquinone*, m.p. 81°, and thence β-n-*heptylanthraquinone*, m.p. 87°. MgPhBr gives (*a*) β-*phenyl*-$\Delta^{\alpha\gamma}$-*butadiene* (*phenoprene*), b.p. 60—61°/17 mm., affording 2-*phenyl*-1 : 4 : 4a : 9a-*tetrahydroanthraquinone*, m.p. 146—147°, and thence 2-phenylanthraquinone, double m.p. 145° (decomp.) and 161—165°, but only 163—164° if previously dried in vac. at 125°, (*b*) δ-*phenyl*-$\Delta^{\alpha\beta}$-*butadiene*, b.p. 72—73°/17 mm., which does not react with naphthaquinone and is hydrogenated to $PhBu^{\alpha}$, (*c*) a *dimeride*, m.p. 62°, b.p. 220—225°/10 mm., of phenoprene, and (*d*) some Ph_2. CH_2Ph·MgCl affords $(\cdot CH_2Ph)_2$ and δ-*benzyl*-$\Delta^{\alpha\beta}$-*butadiene*, b.p. 76—77°/7 mm., oxidised by $KMnO_4$ to BzOH and by O_3 in $CHCl_3$ to γ-*phenylpropaldehyde*, an oil (*oxime*, m.p. 95—97°). M.p. were taken on a Cu block.

R. S. C.

Elimination of the nitro-group from tertiary nitro-compounds. III. H. Kleinfeller and H. Stahmer (Ber., 1933, 66, [*B*], 1127—1137).—Trichloronitro*iso*butane (I) is converted by KOH in EtOH–H_2O or by NaOEt into α-*chloro*-γ-*ethoxy*-β-*ethoxymethyl*-Δ^{α}-*propene* (II), b.p. 81°/11 mm., oxidised by $KMnO_4$ to Cl_2 and AcOH and by H_2O_2 or HNO_3 to $H_2C_2O_4$; ozonisation does not yield $CO(CH_2\cdot OEt)_2$. Treatment of (II) with 3 : 5-dinitrobenzoyl chloride and $ZnCl_2$ at 120° yields 3 : 5-$(NO_2)_2C_6H_3\cdot CO_2Et$, m.p. 89°. Catalytic hydrogenation (PtO_2 in EtOH) follows a complex course, C_2H_6 and $CHMe_3$ being evolved. α-*Bromo*-γ-*ethoxy*-β-*ethoxymethyl*-Δ^{α}-*propene*, b.p. 90—91°/11 mm., is similarly obtained from tribromonitro*iso*butane. Hydrogenation of (II) in presence of KOH–EtOH (Pd–$CaCO_3$) leads to γ-*ethoxy*-β-*ethoxymethyl*-Δ^{α}-*propene* (III), b.p. 160°, also obtained by dehydration with $KHSO_4$ of *αγ*-*diethoxy*-β-*methylpropan*-β-*ol*, b.p. 71—74°/14 mm., prepared from MgMeI and $CO(CH_2\cdot OEt)_2$. (III) is transferred by energetic bromination in $CHCl_3$ into the *bromide* (IV)  $\begin{matrix}CHBr_3\\CBr_3\end{matrix}\!>\!C\!<\!\begin{matrix}O\cdot CH_2\\CH_2\cdot O\end{matrix}\!>\!C\!<\!\begin{matrix}CHBr_3\\CBr_3\end{matrix}$, m.p. 101°. Treatment of (I) with boiling 11% KOH affords α-*chloro*-γ-*hydroxy*-β-*hydroxymethyl*-Δ^{α}-*propene* (V), b.p. 102—105°/0·2 mm. (*di*-3 : 5-*dinitrobenzoate*, m.p. 73—76°), and its *dimeric anhydride* (VI),  $CHCl{:}C\!<\!\begin{matrix}CH_2\cdot O\cdot CH_2\\CH_2\cdot O\cdot CH_2\end{matrix}\!>\!C{:}CHCl$, m.p. 47—48°, which is stable to HCl and Br, but oxidised by HNO_3 to mesoxalic acid. (VI) absorbs almost 6 H_2 in EtOH in presence of PtO_2. (V) is converted by H_2SO_4 into the *trimeric anhydrides*, $OH\cdot CH_2\cdot[C({:}CHCl)\cdot CH_2\cdot O\cdot CH_2]_2\cdot C({:}CHCl)\cdot CH_2\cdot OH$, incipient decomp. 75—80°,  $\underline{CH_2\cdot[C({:}CHCl)\cdot CH_2\cdot O\cdot CH_2]_2C({:}CHCl)\cdot CH_2}$, m.p. 125—130° (decomp.), and a *substance* $C_3H_4O_2$, m.p. 160—165° (decomp.). Treatment of (II) with PCl_5 at 100° in absence of solvent leads to *tetrachloro*iso*butanediol* Et_2 *ether*, b.p. 84—87°/11 mm. (II) and Br in $CHCl_3$ yield *chlorotribromo*iso*butanediol*, b.p. 90°/0·2 mm., and the *substance*  $O\!<\!\begin{matrix}CHBr\\CHBr\end{matrix}\!>\!C\!<\!\begin{matrix}O\cdot CH_2\\CH_2\cdot O\end{matrix}\!>\!C\!<\!\begin{matrix}CHBr\\CHBr\end{matrix}\!>\!O$, m.p. 97°, whereas (IV) is obtained similarly from the corresponding Br-ether.

H. W.

Amyl alcohol. I. M. Korenman (Pharm. Zentr., 1933, 74, 453—454).—The colour reactions of Ekkert (A., 1928, 733) are extended.

J. L. D.

Configurative relationship of *iso*propylcarbinols. P. A. Levene and R. E. Marker (J. Biol. Chem., 1933, **101**, 413—418).—Et *l*-α-hydroxybutyrate with EtI and dry Ag_2O yields *Et* l-α-*ethoxybutyrate*, b.p. 67°/12 mm., $[\alpha]_D^{25}$ −36·45°, converted by MgMeI into l-γ-*ethoxy*-δ-*methylpentan*-δ-*ol*, b.p. 162—163°/760 mm., $[\alpha]_D^{25}$ −8·3°, which affords l-γ-*ethoxy*-δ-*methyl*-Δ^{δ}-*pentene*, b.p. 120—130°, $[\alpha]_D^{25}$ −17·8°, reduced to l-γ-*ethoxy*-β-*methylpentane*, b.p. 126°, $[\alpha]_D^{25}$ −2·78°. *d*-β-Methylpentan-γ-ol, $[M]_D^{18}$ +9·8°, is similarly converted into d-γ-*ethoxy*-β-*methylpentane*, b.p. 124—126°/760 mm., $[\alpha]_D^{25}$ +5·00°. The above syntheses permit correlation of CHEtPr·OH and $CHEtPr^{\beta}\cdot OH$, the results being compared with those of Stevens (A., 1932, 1109). The trustworthiness of the indirect method (A., 1932, 1027) is confirmed.

F. O. H.

Partly acylated sugar alcohols. III. Products of the toluenesulphonation of mannitol αζ-dibenzoate. A. Müller and L. von Vargha (Ber., 1933, 66, [*B*], 1165—1168).—The material described previously as *d*-mannitol αζ-dibenzoate tri-*p*-toluenesulphonate is a mixture of d-*mannitol αζ-dibenzoate* βγδε-*tetra*-p-*toluenesulphonate* (I), m.p. 159°, $[\alpha]_D^{18}$ +42·02° in $CHCl_3$, and *anhydro*-d-*mannitol di*-p-*toluenesulphonate* (II), m.p. 142°, $[\alpha]_D^{18}$ +56·1° in $CHCl_3$. (II) is converted by NaOH–EtOH into *dianhydro*-d-*mannitol* p-*toluenesulphonate*, m.p. 98—99°, $[\alpha]_D^{20}$ −57·17° in $CHCl_3$, under conditions which do not affect (I). Treatment of (I) with boiling Ac_2O and NaOAc affords d-*mannitol diacetate αζ-dibenzoate di*-p-*toluenesulphonate*, m.p. 108—109°, $[\alpha]_D^{20}$ +74·3° in $CHCl_3$.

H. W.

Favourable influence of lead on hydrogenation by sodium amalgam. G. Bertrand and (Mme.) S. Delauney-Auvrey (Compt. rend., 1933, 197, 6—9).—Amalgams were prepared containing 2·5% Na and up to 0·5% Pb from vac.-distilled Hg and pure Na and Pb; with > 0·2% Pb the amalgams acted slowly. In the reduction of galactose in presence of H_2SO_4, addition of 0·1 and 0·2% Pb gave increased yields, *e.g.*, 75·8 and 90·9% of possible dulcitol as against 62·1—64·2% without Pb.

C. A. S.

Quantitative isolation of ether from dilute solutions. A. A. Benedetti-Pichler and F. Schneider (Ind. Eng. Chem. [Anal.], 1933, 5, 255—257).—Et_2O is separated from dil. aq. solutions by distilling from a specially-constructed flask and collecting the distillate in a receiver cooled with $COMe_2$ and solid CO_2, which freezes out the H_2O vapour. The contents of the receiver are then centrifuged. The procedure gives a const. error of −9 mg. with solutions containing 10—300 mg. Et_2O in 60 c.c. H_2O. E. S. H.

Highly polymerised compounds. LXXXI. Eucolloidal polyethylene oxide. H. Staudinger and H. Lohmann (Annalen, 1933, **505**, 41—51).—Sluggish catalysts such as the oxides and carbonates of Ca, Sr, or Zn cause the conversion of $(CH_2)_2O$ into polymerides of very high mol. wt. Since these products are formed at room temp. or at 100°, the type of change depends on the catalyst. Oxides of Fe, Mg, Pb, SiO_2 gel, and C are without action. Al_2O_3 slowly yields hemicolloids. The best results are obtained with ZnO, nearly all of which can be subsequently removed without accompanying depolymerisation; the small residue is regarded as an impurity. Solutions of eucolloidal polyethylene oxides do not follow the Hagen–Poiseuille law; the deviations are slight in dil. solution, but increase with increasing chain-length of the polymerides. In the polymeric-homologous series of polyethylene oxides (n= 2—2700), elasticity and hardness are functions of n. Very hard, tenacious products occur only when n is very great, and the power of forming hard, tenacious films is confined to such materials. All polyethylene oxides are cryst., and differences are not observable between the higher and lower polymerides. A "meander" form of the mol. is postulated which explains the free solubility and low m.p. in contrast with the paraffins and polyoxymethylenes. H. W.

Organic reactions with boron fluoride. IV. Ether cleavage in the presence of organic acids. G. F. Hennion, H. D. Hinton, and J. A. Nieuwland (J. Amer. Chem. Soc., 1933, **55**, 2857—2860; cf. A., 1932, 1125).—Et_2O, $Bu^a{}_2O$, or di*iso*amyl ether with various acids or PhOH and BF_3 ($\nless$ 0·3 mol.; modified prep.) at 200° give up to 55% yields of the esters, possibly by preliminary cleavage of the ether to the alcohol. R. S. C.

Synthesis of dimethyl ether of *n*-pentitol. Lespieau and Wiemann (Compt. rend., 1933, **197**, 69—70).—Hydrogenation of δ-hydroxy-αε-dimethoxy-Δ^β-pentinene (cf. A., 1928, 989) ($Pd–H_2$) gives cis-*δ-hydroxy-αε-dimethoxy-Δ^β-pentene*, b.p. 107°/14 mm., oxidised by $AgClO_3$ in presence of OsO_4 to *βγδ-trihydroxy-αε-dimethoxy-*n*-pentane*, b.p. 129—131°/0·34 mm. H. A. P.

Monoalkyl carbonates. V. Mono-*n*-propyl carbonate. C. Faurholt and I. C. Jespersen (Z. physikal. Chem., 1933, **165**, 79—88; cf. A., 1927, 515).—If CO_2 is passed into aq. PrOH and NaOH there occur simultaneously the reactions $CO_2+PrO'=PrCO_3'$, $CO_2+OH'=HCO_3'$, and $PrO'+H_2O=PrOH+OH'$. Combining the first and last gives $CO_2+PrOH+OH' \longrightarrow PrCO_3'+H_2O$, the rate of which has been measured at 0°. $PrHCO_3$ decomposes rapidly in acid solution, $PrHCO_3=CO_2+PrOH$; in an acetate buffer the rate is proportional to the H˙ activity. In slightly alkaline solution in presence of an appropriate amount of PrOH there is established the equilibrium $NaPrCO_3+H_2O \rightleftharpoons PrOH+NaHCO_3$, the equilibrium const. of which has been measured at 0°. The rate of reaction in strongly alkaline solution has also been determined. R. C.

Ribosephosphoric acid from yeast adenylic acid. P. A. Levene and S. A. Harris (J. Biol. Chem., 1933, **101**, 419—429).—Hydrolysis of yeast adenylic acid (I) (A., 1925, i, 487) yields methylribosidephosphoric acid, converted by exhaustive methylation into tetramethylphosphomethylriboside, $[\alpha]_D^{25}$ −26·4° in abs. EtOH, also produced by similar treatment of NH_4 guanylate or xanthylic acid. Dephosphorylation by $Ba(OMe)_2$ of the riboside from guanylic acid yields dimethylmethylriboside (II), b.p. 90—93/< 1 mm., $[\alpha]_D^{22}$ −48·7° in MeOH, −47·4° in H_2O (that from adenylic acid has $[\alpha]_D^{21}$ −55·8° in H_2O), hydrolysed by 6% aq. HCl to dimethylribose, b.p. 132—136°/< 1 mm., $[\alpha]_D^{21}$ −16·7° in dil. aq. NH_3, which is reduced by Adams' catalyst to dimethylribitol. The product was not optically inactive [due to presence of γ-glucoside in (II)], and hence the structure of (I) cannot be rigidly concluded. Deamination of (I), however, yields inosine-3-phosphoric acid, $[\alpha]_D^{22}$ −41·0° in H_2O, which, in aq. solution at its own p_H, is readily hydrolysed to a ribosephosphoric acid identical with the corresponding acid from xanthylic acid. Thus (I) is 1-adenine-*d*-ribofuranoside-3-phosphoric acid. F. O. H.

Thermal behaviour of sulphur compounds in hydrocarbon solvents. II. *n*-Butyl sulphide in benzene. W. M. Malisoff and E. M. Marks (Ind. Eng. Chem., 1933, **25**, 780—783; cf. A., 1931, 1393).—The thermal stability of *n*-butyl sulphide (I) in C_6H_6 solution is studied at various temp., concns., and times of exposure. For exposures up to 50 sec. in 0·05 mol. solution (I) is thermally stable at 400°, slightly decomposed at 450°, whilst a 30-sec. exposure at 515° yields only a 20% conversion into H_2S. On exposure up to 55 sec. at $\ngtr$ 515° the products are only H_2S and mercaptan unless a large amount of H_2S is present, in which case S and thiophens are also formed. The rates of decomp. are decidedly < those for aliphatic mercaptans under similar conditions. The reactions are partly heterogeneous, being promoted by surface and length of exposure. The inequality of rates of decomp. in C_6H_6 and in n-C_7H_{16} (II) suggests that C_6H_6 may affect the velocity of the reaction or (II) may be an inhibitor. C. E. M.

Sulphoxides and other derivatives of tetrathiolmethylmethane. H. J. Backer and N. D. Dijkstra (Rec. trav. chim., 1933, **52**, 701—708; cf. this vol., 48).—Tetrathiolmethylmethanes (I) (1 mol.) with H_2O_2 (4 mols.) in AcOH at room temp. afford the following tetrasulphoxides, which yield cryst. mercurichlorides: *Me*, m.p. 205° (+2*HgCl₂*, m.p. 143°); *Et*, m.p. 137° (+2*HgCl₂*, m.p. 157·5°); *Prᵅ*, m.p. 117° (+2*HgCl₂*, m.p. 88°; +4*HgCl₂*, m.p. 141°); *Prᵝ*, m.p. 165°; n-*Bu*, m.p. 123° (+*HgCl₂*, m.p. 51°; +2*HgCl₂*, m.p. 97°; +4*HgCl₂*, m.p. 149°); tert.-*Bu*, m.p. 212° (+2*HgCl₂*, decomp. > 300°); n-*amyl*, m.p. 143° (+2*HgCl₂*, m.p. 84°; +4*HgCl₂*, m.p. 128°); n-*hexyl*, m.p. 159·5°. (I) with Br (4 mols.) in C_6H_6 or PhMe afford the following octabromides, decomposed by cold H_2O : *Me*, m.p. 107° (decomp.); *Et*, m.p. 93° (decomp.); *Pr*$^{\alpha}$, m.p. 80° (decomp.); *Pr*$^{\beta}$, m.p. 80° (decomp.); tert.-*Bu*, m.p. 130° (decomp.). $C(CH_2{\cdot}SPh)_4$ (1 mol.) in CCl_4 with Br (4 mols.) affords *tetra*-p-*bromophenylthiolmethylmethane*, m.p. 110° [also formed by interaction (II) of *p*-$C_6H_4Br{\cdot}SNa$ and $C(CH_2Br)_4$ at 150° during 8 hr.] [*sulphone*, m.p. 328°, which is not obtained from $C(CH_2{\cdot}SO_2Ph)_4$ and Br in CCl_4]. By a method similar to (II), the *tetra*-p-*chlorophenyl*, m.p. 96° (*sulphone*, m.p. 276°), and the *tetra*-p-*tolyl* compounds, m.p. 103° (*sulphone*, m.p. 249°), are prepared. J. L. D.

Mercaptides of selenium and tellurium. T. Bersin and W. Logemann (Annalen, 1933, 505, 1—16).—Absorption of O_2 by Na α-thiolpropionate (I) is not accelerated by $CH_2I{\cdot}CO_2Na$ (II). Repetition of the observations with thiolacetanilide (III) shows this substance to behave similarly when sufficiently purified; the previously observed activity is due to traces of Se present in the NH_4CNS used in the prep. Addition of Na_2SeO_3 (IV) increases the rate of oxidation of (III). If the amount of (IV) is reduced so that only a slight acceleration is observable, addition of (II) causes absorption at a marked rate. (I) behaves similarly. Se and Te likewise accelerate, surpassing Cu and As. (IV) and (I) under N_2 or O_2 give a ppt. of red Se after a transient yellow colour. If the amount of (IV) is diminished and shaking is continued in O_2, the ppt. re-dissolves and the solution contains only (IV) and disulphide. If the concn. of (I) is sufficiently diminished, Se is not pptd., but sufficient O_2 is invariably absorbed for the oxidation of Se to SeO_2 and 2RSH to R_2S_2. Protracted action carries the oxidation beyond the S_2 stage. H_2TeO_3 behaves similarly, but the intermediate compound is more stable. Also, in the presence of an equiv. amount of Na_2TeO_3, the rate of absorption of O_2 exhibits a sharp decline corresponding with the point of complete dissolution of the pptd. Te. The intermediate compound of (IV) and (I) or (II) is too unstable for isolation. Na_2TeO_3 and (I) yield *Te di-α-carboxyethyl disulphide*, $Te(S{\cdot}CHMe{\cdot}CO_2H)_2$, m.p. 114°, which gives the *product* $Te(S{\cdot}CHMe{\cdot}CO_2H)_2,SH{\cdot}CHMe{\cdot}CO_2H$, decomp. 84°, readily hydrolysed by H_2O. SeO_2 and 3-bromo-2-hydroxy-5-methylthiophenol in Et_2O yield *Se di-3-bromo-2-hydroxy-5-methylphenyl disulphide*, m.p. 98°. H. W.

Hexadecanesulphonic acid. R. C. Murray (J.C.S., 1933, 739—740).—An improved prep. is described for hexadecyl mercaptan, m.p. 47—48° (*Pb mercaptide*), containing approx. 25% disulphide, and oxidised (98% yield) to the sulphonic acid, which may be determined as the Ba salt. A. A. L.

Determination of formic, acetic, and propionic acids in a mixture. O. L. Osborn, H. G. Wood, and C. H. Werkman (Ind. Eng. Chem. [Anal.], 1933, 5, 247—250).—HCO_2H is determined by oxidising with HgO and absorbing the CO_2 in aq. KOH. AcOH and $EtCO_2H$ are determined by the partition method, using Et_2O and titrating with 0·05*N*-NaOH and phenolphthalein. E. S. H.

Identification of hexoic [acids]. M. Hommelen (Bull. Soc. chim. Belg., 1933, 42, 243—250).—The prep. of the following acids is described: *γ-methylvaleric* (I) (b.p. 199·1°/752 mm., m.p. −33°), β-*methylvaleric* (II) (b.p. 197·8°, m.p. −41·6°), ββ-*dimethylbutyric* (III) (b.p. 183·1—183·8°/741 mm., m.p. +5·6°), *α-ethylbutyric* (IV) (b.p. 192·6—193·0°/754 mm., m.p. −31·8°), *αβ-dimethylbutyric* (V) (b.p. 191·4—191·9°/760 mm., m.p. −1·5°), *α-methylvaleric* (VI) (b.p. 192·0—193·6°/748 mm.), *αα-dimethylbutyric* (VII) (b.p. 186·8—187·2°/750 mm., m.p. −15·0°). Data are given for derivatives as follows: (*a*) b.p. of *chlorides*, (I) 143·8—144·6°/745 mm., (II) 142·5—143·0°/749 mm., (III) 129·5—130·3°/746 mm., (IV) 138·0—138·8°/750 mm., (V) 140—140·8°/745 mm., (VI) 135·9—136·6°/751 mm., (VII) 131·8—132·4°/748 mm.; (*b*) m.p. of *amides*, (I) 118·8°, (II) 124·9°, (III) 132·0°, (IV) 111·8°, (V) 79·6°, (VI) 130·9°, (VII) 99·8°; (*c*) m.p. of *anilides*, (I) 112·0°, (II) 95·2°, (III) 87·0°, (IV) 126·8°, (V) 91·4°, (VI) 131·6°, (VII) 78·4°; (*d*) m.p. of p-*toluidides*, (I) 63·0, (II) 80·5°, (III) 74·8°, (IV) 116·2°, (V) 83·3°, (VI) 134·4°, (VII) 112·6°. E. S. H.

Ester-interchange. IV. Ester-interchange between two fats, and between ethylene glycol and a mixture of two fats. V. Ether-interchange. R. Oda (J. Soc. Chem. Ind. Japan, 1933, 36, 331—334B, 334B; cf. B., 1933, 197, 476).—IV. Olive oil (I) or linseed oil (II) at 200° in presence of H_2 and a little K_2CO_3 undergoes ester-interchange (III) with coconut oil (IV), but not with hardened oil. From experiments with mixtures of two fats with glycol it is concluded that the acids of (IV) undergo (III) with glycol more easily than those of (I) or (II).

V. An extension of the double linking rule (this vol., 256) indicates that certain ethers should undergo (I) in a similar manner to esters. EtOBz and PrOBz with EtOH at 200° give a little Et_2O and EtOPr, respectively. A. A. L.

Ester-interchange. VI. Ester-interchange between fatty oils, fatty acids, and ethylene glycol. R. Oda (J. Soc. Chem. Ind. Japan, 1933, 36, 376—377B; cf. preceding abstract).—Interchange of free and combined fatty acid radicals occurs on autoclaving coconut oil (I) with oleic acid (II) at 200°, and to a smaller extent between linseed oil and stearic acid. With castor oil and (II), ester-interchange accompanies ester formation at the OH group: similarly, both reactions take place when a mixture of (I), (II), and $C_2H_4(OH)_2$ is heated at 200° for 2 hr. E. L.

Olefinic compounds. II. Orienting influence of the carboxyl group. G. F. Bloomfield, E. H. Farmer, and C. G. B. Hose (J.C.S., 1933, 800—806; cf. A., 1932, 930).—α-Methylacrylic acid, from α-bromo*iso*butyric acid by an improved process, with HOCl gives α-chloro-β- and β-chloro-α-hydroxy-*iso*butyric acid (90%), m.p. 110°, the latter being also obtained by hydrolysis of chloroacetone cyanohydrin. Et α-methylacrylate similarly gives (?) Et αβ-dichloro-, β-chloro-α-hydroxy-, and α-chloro-β-hydroxy-*iso*butyrate (70% of the chlorohydrins), separated as the corresponding acids. Tiglic acid gives *α-chloro-β-* (I), m.p. 113° (38%), and *β-chloro-*

α-*hydroxy-α-methylbutyric acid* (II), m.p. 89°. The proportion of isomerides is found by determination of the Cl content after reduction with Na–Hg in presence of CO_2, only the α-Cl-acids being attacked. Et tiglate gives a (?) dichloride and equal quantities of the Et esters of (I) and (II), isolated as the acids, one of which is a *stereoisomeride* of (II), m.p. 114°. The proportions were found by the above reduction method, and by actual separation. Na tiglate gives (I) and (II) (80%), determined by the reduction method. Crotonic acid gives β-chloro-α- and α-chloro-β-hydroxybutyric acid (26% by the reduction method); this mixture when oxidised with $K_2Cr_2O_7$ or HNO_3 gave AcOH and $CHMeCl·CO_2H$, isolated as $CHMe(CO_2H)_2$. ββ-Dimethylacrylic acid gives α-chloro*iso*butylene and other neutral compounds, impure β-*chloro*-α-, and α-*chloro*-β-*hydroxy*-β-*methylbutyric acid* (80%), m.p. 69°, converted by conc. H_2SO_4 into α-chloro-ββ-dimethylacrylic acid. In determining the isomerides the neutral compounds are considered to arise from the latter acid. It is suggested that the O of the CO group has no attraction for the components of HOCl, so that the proportion of isomerides is a measure of the orienting influence of the CO_2H group. This influence is greatly affected by the state of ionisation of the CO_2H group, and appears to be small with the CO_2Et group. Δ^{α}-Acids, and especially their esters, add more slowly than the Δ^{β}- and Δ^{γ}-compounds. A. A. L.

Olefinic acids. VII. Preparation of Δ^{β}-acids. R. P. Linstead, E. G. Noble, and (in part) E. J. Boorman. **IX. Addition of hydrogen bromide to unsaturated acids.** E. J. Boorman, R. P. Linstead, and H. N. Rydon. **X. Formation of lactones from Δ^{α}- and Δ^{β}-*n*-butenoic and -pentenoic acids.** E. J. Boorman and R. P. Linstead. **XI. Formation of lactones from Δ^{γ}-unsaturated acids, and an example of ring–chain (lacto–enoic) tautomerism.** R. P. Linstead and H. N. Rydon (J.C.S., 1933, 557—561, 568—576, 577—580, 580—586; cf. A., 1932, 251).—VII. EtCHO and malonic acid in presence of $N(C_2H_4·OH)_3$ (cf. A., 1931, 935) give β-ethylglutaric acid and Δ^{β}-*n*-pentenoic acid, m.p. 1°, b.p. 90°/10 mm. (32—36% yield). Δ^{β}-*n*-Hexenoic acid, m.p. 12°, b.p. 110°/15 mm. (40—52% yield), and β-*n*-propylglutaric acid (and its anhydride) are similarly obtained, whilst vinylacetic acid is obtained only in small yield by this process, being best prepared by an improvement in Bruylants' method (A., 1924, i, 1053). Other methods for Δ^{β}-olefinic acids are less good.

IX. With the exception of Δ^{α}-acids, addition of HBr is independent of the position of the double linking with respect to CO_2H. In hydrocarbon solvents the acids behave as H esters, so that Br goes entirely to the C atom of the double linking more distant from CO_2H. Addition is considered to be controlled by the polar effect of CO_2H acting either through the C chain, or as a direct field effect if > one CH_2 intervenes. In other solvents (H_2O, AcOH, Et_2O), or with the free acid, addition proceeds according to the Markovnikov rule, being controlled by the no. of the alkyl substituents at the double linking. Application of these rules provides convenient preps. for acids with Br distant from CO_2H. A method for the analysis of mixtures of β- and γ-Br-acids depends on the formation of OH-acid by the former, and lactone by the latter, when the Ba salts are boiled with H_2O. The hydrobromides obtained in the following reactions are individuals except where stated. Crotonic acid at 80° with HBr gives β-bromobutyric acid (I) (Et ester, b.p. 81°/17·5 mm.). Similarly, vinylacetic acid (II) alone, with 0·5% H_2O, in Et_2O, or in AcOH gives (I), whilst in petrol or PhMe it gives γ-bromobutyric acid (III), converted by boiling with $Ba(OH)_2$ into the γ-lactone, m.p. −48°. The Et ester of (II) gives the Et ester of (III), b.p. 94°/18 mm., converted by suitable treatment with Et sodiomalonate into adipic acid, a method also applied to the synthesis of glutaric and β-methylglutaric acids. Δ^{α}-*n*-Pentenoic acid, m.p. 9·5°, b.p. 106°/20 mm., alone gives β-bromovaleric acid (IV). Δ^{β}-*n*-Pentenoic acid alone or with 0·5% H_2O gives 8% of (IV) and 92% γ-bromovaleric acid (V), the Et ester of which by the above treatment gives β-methyladipic acid. (V) is converted as for (III) into γ-valerolactone, m.p. −35·5°, b.p. 92—93°/18 mm. Δ^{γ}-*n*-Pentenoic acid [Et ester (VI), b.p. 144—144·5°], alone, with 0·5% H_2O, or in Et_2O gives (V), whilst in PhMe it gives δ-bromovaleric acid (VII), m.p. 40°, also obtained from δ-valerolactone with HBr. (VI) alone gives the Et ester of (VII), converted as above into pimelic acid. Δ^{α}-*iso*-Hexenoic acid alone gives β-bromo*iso*hexoic acid, converted (also as Na salt) by boiling H_2O into the β-hydroxy-acid and a little (?) β-lactone. Δ^{β}-*iso*-Hexenoic acid (pyroterebic acid), m.p. −2°, b.p. 84°/4 mm., alone or with 0·5% H_2O gives γ-bromo*iso*hexoic acid, also obtained from, and converted into, the γ-lactone, m.p. 8·4°, b.p. 94°/20 mm. Δ^{γ}-*iso*-Heptenoic acid (see below) alone or with 0·5% H_2O gives δ-*bromo*-δ-*methylhexoic acid*, m.p. 45°, also obtained from the δ-lactone. γ-*Bromo*-δ-*methylhexoic acid*, m.p. 41°, is obtained from the γ-lactone.

X (cf. A., 1932, 251). Vinylacetic acid when boiled alone, with 50% H_2SO_4, or in decahydronaphthalene yields crotonic acid without appreciable lactone formation, whilst in cold 60% H_2SO_4 tautomeric change is slow, and unaccompanied by lactonisation. Crotonic acid and γ-butyrolactone, m.p. −48°, b.p. 83·5°/12 mm., are stable under similar conditions. The latter is obtained by the action of KCN on trimethylene chlorohydrin, followed by hydrolysis and distillation of the acid. Δ^{α}-*n*-Pentenoic acid is stable to cold 60% H_2SO_4, but with boiling 50% H_2SO_4 gives γ-valerolactone (I), m.p. −36°, b.p. 102—103°/28 mm. (hydroxyamide, m.p. 51·5—52°), also obtained by the reduction of lævulic acid (improved prep.). Δ^{β}-*n*-Pentenoic acid is stable when boiled alone, gives (I) slowly with cold 60% H_2SO_4, and rapidly with hot 50% H_2SO_4. The results are correlated with theory previously discussed. The rates of formation of lactone from γ-hydroxy-butyric and -valeric acids are recorded, and the amounts of hydrolysis of the above lactones by H_2O at 100° are determined by a method of direct titration with $Ba(OH)_2$.

XI. An extension of previous theory indicates that if R=R′=H in the acid $CRR'{:}CH·[CH_2]_2·CO_2H$

it should give a γ-lactone, whereas if R and R′ are alkyl groups a δ-lactone should be formed. Δ^{γ}-*n*-Pentenoic acid, m.p. −22·5°, b.p. 90°/16 mm. (from Et allylmalonate), gives γ-valerolactone slowly when boiled alone in the absence of air, or rapidly with H_2SO_4. Dimethylmalonic acid, obtained by an improved method from the ester (A., 1922, i, 978; also obtained from dimethyltrimethylene dibromide), gives δ-*iso*heptolactone (I), m.p. 28°, b.p. 94°/6 mm. (? second form, m.p. 8°), and Δ^{γ}-*iso*heptoic acid (II), m.p. −33°, b.p. 105°/5 mm., separated by acidifying the $NaHCO_3$ extract in presence of a solvent, and converted into (I) with H_2SO_4. (I) is also obtained from *iso*amylmalonic acid, m.p. 94°, which is converted into *iso*heptoic acid. Oxidation of the K salt of this with $KMnO_4$ gives (I). The "lacto–enoic" tautomerism (I) $\rightleftharpoons$ (II) takes place at the b.p., and was studied quantitatively. A method for the analysis of mixtures of (I) and (II) is described. Trimethylene chlorohydrin with $CHNa(CO_2Et)_2$ gives a *substance*, $C_{11}H_{16}O_2$, m.p. 148°. An improved prep. is described for δ-*n*-valerolactone, m.p. −12·5°, b.p. 88°/4 mm. (A., 1928, 737), from Et γ-phenoxypropylmalonate (acid, m.p. 65—66°; cf. A., 1928, 990). β-Carbethoxypropionyl chloride with $CHMe_2{\cdot}ZnI$ gives γ-keto*iso*heptoic acid, which, after reduction with Na–Hg, gives the γ-lactone, b.p. 98°/15 mm. The hydrolysis of the above lactones and the lactonisation of the corresponding OH-acids were followed quantitatively. A. A. L.

Catalytic hydrogenation of unsaturated compounds. I. Additive mode in relation to selectivity of attack and catalyst activity. E. H. Farmer and R. A. E. Galley (J.C.S., 1933, 687—696; cf. A., 1932, 365).—In mixtures of Δ^{γ}-pentenoic acid or allyl alcohol with a hexenoic acid (I) the former is reduced first, whilst the components of mixtures of (I) are hydrogenated side by side. This is in agreement with the principle that monosubstituted olefines are selectively reduced before disubstituted etc. (cf. A., 1925, i, 350). In the reduction of sorbic acid (II), hexoic acid (III) and (I) are produced side by side. Since the amount of H required to effect complete disappearance of the (II) is unchanged by previous addition of (I), all the (III) is formed by αβγδ addition to (II) so long as some is present, and not by reduction of the (I). With an "aged" catalyst (from PtO_2,H_2O) αβγδ addition is decreased, whilst αβ, αδ, and γδ additions are increased, the last to the greatest extent. Hence the state of the catalyst may affect the additive mode with a polyolefine. The bearing of this on the assessment of constitutive influences is discussed. The rate of reduction of (I) increases with increasing remoteness of the double linking from the acid group. The rate of hydrogenation is independent of the concn. of the olefine within wide limits, but the sudden increase in rate just before saturation with certain substances is confirmed (*loc. cit.*). A. A. L.

So-called polyundecenoic acids. A. Barbot (Compt. rend., 1933, 197, 65—67).—The spongy residue left on distillation of castor oil on alcoholysis (EtOH) gives 8 wt.-% of glycerol, Et heptoate (0·4%), *n*-nonoate (0·5%), undecenoate (I) (11·1%), palmitate (2·4%), ricinoleate (II) (2·4%), oleate (III) (6·5%), stearate (0·8%), the Et ester of an unidentified acid, m.p. 85—86° (0·4%), and an undistillable residue (IV) (75%), mol. wt. approx. 700°, apparently the ester of a dibasic acid. Interruption of the distillation at an early stage gives the same products in very different proportions, (I), (II), (III), and Et linoleate comprising the bulk of the product. Abundant evolution of H_2O occurs during the distillation, and it is concluded that (IV) is formed by condensation of linoleic acid with itself or with other unsaturated acids produced by decomp. of ricinoleic acid. H. A. P.

Calorimetric researches. XX. Alternation phenomena. VI. Alternations in the properties of *n*-monoalkylmalonic acids. P. E. Verkade and J. Coops, jun. (Rec. trav. chim., 1933, 52, 747—767).—The *n*-monoalkylmalonic acids fall into two groups, that with term no. (cf. A., 1930, 848) 2—5, and that from 6 onwards. The heats of combustion are determined (cf. A., 1925, ii, 490); those from the "lower" group exhibit definite, although weak, odd alternation, whereas those of the "higher" group are const. These results strongly contrast with those of Coster and van der Ziel (A., 1932, 682) and previous work on the alternation of other physical properties. The significance of the results is discussed and Malkin's views (A., 1932, 326) are criticised. J. L. D.

Modes of addition to conjugated unsaturated systems. V. Hydrogenation of ethyl muconate and of sorbic and β-vinylacrylic acids in presence of platinum. C. K. Ingold and L. D. Shah (J.C.S., 1933, 885—890).—Treatment of Et muconate, sorbic (I) or β-vinylacrylic acid with 1 mol. of H_2 in presence of Pt gives equal proportions of tetrahydro-derivative and unchanged material, the amount of dihydro-compounds being < a few % (cf. A., 1932, 365; this vol., 935). Analyses by ozonisation, followed by treatment with H_2O_2, and with $KMnO_4$ in the case of (I) (*loc. cit.*) are described. The mixtures of unchanged and hydrogenated substances could not be completely separated by distillation. $CH_2(CO_2H)_2$ may be titrated with Br in $CHCl_3$ in the presence of HCl. Similar results are obtained with (I) and an "aged" catalyst. Reduction of dihydro-derivatives is slower than the complete reduction of butadiene derivatives. *Et* Δ^{α}-*dihydromuconate* (from the chloride) has b.p. 125—126°/14 mm. The results are in agreement with theory previously discussed. A. A. L.

Emetics derived from mandelic and malic acids. Volmar and Betz.—See this vol., 948.

Synthesis of substances analogous to bile acid degradation products. II. Synthesis of some straight-chain polycarboxylic esters. J. W. Baker. **III. Attempted use of diallyl as an agent to introduce the requisite side-chain in the synthesis of the acid $C_{13}H_{20}O_6$.** J. W. Baker and H. Burton (J.C.S., 1933, 811—815, 815—818).—II. $CH_2(CO_2Me)_2$ and Me γ-bromovalerate condense to *Me* β-*methyl*-n-*butane*-ααδ-*tricarboxylate*, b.p. 145°/3 mm. $CH_2(CO_2Me)_2$ and $CHMeBr{\cdot}CO_2Me$ form *Me* n-*propane*-ααβ-*tricarboxylate*, m.p. 48—49° [*triamide*, m.p. 249° (decomp.); *amide-imide*, m.p. 162°], brominated to the α-*Br*-ester, b.p. 150°/7 mm., which with C_5H_5N gives *Me* Δ^{a}-*propene*-ααβ-*tricarboxylate* (I), b.p. 178°/53 mm. [*amide*, m.p. 198° (decomp.)]. (I) condenses with $CH_2Ac\cdot CO_2Me$ to Me paraorsellinate and with HBr gives *Me* β-*bromo*-n-*propane*-ααβ-*tricarboxylate* (II), b.p. 158—165°/5 mm., m.p. 68° (*l*-ester, b.p. 165—175°/10 mm., m.p. 72°). (II) condenses with $CH_2(CO_2Me)_2$ to *Me* β-*methyl*-n-*propane*-ααβγγ-*pentacarboxylate*, m.p. 58°, and with Me β-methyl-*n*-butane-ααδ-tricarboxylate to *Me* βγ-*dimethyl*-n-*butane*-ααβγδδ-*hexacarboxylate*, m.p. 179°. $CH_2Ac\cdot CO_2Me$ and $CHMeBr\cdot CO_2Me$ give *Me* β-*keto*-n-*pentane*-γδ-*dicarboxylate*, b.p. 146°/30 mm. (*semicarbazone*, m.p. 159°). Et ethane-ααβ-tricarboxylate with Et bromosuccinate yields *Et* n-*butane*-αβγγδ-*pentacarboxylate*, b.p. 210°/5 mm., but with Et β-bromo-*n*-propane-αβ-dicarboxylate the required product is not obtained. Bromination of Et β-methyl-*n*-propane-αγγ-tricarboxylate affords the γ-*Br*-ester, b.p. 184°/9 mm., which does not give the required condensation product with Et αβ-dicyano-β-methylglutarate (III). Hydrolysis of (III) gives a *substance*, m.p. 109—110°, and subsequently an *acid*, $C_7H_9O_4N$, m.p. 133°.

III. Diallyl and HBr give the *mono*- (I), b.p. 41—43°/13 mm., and the *di-hydrobromide*, b.p. 82—84°/5 mm. Ozonolysis of diallyl yields some MeCHO, showing the presence of a small amount of isomerides. Decomp. of the ozonide of (I) affords some MeCHO and a Br-aldehyde. The *trimeride* of β-bromo-*n*-butaldehyde, m.p. 98°, prepared from crotonaldehyde and HBr, is not found in the ozonolysis product, indicating that the amount of $CHMeBr\cdot CH_2\cdot CH{:}CHMe$ is small. *Me* cyclo*pentanone*-2 : 3-*dicarboxylate*, b.p. 162°/15 mm. (*semicarbazone*, m.p. 188—189°), prepared from *Me* n-*butanetricarboxylate*, b.p. 168°/16 mm., by the Dieckmann reaction, is methylated to the 2-*Me* derivative (II), b.p. 146°/4 mm. [*semicarbazone*, m.p. 234° (decomp.)]. Condensation of (II) and (I) and subsequent ozonolysis and oxidation does not give the required OH-acid ester or the unsaturated derivative, but *n*-pentane-αγδ-tricarboxylic acid or unchanged ester. F. R. S.

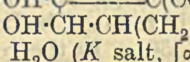
Influence of solvents and other factors on the rotation of optically active compounds. XXXI. Rotation dispersion of the nitrobenzyl tartrates. T. S. Patterson and D. McCreath (J.C.S., 1933, 760—768).—*m*-$NO_2\cdot C_6H_4\cdot CH_2\cdot OH$ and *d*-tartaric acid at 140° for 15 hr. in a current of dry air give m-*nitrobenzyl* d-*tartrate*, m.p. 119° (Ac_2 derivative, m.p. 107°; Bz_2 derivative, m.p. 109°). *o*-Nitrobenzyl *d*-tartrate (*Ac* derivative, m.p. 118—120°; Ac_2 derivative, m.p. 75°) is similarly prepared. Rotation–temp. curves for the *m*- and *p*-NO_2-esters and their derivatives in C_5H_5N, quinoline, and $MeNO_2$ lie in a comparatively restricted part of the general curve for tartrates already described, whilst the *o*-NO_2-esters lie in widely separated regions. The curves for *o*-nitrobenzyl dibenzoyl-*d*-tartrate in quinoline suggest that the general curves should be extended to include a second point of visible anomalous dispersion, and possibly should rise to another max. with fall of temp. A. A. L.

Primary process in the oxidation of tartrates in alkaline solution at a high anode potential. V. Sihvonen.—See this vol., 914.

Derivatives of hydroxymethoxysuccinic and methoxymalonic acids. J. Pryde and R. T. Williams (J.C.S., 1933, 642—644).—The [α] of derivatives of α-hydroxy-β-methoxysuccinic acid (*Me* ester, b.p. 119—122°/1·6 mm.; *diamide*, m.p. 190—191°; *methylamide*, m.p. 129°) are approx. the means of the pairs of corresponding derivatives of tartaric and dimethoxysuccinic acids (cf. J.C.S., 1915, 109, 5). Tartronic acid (improved prep.) with Ag_2O and MeI gives *Me* αβ-*dimethoxyethane*-ααββ-*tetracarboxylate*, m.p. 76°. A. A. L.

Constitution of vitamin-*C*. V. F. Micheel and K. Kraft (Z. physiol. Chem., 1933, 218, 280—282; cf. this vol., 698).—Catalytic hydrogenation of ascorbic acid yields *l*-idonic acid, whereas the authors' proposed constitution should give anhydrohexonic acid. Hydrogenation in AcOH gives a cryst. acetylhexonolactone, which from its stability contains a 1 : 4-ring. Oxidation with $Pb(OAc)_4$ of dimethylascorbic acid affords CH_2O. In the light of this evidence the constitution advanced by Hirst *et al.* (cf. this vol., 594) is accepted. J. H. B.

Synthesis of ascorbic acid. W. N. Haworth and E. L. Hirst (Chem. and Ind., 1933, 645—646).—*d*- and *l*-Xylosone, aq. KCN, and $CaCl_2$ give a reducing acid converted by 8% HCl at 50° into ascorbic acid, identical with the natural acid (cf. this vol., 698). The substance of Reichstein *et al.* (this vol., 594) is a derivative of *d*-ascorbic acid. F. R. S.

Preparation from glucose of an acid $C_6H_8O_6$ equal to ascorbic acid in reducing power. K. Maurer and B. Schiedt (Ber., 1933, 66, [*B*], 1054—1057).—Me α-ketogluconate is converted by NaOMe in MeOH, C_5H_5N, or their mixtures into an *acid*, probably  $\begin{matrix}OH\cdot C{=\!=\!=}C(CO_2H)\\ OH\cdot CH\cdot CH(CH_2\cdot OH)\end{matrix}{>}O$, m.p. 168°, $[\alpha]_D$ $-16\cdot 3°$ in H_2O (*K* salt, $[\alpha]_D$ $+91\cdot 8°$ in H_2O), which gives all the reactions of vitamin-*C*. Treatment of the *Na* salt with H_2SO_4, $COMe_2$, and anhyd. $CuSO_4$ gives a strongly reducing *substance*, m.p. (indef.) 150—160°, $[\alpha]_D$ $-16\cdot 8°$ in H_2O, which is not a mono*iso*propylidene compound; it appears to acquire 2 Me when treated with CH_2N_2. H. W.

Preparation of aldehydes and ketones by dehydrogenation of alcohols over copper–chromium oxide. H. Adkins, C. E. Kommes, E. F. Struss, and W. Dasler (J. Amer. Chem. Soc., 1933, 55, 2992—2994).—Dehydrogenation of alcohols by $CuO–Cr_2O_3$ may lead to four products, *e.g.*, $Bu^aOH \longrightarrow$ (*A*) $Pr^a\cdot CHO+H_2$ or (*B*) $C_4H_8+H_2O$; $2Pr^a\cdot CHO \longrightarrow$ (*C*) $CHPr^a{:}CEt\cdot CHO+H_2O$ or (*D*) $Pr^a\cdot CO_2Bu$. With primary alcohols at 300° reaction (*B*) occurs only slightly. At 300—400°/100—300 atm. reactions (*C*) and (*D*) mainly occur, and even at 1 atm. reaction (*D*) may take place to 20%, although it rarely exceeds 10%. Reaction (*C*) does not usually occur greatly at 1 atm. with primary alcohols, but *cyclo*hexanol at 360° gives 2-*cyclo*hexylidene*cyclo*hexan-1-one, b.p. 274—276° (20%), *cyclo*hexanone (I) (56%), and *cyclo*hexene (II), b.p. 81—83° (6%); at 360° and (?) 300 atm. it gives

26% of (I) and 51% of (II). The activity of the catalyst can be revived by heating in H_2O at 250° for 1 hr. R. S. C.

Anhydrous formaldehyde. F. Walker (J. Amer. Chem. Soc., 1933, **55**, 2821—2826).—The preps. of liquid CH_2O (I) and its anhyd. polymeride are modified. The solubility of (I) in H_2O, MeOH, Pr^aOH, and Bu^aOH is recorded, the heat of dissolution for these solvents being 14·2—15·0 kg.-cal. (I) does not react with ice and is fairly stable when pure. Primary aliphatic amines cause very rapid, *tert.* less rapid, polymerisation. The polymerides can be differentiated by the rate of their reaction with H_2O. R. S. C.

Reductone (enol-tartronaldehyde) and ascorbic acid. H. von Euler and C. Martius (Annalen, 1933, **505**, 73—87; cf. this vol., 699).—Equally conc. solutions of fructose, glucose, mannose, and maltose when heated with the same amount of alkali under similar conditions consume equal amounts of 2 : 6-dichlorophenol-indophenol (I), galactose somewhat less, and hexose phosphate only so much as corresponds with the amount of ester hydrolysed. Glyceraldehyde, AcCHO, and, particularly, dihydroxyacetone require about twice as much (I). Pentoses behave similarly to hexoses. The resulting reductone (II) differs quantitatively from ascorbic acid in behaviour towards I and (I). Sudden polymerisation occurs when conc. acid solutions of (II) are heated to rather above 100°; the viscous, amorphous products are devoid of reducing power, which they regain when treated with alkali. The high m.p. is explained by polymerisation during heating. (II) does not show antiscorbutic action. H. W.

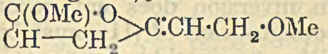
Determination of acetone [in the presence of acetaldehyde]; catalysts in the synthesis of acetone from acetaldehyde. S. Yamada (J. Soc. Chem. Ind. Japan, 1933, **36**, 193—195B).—MeCHO is determined in presence of $COMe_2$ by oxidation with Ag_2O. The total aldehyde and ketone is then determined with $NaHSO_3$ and I, and the $COMe_2$ by difference. A mixture of ZnO and CaO is more effective than either alone as a catalyst in the conversion of MeCHO into $COMe_2$ with steam. A. A. L.

Preparation of mesityl oxide by Bodroux and Taboury's method. R. Jacquemain (Compt. rend., 1933, **196**, 1622—1624).—Fractionation of the product gives 18% of mesityl oxide (I), 40% of $COMe_2$, and 14% of a forerun containing $COMe_2$ (59·1%), H_2O (2·7%), and (I) (29·5%). The last fraction, b.p. > 132°, contains β-hydroxy-δ-keto-β-methylpentane and *ketones*, $C_9H_{18}O$ and $C_{12}H_{18}O$, b.p. 80°/6 mm. and 104—106°/6 mm. (*semicarbazones*, m.p. 206° and 150°, respectively) (cf. A., 1909, i, 699). R. S. C.

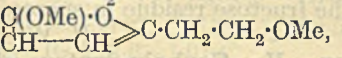
Formation of sugar from formaldehyde in presence of alcohols. G. Gorr and J. Wagner (Biochem. Z., 1933, **262**, 351—354).—Details of the rapid polymerisation of CH_2O into sugar by heating with various alcohols and CaO are given. Using 30% CH_2O and MeOH the yield of sugar calc. as glucose was 82—93% of the aldehyde. P. W. C.

Reducing sugars. III. L. Marchlewski and W. Urbańczyk (Biochem. Z., 1933, **262**, 248—259; cf. this vol., 810).—Addition of 0·5*N*-NaOH to *l*-arabinose (I) solutions leads to the appearance in the originally continuous spectrum of two bands, max. at 2690 and 3095 Å., and on keeping for 2 hr. with NaOH rhamnose solutions show a band at 2675 Å. With (I) immediate neutralisation restores the continuous spectrum. P. W. C.

Transformation of glucals into γ-keto-acids. M. Bergmann and H. Machemer (Ber., 1933, **66**, [*B*], 1063—1065).—Glucal triacetate is converted by boiling 0·5% HCl–MeOH into a *substance*, possibly



$\begin{array}{l}\text{C(OMe)·O}\\ \text{CH—CH}_2\end{array}\!>\text{C:CH·CH}_2\text{·OMe}$ or



$\begin{array}{l}\text{C(OMe)·O}\\ \text{CH—CH}\end{array}\!\geqslant\text{C·CH}_2\text{·CH}_2\text{·OMe}$, b.p. 53°/1·5 mm., and *Me δ-methoxymethyl-lævulate* (I), b.p. 90°/3 mm. [*phenylhydrazone*, m.p. 74°; *semicarbazone*, m.p. 117° (corr.)]. (I) is obtained in similar yield from ψ-glucal triacetate, in poorer yield from glucodeose or galactal triacetate. Xylal diacetate similarly affords Me lævulate, b.p. 85°/14 mm. [phenylhydrazone, m.p. 105°; semicarbazone, m.p. 151° (corr.)], also obtained from arabinal diacetate. H. W.

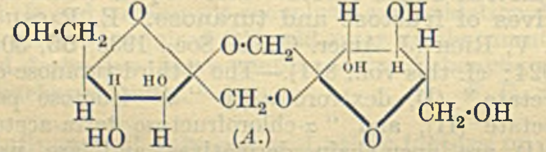
Simultaneous preparation of 2 : 3 : 4- and 2 : 3 : 6-trimethylglucose. G. J. Robertson (J.C.S., 1933, 737—739).—2 : 3-Dimethyl-α-methylglucoside in C_5H_5N with CPh_3Cl gives 6-*triphenylmethyl*-2 : 3-*dimethyl-α-methylglucoside*, m.p. 169—170°, $[\alpha]_D$ +66·4° in $CHCl_3$ [4-*Bz* derivative, m.p. 60°; 4-*Ac* derivative (I), m.p. 153—154°]. 4-*Acetyl*-2 : 3-*dimethyl-α-methylglucoside* [from (I)] on repeated methylation with MeI and Ag_2O yields a Me_3 derivative, from which 2 : 3 : 6- (separated by conversion into the methylglucoside) and 2 : 3 : 4-trimethylglucose (1 : 6-dinitrate, m.p. 84° and 86°) are obtained in approx. equal amounts. The wandering of Ac groups during treatment with MeI and Ag_2O is discussed. A. A. L.

Ketone sugar series. III. Open-chain derivatives of fructose and turanose. E. Pacsu and F. V. Rich (J. Amer. Chem. Soc., 1933, **55**, 3018—3024; cf. this vol., 811).—The "third turanose octa-acetate" (I), dextrorotatory "α" fructose penta-acetate (II), and "α-chlorofructose tetra-acetate" (III) are open-chain derivatives and are named *keto*turanose octa-acetate, *keto*fructose penta-acetate, and 6-chloro*keto*fructose tetra-acetate, respectively. (I) is hydrogenated (Pt) in EtOH to a mixture, yielding on acetylation 5-*glucosido-sorbitol nona-acetate* (IV), m.p. 116·5°, $[\alpha]_D^{20}$ +70·9° in $CHCl_3$, and -*mannitol nona-acetate*, m.p. 142°, $[\alpha]_D^{20}$ +89·3° in $CHCl_3$. (IV) when deacetylated by 5% H_2SO_4 and then with yeast gives *d*-sorbitol hexa-acetate. The prep. of fructose tetra-acetate, $[\alpha]_D^{20}$ $-101·6° \longrightarrow -99·9°$ in C_5H_5N, −97·2° in C_6H_6, and −74·4° (stable) in H_2O, is modified. (II) by reduction and acetylation gives similarly sorbitol and mannitol hexa-acetates. β-Fructose penta-acetate is not reduced similarly. (III) with AgOAc and Ac_2O gives β-fructose penta-acetate and on reduction and acetylation a mixture of (probably) 6-chloro-sorbitol and -mannitol tetra-acetates. R. S. C.

Alcoholysis of sucrose. I. E. Berner (Ber., 1933, **66**, [*B*], 1076—1080).—The action of MeOH on

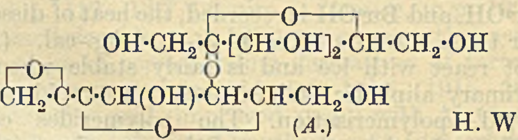
sucrose (I) at 150—155° during 8—10 hr. causes change of about half of (I) into glucose and γ-methylfructoside (II) $[\alpha]_D \not> +54°$. Prolongation of the reaction is accompanied by isomerisation of (II), which is partly prevented by the alkali of the glass. Since the determinations of reducing sugar and of aldose (Willstätter–Schudel) gives identical results, free fructose is not formed. (II) is identified by conversion into 1 : 3 : 4 : 6-tetramethyl-methylfructoside and -fructose. In accordance with Hudson's rule, (II) is regarded as α-methylfructofuranoside. Provided that a Walden inversion does not occur during alcoholysis, the configuration of (II) must be identical with that of the fructose residue in sucrose.
H. W.

Natural polylævans. V. Carbohydrates of the Jerusalem artichoke. II. H. H. Schlubach and H. Knoop (Annalen, 1933, 504, 19—30).—Repeated dissolution in MeOH of the dextrorotatory material (I) derived from the Jerusalem artichoke and subsequent pptn. with Et_2O permits the separation of mannitol without leading to a product of established homogeneity. Characterisation of fructose anhydrides is facilitated by hydrolysis with N-H_2SO_4 in 1% solution at 20° or 60°, respectively, the course of the change being followed by determination of reducing power (Bertrand) rather than of $[\alpha]$. The fructose anhydrides are thereby differentiated into two distinct classes: irisin, sucrose, inulin, and the dilævan of artichoke are readily hydrolysed, whereas (I) and Jackson's difructose anhydride I and III are difficultly hydrolysed. A simple relationship does not exist between the rates of hydrolysis at the different temp. Treatment of (I) with Ag_2O and MeI yields mainly a *hexamethyldifructose anhydride*, b.p. 143°/0·18 mm., $[\alpha]_D^{20}$ +149·2° in $CHCl_3$, hydrolysed by N-H_2SO_4 at 95° chiefly to 3 : 4 : 6-trimethylfructose, b.p. 90°/0·1 mm., $[\alpha]_D^{20}$ +24·9° in $CHCl_3$ (phenylosazone, m.p. 77—79°). (I) has therefore the constitution A. Jackson's compound III is probably identical with (I) and is an accompaniant of his inulin, whilst his substance I is regarded as a reversion product.
H. W.



(A.)

Fructose anhydrides. XII. Constitution of irisin. H. H. Schlubach, H. Knoop, and M. Y. Liu (Annalen, 1933, 504, 30—37).—Extraction of the powdered rhizomes of *Iris pseudoacorus* mixed with $CaCO_3$ by EtOH and successive treatment of the extracts with $Pb(OAc)_2$, H_2S, and NH_3 leads to irisin (I), which, after repeated dissolution in H_2O and pptn. with EtOH, has m.p. 210° (decomp.) after softening at 160°, $[\alpha]_D^{20}$ −53·3° in H_2O, ash 0·08%. Under standard conditions it is more readily hydrolysed than any other fructose derivative; the discrepancy between the results obtained by using Bertrand's method and measuring $[\alpha]_D$ points to the production of intermediate compounds during hydrolysis. (I), Ac_2O, and C_5H_5N afford irisin acetate, m.p. 217°, $[\alpha]_D^{20}$ −23·1° in AcOH, which, with Me_2SO_4 and NaOH in $COMe_2$, gives *methylirisin* (II), m.p. 187—188·5°, $[\alpha]_D^{20}$ −63·2° in $CHCl_3$. (II) is hydrolysed by $H_2C_2O_4$ in boiling 70% EtOH to 1 : 3 : 4 : 6-tetramethyl- and an unidentified dimethyl-fructose. The fundamental unit of (I) has probably the structure A.



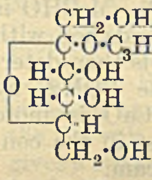
(A.)

H. W.

Optical superposition and the 4 : 6-benzylidenemethylglucosides. D. S. Mathers and G. J. Robertson (J.C.S., 1933, 696—698).—4 : 6-Benzylidene-α-methylglucoside 2 : 3-di-p-toluenesulphonate, m.p. 148—149°, has $[\alpha]_D$ +13° in $CHCl_3$ (cf. A., 1929, 50). A comparison of mol. rotations of 4 : 6-benzylidene-α- and -β-methylglucosides, and their Bz_2, Me_2, Ac_2, and di-p-toluenesulphonyl derivatives shows that the rule of optical superposition is not applicable, probably owing to the influence of :CHPh.
A. A. L.

Properties of d-β-5-chloro-, -5-bromo-, and -5-iodo-salicylglucosides. P. Delauney (Compt. rend., 1933, 197, 70—72; cf. A., 1927, 174; 1928, 201; 1930, 57).—Solubility in H_2O and EtOAc, m.p., $[\alpha]_D$, reducing power, and behaviour on hydrolysis with dil. H_2SO_4 and emulsin are given. All crystallise with $1H_2O$. d-β-5-Iodosalicylglucoside has m.p. 172° (block, anhyd.).
H. A. P.

Alcoholytic degradation of inulin. E. Berner (Annalen, 1933, 505, 58—72).—Treatment of inulin (I) with glycerol (II) in the proportion used by Vogel and Pictet occasions slight degradation, leading to products of widely differing mol. wt. Increase in the amount of (II) and prolongation of the time of reaction leads to *glycerylfructofuranoside* (III), which is treated with Ac_2O and C_5H_5N and then with Me_2SO_4 and NaOH in $COMe_2$, thereby giving *glycerylfructofuranoside Me_6 ether*, b.p. 126°/0·03 mm., $[\alpha]_D^{20}$ +19·4° in $CHCl_3$, hydrolysed by 1% HCl to 1 : 3 : 4 : 6-tetramethylfructofuranose, b.p. 99°/0·05 mm., $[\alpha]_D^{20}$ +27·1° in H_2O (final val.), further identified as 5-methoxymethylfurfuraldehydesemicarbazone, m.p. 165—166°. Depolymerisation of (I) is greatly accelerated by a little H_3PO_4 (d 1·75). Treatment of (I) with $[\cdot CH_2\cdot OH]_2$ is described. Anhyd. MeOH and (I) at 170—175° yield γ-methylfructoside, $[\alpha]_D^{20}$ +41·3° in H_2O, converted by Me_2SO_4 and 30% NaOH into tetramethylmethylfructofuranoside, b.p. 85°/0·04—0·05 mm., $[\alpha]_D^{20}$ +76·3° in H_2O, whence 1 : 3 : 4 : 6-tetramethylfructose, b.p. 95°/0·1 mm., $[\alpha]_D$ about +40° in H_2O. (I) is therefore a α-fructofuranose anhydride of high mol. wt. Trimethylinulin is more stable than (I), but is degraded by MeOH at 220—230° to a trimethylmethylfructoside, b.p. 100°/0·03 mm., $[\alpha]_D$ +44° in $CHCl_3$
H. W.



(III.)

Factors influencing the conversion of cellulosic material into sugar. G. J. Ritter, R. L. Mitchell, and R. M. Seborg (J. Amer. Chem. Soc., 1933, **55**, 2989—2991).—With the 2-hr. treatment of spruce cellulose with 72% H_2SO_4 the optimum temp. is 35°, with 6-hr. treatment 16° (99·7% conversion), conversion being partial below the optimum temp. and reduced by charring above it. R. S. C.

Complete nitration of cellulose. A. Bouchonnet, M. Trombe, and G. Petitpas (Compt. rend., 1933, **197**, 63—65).—Nitration of cellulose (linters) with a mixture of 50 parts of 99·9% HNO_3, 25 of AcOH, and 25 of Ac_2O for 5 hr. at 15°, and stabilisation with EtOH gives a stable trinitrate with the calc. N content. Only slightly inferior results are obtained with ramie and α-cellulose. H. A. P.

Osmometric investigation of dilute solutions of polymeric carbohydrates. IV. Mol. wt. of crystalline cellulose acetate II. K. Hess and M. Ulmann (Annalen, 1933, **504**, 81—94).—The mol. wt. of cryst. cellulose acetate II (I) in glacial AcOH depends greatly on the concn. In solution more conc. than 0·25% at 20°, osmotic pressure is scarcely detectable, so that the colloidal state must be assumed. Between 0·25 and 0·19%, 0·16 and 0·08%, and 0·07 and 0·01% the apparent mol. wt. corresponds with $(C_6)_{16}$, $(C_6)_8$, and $(C_6)_2$, respectively. Since the region of concn. within which a colloidal solution passes into one with mols. $(C_6)_{16}$ is very narrow, a possible equilibrium between colloidal and cryst. phases must be assumed which is very readily displaced in either direction by slight changes of concn. An almost instantaneous change is indicated. The changes $(C_6)_{16} \longrightarrow (C_6)_8 \longrightarrow (C_6)_2$ are even more definitely marked, and in suitably conc. solution are functions of the time. Delay in the establishment of equilibrium is frequently observed. Thus, in 0·07% solution the $(C_6)_8$ stage may persist at 20°; if the solution is warmed for 1 hr. at 50° and then cooled to 20°, the $(C_6)_2$ stage is attained. Freezing and subsequent thawing of the solution leads to the $(C_6)_8$ condition, which gradually passes within a few hr. to $(C_6)_2$, and then remains const. Evaporation of a solution of $(C_6)_2$ leads to regeneration of (I), m.p. 280—286° (decomp.), $[\alpha]_D^{20}$ +23·0° in $CHCl_3$. In analogy with "hendecamethylcellotriose" the possible dispersal of (I) to the (C_6) stage is discussed. Since (I) has low viscosity and does not form films or swell, it appears that there is no relation between these properties and mol. size. H. W.

Primary, secondary, and tertiary cellulose acetates. I. Sakurada and T. Furukawa (J. Soc. Chem. Ind. Japan, 1933, **36**, 400—403B).—Primary (I), *sec.* (II), and *tert.* (III) cellulose acetates were prepared by acetylation (60·5% AcOH), by partial hydrolysis (56·3%), and by subsequent re-acetylation (61·8%). (I) and (III) were similar in solubility and swelling in a no. of solvents and in their *X*-ray diagrams. (I) and (III) swell > (II) in non-polar liquids but less in polar liquids. The different solubilities of (I) and (II) are due to different mol. arrangements conditioned by the different Ac contents. A. G.

Identification of amines as 3 : 5-dinitrobenzoates. C. A. Buehler, E. J. Currier, and R. Lawrence (Ind. Eng. Chem. [Anal.], 1933, **5**, 277—278).—The m.p. of the amine salts of 3 : 5-dinitrobenzoic acid are recorded: NH_2Ph 134·7°, *o*- 134·9°, *m*- 139·0—144·0°, and *p*-$C_6H_4Me\cdot NH_2$ 145·0—147·4°, *m*-4-xylidine 169·6—170·4°, *o*- 152·7°, *m*- 121·8°, and *p*-$C_6H_4Cl\cdot NH_2$ 133·0°, *p*-$C_6H_4Br\cdot NH_2$ 126·9°, *m*- 112·0—114·4°, *p*-$C_6H_4(NH_2)\cdot NO_2$ 128·6°, *p*-$NH_2\cdot C_6H_4\cdot OH$ 178·2—178·8°, *o*- 205·2—205·6°, *m*- 167·0—172·2°, *p*-$NH_2\cdot C_6H_4\cdot CO_2H$ 196·7°, NHMePh 121·8°, NMe_2Ph 114·8—115·6°, $NHPh\cdot CH_2Ph$ 133·0°, NHPhAc 129·1—130·1°, *o*- 177·3°, *m*- 158·7°, *p*-$C_6H_4(NH_2)_2$ 177·3—178·0°, α- 200·5°, β-$C_{10}H_7\cdot NH_2$ 156·5—157·2°, benzidine 205·7°, C_5H_5N 171·3°, quinoline 151·4—152·2°, NH_3 246·7°, $CH_2Ph\cdot NH_2$ 210·0°, $NHEt_2$ 163·4°, NEt_3 138·0—150·0°, $CO(NH_2)_2$ 120·5°, NH_2Ac 93·9—103·0°, NH_2Bz 138·6—140·4°. E. S. H.

Acyl peroxides and secondary amines. S. Gambarjan and L. Kazarjan (J. Gen. Chem. Russ., 1933, **3**, 222—228).—The reaction between Bz_2O_2 (I), Ac_2O_2 (II), and BzO_2Ac (III) and *sec.* amines yields acyldialkylhydroxylamines. (III) gives in every case the Ac, not the Bz, compound and BzOH, and under more drastic conditions the corresponding dialkylacetamide. $C_5H_{11}N$ was the most active amine examined; *tert.* amines also react. (I) and $NHEt_2$ in Et_2O gave *N*-benzoyloxydiethylamine, b.p. 92°/0·12 mm. (II) and $NHEt_2$ give without cooling NEt_2Ac, and with cooling *acetoxydiethylamine*, b.p. 32°/0·01 mm., also obtained from (III) and $NHEt_2$. (I) and $NHPr^a_2$ give N-*benzoyloxydipropylamine*, b.p. 40—41°/0·01 mm., also obtained from (III) and $NHPr^a_2$. (I) and $C_5H_{11}N$ give *N*-benzoyloxypiperidine (A., 1925, i, 1260). (II) and $C_5H_{11}N$ give without cooling *N*-acetylpiperidine, b.p. 44°/0·01 mm., and with cooling *N*-acetoxypiperidine, b.p. 50—51°/0·01 mm., also obtainable from (III) and $C_5H_{11}N$. (I) and NEt_3 give $NHEt_2$. G. A. R. K.

Reaction of alkylchloroamines with Grignard reagents. G. H. Coleman (J. Amer. Chem. Soc., 1933, **55**, 3001—3005).—The following % yields of (*a*) primary, (*b*) *sec.*, and (*c*) *tert.* amines were obtained. (*a*), (*b*), and (*c*): $NEtCl_2$ with $MgPr^aCl$ 52, 12, and 8, $MgBu^aCl$ 36, 11, and 9, *n*-$C_5H_{11}\cdot MgCl$ 34, 12, and 8, and $CH_2Ph\cdot MgCl$ 28, 19, and 6; $NMeCl_2$ with $MgBu^aCl$ 43, 22, and 5, and $CH_2Ph\cdot MgCl$ 43, 25, and 3. (*a*) and (*b*): $CH_2Ph\cdot MgCl$ with NHMeCl 70 and 14, and NHEtCl 75 and 12; $MgBu^aCl$ with NHMeCl 72 and 14. (*b*) and (*c*): $CH_2Ph\cdot MgCl$ with NMe_2Cl 95 and 5, NEt_2Cl 76—90 and 5—7, and NPr^a_2Cl 78 and 5; $MgBu^aCl$ with NBu^a_2Cl 85 and 4, respectively. The following b.p. are recorded: *n*-ethylamylamine, 134—136°/745 mm., $NHMe\cdot CH_2Ph$ 77·5—78°/17 mm., $NMe_2\cdot CH_2Ph$, 98—99°/24 mm., $NHEt\cdot CH_2Ph$ 88·5—89°/18 mm., $NEt_2\cdot CH_2Ph$ 96—98°/17 mm., and $NPr^a_2\cdot CH_2Ph$ 120—122°/17 mm. R. S. C.

Stereochemistry of organic compounds. III. Spatial configuration of aliphatic and alicyclic amino-acids. L. Orthner and R. Hein (Biochem. Z., 1933, **262**, 461—479).—The acid and basic dissociation consts. of various aliphatic and alicyclic NH_2-acids are calc. from the hydrolysis const. of their hydrochlorides and Na salts, and it is shown that the strength of the CO_2H group in these compounds is increased in comparison with that of the corresponding carboxylic acids, the extent of the increase decreasing as the NH_2 group passes from the α- to the δ-position. The basic nature of the NH_2 group is increased as the CO_2H group passes from the α- to the δ-position. In aq. solutions the C chains are so arranged that the NH_2 and CO_2H groups are as far removed from one another as is possible. P. W. C.

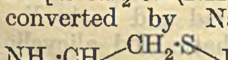
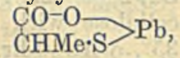
Hydrolysis of amino-acids by aqueous extracts of bone charcoal. E. BAUR and K. WUNDERLY (Biochem. Z., 1933, 262, 300—307).—Aq. extracts of bone black hydrolytically deaminate glycine, alanine, aspartic acid, leucine, and phenylalanine (I), the activity except in the case of (I) being < that of the charcoal itself. The salts contained in the extracts have relatively a feeble deaminating activity. P. W. C.

Amino-acids and related compounds. III. Electrolytic oxidation of arginine. IV. Electrolytic reactions of leucic acid. Y. TAKAYAMA (Bull. Chem. Soc. Japan, 1933, 8, 169—173, 173—178; cf. this vol., 720).—III. Electrolysis of arginine sulphate in dil. H_2SO_4 using PbO_2–Pb electrodes at 2 amp. per sq. dm. and 25° gives NH_3, guanidine, and succinic acid. γ-Guanidinobutyric acid was not detected as an intermediate product.

IV. Electrolysis of leucic acid (I) as above but at 38·5° gives *iso*valeric acid, its *iso*amyl ester, *iso*amyl alcohol, iso*valeryl-leucic acid* (II), b.p. 165—175°/24 mm. (*Ag* salt), and gases. (II) was synthesised for comparison from (I) and *iso*valeryl chloride. H. A. P.

Synthesis of aspartic acid. M. S. DUNN and S. W. FOX (J. Biol. Chem., 1933, 101, 493—497).—Aspartic acid (I) is readily prepared (59% yield) by heating for 24 hr. in sealed vessels at 100° NH_3 (4·8 mols.) and Et_2 fumarate (1·0 mol.) in abs. EtOH to yield crude diketopiperazinediacetamide, which is hydrolysed by 6*N*-NaOH and (I) separated by its Cu salt. F. O. H.

Hydroxyamino-acids. E. ABDERHALDEN and F. BROICH (Biochem. Z., 1933, 262, 321—328).—The formation of Bz_2 derivatives of serine and *iso*serine on benzoylating in slightly alkaline solution is confirmed. *O*-Bz in these compounds is, however, immediately removed by stronger alkali. Serine is readily decomposed both by acids and alkalis, forming on heating with 25% H_2SO_4 lactic and pyruvic acids, CO_2, glycine, and NH_3. Serine ester on distillation at 2 mm. is considerably decomposed, and the amount of serine isolated from proteins containing it is only about ⅓ the actual content. P. W. C.

Sulphur–lead union. H. BAUER and K. BURSCHKIES (Ber., 1933, 66, [*B*], 1041—1046).—Cysteine (I) and $Pb(OAc)_2$ in H_2O yield the insol. *salt*, $\mathrm{Pb{:}[\cdot S\cdot CH_2\cdot CH(NH_2)\cdot CO_2\cdot]_2{:}Pb}$, decomp. 215—220°, converted by Na_2CO_3 into (I) and the *salt*  $\mathrm{NH_2\cdot CH{<}\begin{matrix}CH_2\cdot S\\ CO{-}O\end{matrix}{>}Pb}$, sol. without decomp. in Na_2CO_3, NaOAc, and NaCl, but from which all the Pb is pptd. by H_2S. α-Thiolpropionic acid similarly yields the compounds $\mathrm{Pb{:}[\cdot S\cdot CHMe\cdot CO_2]_2{:}Pb}$ and  $\mathrm{\begin{matrix}CO{-}O\\ CHMe\cdot S\end{matrix}{>}Pb}$, whereas *o*-thiolbenzoic acid gives a *Pb* salt $C_7H_4O_2SPb$, decomp. 350°, completely decomposed by Na_2CO_3. *Pb 3-amino-4-thiolbenzenesulphonate* is partly stable to Na_2CO_3. The *Pb* salt of 2-*aminothiophenol*, m.p. 185—186° (decomp.), is decomposed by Ac_2O, and the NH_2 group cannot be substituted by HCHO–$NaHSO_3$, whereas *Pb* p-*aminophenyl sulphide*, m.p. 185° (decomp.), gives an Ac_2 derivative, decomp. 330—331°, and the *substance* $(SO_3Na\cdot CH_2\cdot NH\cdot C_6H_4\cdot S)_2Pb$. *Pb* m-*aminophenyl sulphide*, decomp. 174°, occupies an intermediate position. H. W.

Crystalline derivatives of dithiocyanostearic acid. I. Synthesis of thiocyanogen derivatives of benzoylmethyl and *p*-halogenobenzoylmethyl esters of oleic acid. W. KIMURA (J. Soc. Chem. Ind. Japan, 1933, 36, 234—236B).—Na oleate with ω-bromoacetophenone or its *p*-halogen derivatives, followed by treatment with $(CNS)_2$ (cf. B., 1930, 429), gives *benzoylmethyl*, m.p. 54°, and p-*iodo*-, m.p. 48°, p-*bromo*-, m.p. 43·5°, and p-*chloro-benzoylmethyl* ηθ-*dithiocyanostearate* (oily). A. A. L.

Salts of diguanide and of guanidine. C. MANUELLI (Annali Chim. Appl., 1933, 23, 235—244).—Priority is claimed for the industrial prep. of guanidine nitrate by heating a mixture of NH_4NO_3 and dicyanodiamide (I) and of the interpretation of the reaction through the intermediate formation of diguanide nitrate. The *mono*- and *di-nitrates* and the $(NO_2)_2$-derivative of diguanide (II), and some guanidine salts are described. The analytical reactions of guanidine, (II), and (I) have been studied. O. J. W.

Additive compounds of mercuric cyanide with hydriodides of organic bases. G. RAGNI (Gazzetta, 1933, 63, 303—304).—$Hg(CN)_2$ forms with guanidine and dicyanodiamide hydriodides the *complexes* $CH_6N_3I,Hg(CN)_2$, m.p. 210° (decomp.), and $C_2H_7ON_4I,Hg(CN)_2$, decomp. about 300°; the conductivity of the former shows that it is strongly dissociated in solution. E. W. W.

Nitriles of Δ^{α}- and Δ^{β}-olefinic acids. R. A. LETCH and R. P. LINSTEAD (J.C.S., 1933, 612—614; cf. A., 1932, 371).—A reply to Bruylants (A., 1932, 1119). The bromometric method for the determination of Δ^{β}-nitriles (A., 1931, 205) is applicable provided sufficient time is allowed for complete reaction. A. A. L.

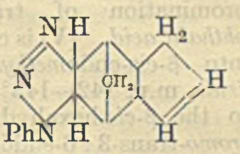
Relative reactivity of various functional groups towards a Grignard reagent. C. E. ENTEMANN, jun., and J. R. JOHNSON (J. Amer. Chem. Soc., 1933, 55, 2900—2903).—When 1 mol. of MgMeBr in Et_2O reacts with 1 mol. each of two reactants, PhX, the proportions of the products formed indicate the following reactivities: X=CHO>COMe>NCO>COF>COPh>COCl, COBr>CO_2Et>CN. The order, COF>COCl, shows that Grignard reactions proceed by addition rather than by direct metathesis. R. S. C.

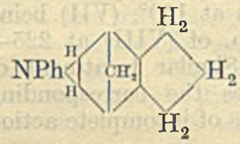
Reactions catalysed by aluminium chloride. VI. Isomerisation of *cyclo*hexane into methyl*cyclo*pentane. C. D. Nenitzescu and I. P. Cantuniari. **VII. Hydrogenation phenomena in the customary Friedel–Crafts reaction.** C. D. Nenitzescu and D. A. Isăcescu (Ber., 1933, **66**, [*B*], 1097—1100, 1100—1103).—VI. *cyclo*Hexane (I) is scarcely affected by protracted ebullition with freshly-sublimed, anhyd. $AlCl_3$. With $AlCl_3$ containing H_2O, equilibrium is established when about 1/5 of (I) has been converted into methyl*cyclo*pentane (II) containing a little *n*-hexane. Under similar conditions (I) is formed from (II). The transformation of (I) into (II) is not due to the smaller strain of the *cyclo*pentane ring; the strain-free *cyclo*hexane ring appears more stable and less reactive.

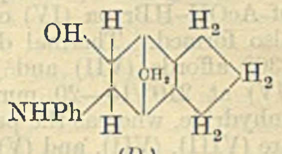
VII. Treatment of C_6H_6 with allyl chloride (I) in presence of $ZnCl_2$ or preferably $FeCl_3$ leads to $CHPhMe\cdot CH_2Ph$ (II) and β-*chloropropylbenzene* (III), b.p. 79°/10 mm., characterised by transformation into propenylbenzene, b.p. 73°/20 mm., and thence into $CHPhBr\cdot CHMeBr$, m.p. 66·5°. Anhyd. $AlCl_3$, C_6H_6, and (I) afford almost exclusively (II), the intermediate production of (III) being postulated. With moist $AlCl_3$ the production of (II) is accompanied by that of PhPr (IV) and 9 : 10-*diethylanthracene* (V), m.p. 146°. Formation of (IV) is intimately connected with that of (V). H. W.

Polymerisation of cyclic hydrocarbons. V. Degradation of polymeric *cyclo*pentadienes with selenious acid. K. Alder and G. Stein [with W. Grassmann]. **VI. Stereochemistry of *cyclo*pentadiene polymerisation.** K. Alder and G. Stein [with W. Eckardt, R. von Buddenbrock, and S. Schneider] (Annalen, 1933, **504**, 205—215, 216—257).—V. Dihydro-α-di*cyclo*pentadiene (I) is converted by H_2SeO_3 in boiling MeOH into *dihydro-α-di*cyclo*pentadien-3-ol Me ether*, b.p. 106—109°/15 mm.; the *Et ether*, b.p. 106—109°/15 mm., and *amyl ether*, b.p. 122—138°/13 mm., are obtained similarly. Treatment of (I) with Ac_2O and H_2SeO_3 leads to *dihydro-α-di*cyclo*pentadien-3-yl acetate*, b.p. 116—120°/12 mm., hydrolysed by KOH–MeOH to *dihydro-α-di*cyclo*pentadien-3-ol*, b.p. 114°/12 mm., m.p. about 30°, which is oxidised by CrO_3 in AcOH to *dihydro-α-di*cyclo*pentadien-3-one* (II), b.p. 110°/12 mm., m.p. about 40° (*semicarbazone*, m.p. 213—214°). (II) is hydrogenated to tetrahydro-α-di*cyclo*pentadien-3-one, m.p. 99°, and oxidised by $KMnO_4$ in $COMe_2$ to α-*cis*-3 : 6-*endo*methylenehexahydro-*o*-phthalic acid, m.p. 165° (anhydride, m.p. 170°). A mixture of (I) and dihydro-β-di*cyclo*pentadiene is similarly treated, and β-*cis*-*endo*methylenehexahydro-*o*-phthalic acid, m.p. 151° (anhydride, m.p. 80°), is isolated from the product of the oxidation of the ketone mixture. Dihydro-α-tri*cyclo*pentadiene is transformed successively into *dihydro-α-tri*cyclo*pentadien-3-yl acetate*, b.p. 180—185°/11 mm., *dihydro-α-tri*cyclo*pentadien-3-ol*, m.p. 135°, *dihydro-α-tri*cyclo*pentadien-3-one*, m.p. 162°, and the α_1-*cis*-dicarboxylic acid (cf. *A*), m.p. 174° (anhydride, m.p. 156°; Me_2 ester, m.p. 101°, transformed by NaOEt into the *trans*-acid, m.p. 248—249°). Similarly, dihydro-β-tri*cyclo*pentadiene yields successively *dihydro-β-tri*cyclo*pentadien-3-yl acetate*, b.p. 180—182°/11 mm., *dihydro-β-tri*cyclo*pentadien-3-ol*, m.p. 140°, *dihydro-β-tri*cyclo*pentadien-3-one*, and the β-*cis*-*dicarboxylic acid* (cf. *A*), m.p. 184—185° (decomp.) [*anhydride*, m.p. 143—144°; *Me_2* ester, m.p. 95—96°, converted by NaOEt in boiling EtOH into the *trans*-acid, m.p. 248—249° (see above)].


(*A*.)


(*B*.)


(*C*.)

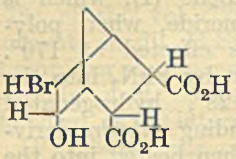

(*D*.)

VI. The evidence obtained above gives proof of the existence of β-di*cyclo*pentadiene (I), which is isolated, mixed with the α-isomeride, when polymerisation of *cyclo*pentadiene is effected at 170°. (I) is characterised by conversion by PhN_3 into the *hydrotriazole* (*B*), m.p. 127—128°, hydrogenated (Pd in EtOH) to the corresponding *dihydro*-derivative, m.p. 142°, which passes when heated into the *phenylimine* base (*C*), m.p. 68°, b.p. 180—190°/15 mm., and when treated with dil. H_2SO_4 into the *OH*-base (*D*), m.p. 95°. Hydrogenation of the mixed di*cyclo*pentadienes and treatment of the product with Br does not lead to a homogeneous β-Br-derivative. The conversion of dihydro-β-di*cyclo*pentadiene into the β-acid (see above) is very circuitous. Reduction of 3 : 6-*endo*methylene-Δ^1-tetrahydrophthalic acid or its anhydride leads exclusively to the known α-*cis*-3 : 6-*endo*methylenehexahydrophthalic acid (anhydride, m.p. 167°). Condensation of *cyclo*pentadiene with Me_2 maleate affords Me_2 α-*cis*-3 : 6-*endo*methylene-Δ^4-tetrahydrophthalate, b.p. 145—147°/18 mm., reduced (Pd–H_2) to the H_6-ester, b.p. 142—143°/15 mm., which is isomerised and hydrolysed by NaOMe to the *trans*-acid (II). Distillation of (II) gives a mixture of anhydrides from which, by treatment with H_2O, β-cis-3 : 6-endo*methylenehexahydrophthalic acid* (II), m.p. 152—153° (decomp.) (*anhydride*, m.p. 78—79°; *Me H* ester, m.p. 96—97°), is obtained. Treatment of (II) with conc. HCl at 180—190° or, successively, with CH_2N_2 and NaOMe affords the *trans*-acid, m.p. 193—194°. The α-*cis*-acid at 215—220° passes exclusively into the α-*cis*-anhydride, m.p. 167°.

Distillation of *trans*-3 : 6-*endo*methylene-Δ^4-tetrahydrophthalic acid gives mainly *cyclo*pentadiene and fumaric acid with a small amount of α-*cis*-anhydride. On the assumption that the transition of CO_2H from the α- into the β-position is possible only when the Δ^4 double linking is saturated, α-*cis*-*endo*methylene-Δ^4-tetrahydrophthalic anhydride (III) is converted by Br in $CHCl_3$ (free from H_2O and EtOH) into *dibromo-α-*cis-endo*methylenehexa-*

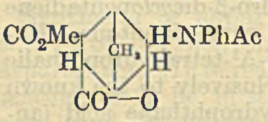
hydrophthalic anhydride, m.p. 206°, converted by Zn dust and AcOH into (III) [corresponding *acid* (IV), m.p. 188° (decomp.), transformed by AcCl into (III)]. (IV) passes at 210—220° into *dibromo*-β-cis-endo*methylenehexahydrophthalic anhydride* (V), m.p. 248—249° [corresponding *acid* (VI), m.p. 248° after loss of H_2O at 220°], and the *bromo*-trans-*lactonic acid*, $C_9H_9O_4Br$ (VII), m.p. 186°, also obtained by bromination of trans-endo*methylene*-Δ^4-*tetrahydrophthalic acid*. (V) is converted by Zn dust and AcOH into β-cis-endo*methylene*-Δ^4-*tetrahydrophthalic anhydride*, m.p. 142—143° (acid, m.p. 148°, hydrogenated to the β-*cis*-hexahydro-acid, m.p. 152—153°). *Dibromo*-trans-3 : 6-endo*methylenehexahydrophthalic acid* (VIII), m.p. 244° (decomp.), is prepared by the action of AcOH–HBr on (IV) or (VI) at 160°, (VII) being also formed. Thermal decomp. of (VIII) at 225—230° affords (VII) and (V). Similar treatment of (IV) at 210°/15—20 mm. gives the corresponding anhydride, whereas the products of incomplete action are (VIII), (VII), and (V).

Bromination of (III) in H_2O gives the *bromohydroxy-acid* (IX), m.p. 116° (decomp.), which passes readily into the *bromo*-cis-*lactonic acid*, $C_9H_9O_4Br$, m.p. 157° (*Me* ester, m.p. 77°). The *trans*-Δ^4-acid is similarly readily converted into the corresponding lactone.



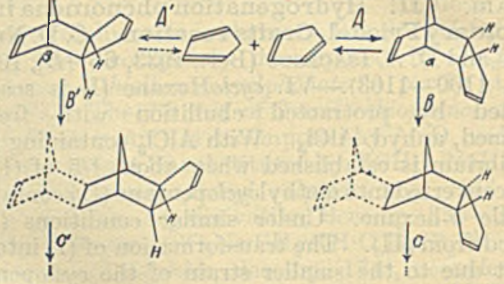
(IX.)

Addition of PhN_3 to Me_2 *trans* - 3 : 6 - *endo*methylenehexahydrophthalate occurs smoothly with production of the *hydrotriazole*, $C_{17}H_{19}O_4N_3$, m.p. 115°, which readily passes into the *base*, $C_{17}H_{19}O_4N$, m.p. 156°, transformed by boiling Ac_2O into the *compound* (X), m.p. 188—189°. Conditions are therefore similar to those of the *cis*-α-series. The β-*cis*-anhydride similarly yields a *hydrotriazole*, m.p. 220° (decomp.), readily passing into the *phenylimine* base, m.p. 189° (decomp.), transformed by CH_2N_2 into the corresponding *Me*$_2$ ester, m.p. 138°, which is stable to boiling Ac_2O.



(X.)

Treatment of Me_2 α-*cis*-3 : 6-*endo*methylene-Δ^4-tetrahydrophthalate with BzO_2H in $CHCl_3$ leads to the corresponding *oxide*, b.p. 162—169°/13 mm., converted by boiling Ac_2O into the *acetylated Me ester lactone*, m.p. 64—65°. Likewise the Me_2 *trans*-ester yields an *oxide*, b.p. 150—160°/15 mm., and the trans-*acetyl-lactone acid*, m.p. 152° (*Me* ester, m.p. 98°). *Me*$_2$ β-cis-3 : 6-endo*methylene*-Δ^4-*tetrahydrophthalate*, b.p. 136°/13 mm., m.p. 51—52° (from the anhydride and MeOH–H_2SO_4), affords an *oxide*, m.p. 86—87°, stable to boiling Ac_2O. Oxidation of *cis*-α-acid with $KMnO_4$ in alkaline solution and treatment of the product with AcCl gives the *diacetoxy*-α-cis-*anhydride*, m.p. 161—162° [corresponding *acid*, m.p. 197° (decomp.)]. Similar treatment of the *trans*-acid and β-*cis*-anhydride yields the *diacetoxy*-trans-*acid*, m.p. 205—206°, and the *diacetoxy*-β-cis-*anhydride*, m.p. 155—156°; lactone formation does not occur in any instance. Determination of the configuration of the acids establishes that of the *cyclo*pentadiene polymerides in the sense of the following scheme, in which the only doubtful positions are indicated by the dotted lines :



Formation of α-di*cyclo*pentadiene is reversible; at room temp. the equilibrium is almost completely in favour of the α-dimeride, and is noticeably displaced towards the monomeride only at 140—160°. In a closed vessel at 170° equilibrium is disturbed by the formation of the α-tri*cyclo*-compound, which is stable at this temp., but is capable of further addition of monomeride. The only complication arises from the ability of the monomeride to yield the β- as well as the α-dimeride at higher temp. H. W.

Slow oxidation of aromatic hydrocarbons at high pressures. D. M. Newitt and P. Szegö (Chem. and Ind., 1933, 645).—Oxidation of PhMe by air at 210°/50 atm. gives chiefly $CH_2Ph{\cdot}OH$, with some PhCHO, BzOH, and 2 : 4-dihydroxytoluene, corresponding with 60% of PhMe burned. The mechanism is one of hydroxylation of side-chain and nucleus. F. R. S.

Bromination of bromobenzene in the gaseous phase at high temperatures. *m*-Directing influence of the bromine atom above 450°. J. P. Wibaut, L. M. F. van de Lande, and G. Wallagh (Rec. trav. chim., 1933, 52, 794—807).—Freezing curves for *o*- and *m*-$C_6H_4Br_2$ are determined; the m.-p. curve shows that an additive *compound*, m.p. −15·9°, of 2 mols. *m*- and 1 mol. *o*- is formed. Employing the *p*–*o* curve of van der Linden (A., 1912, i, 20) as well, the % composition of a mixture of isomerides is determined to 2%. Interaction of Br (1 mol.) and PhBr (2 mols.) at 480° by a streaming technique (cf. A., 1932, 1260) affords a little 1 : 3 : 5-$C_6H_3Br_3$, but mainly $C_6H_4Br_2$. At 400°, *o*-*p*-substitution predominates, but > 450° the *m*-isomeride is the main product, the proportions of isomerides varying only slightly from 450° to 630°, so that Scheffer's suppositions (cf. A., 1926, 913) do not apply over a wide temp. range. J. L. D.

Decomposition of iodobenzene dichloride. VII. Action of solutions in various solvents on Zerevitinov's reagent. VIII. Analogy with the action of equimolecular solutions of chlorine, iodine, and iodine mono- and tri-chloride on the same reagent. E. V. Zappi and H. Degiorgi (Anal. Asoc. Quím. Argentina, 1933, 21, 12—23).—When a solution of $PhICl_2$ in a polar solvent is treated with MgMeI, only one Cl reacts. In a non-polar solvent, only about 20% of the theoretical quantity of C_2H_6 is produced. The substance is therefore [PhICl]Cl. H. F. G.

Tervalent carbon. XII. Rate of dissociation and energy of activation of hexaphenylethane. K. Ziegler, P. Orth, and K. Weber. **XIII. Chain reactions during the autoxidation of radicals.** K. Ziegler and L. Ewald. **XIV. Rates of autoxidation and decomposition of dissociable ethanes.** K. Ziegler, L. Ewald, and A. Sieb. **XV. New tautomerism of dichromenylenes.** K. Ziegler and H. Lüttringhaus (Annalen, 1933, 504, 131—161, 162—181, 182—189, 189—204; cf. A., 1930, 711, 762).—XII. The rate of absorption of NO by C_2Ph_6 in PhMe at 0° is not entirely controlled by the rate of union of CPh_3 with NO. In presence of NH_2Ph the change is strictly unimol. with NO at 1 atm. or more, but not at 0·2 atm. Similar observations are made in $CHCl_3$. Under 1 atm. the rate of the "removal" reaction exactly suffices to render NO a useful reagent. The vol. of NO absorbed exceeds 1 mol. (in presence of NH_2Ph exceeds 3 mols.), so that primary formation of $CPh_3{\cdot}NO$ is followed by one or two changes shown to be immeasurably rapid in comparison with that of radical formation. The half-period of the change in $CHCl_3$ at 0° is 3·30 min., whereas the I method indicates 2·75 min., attributed to errors in the latter process. Observations in CCl_4, $CHCl_3$, $C_2H_4Br_2$, NH_2Ph, EtOH, PhMe, $PhNO_2$, $NPhMe_2$, $CH_2Cl{\cdot}CH_2{\cdot}OH$, $CH_2(CO_2Et)_2$, $OH{\cdot}CH_2{\cdot}CH_2{\cdot}OMe$, C_5H_5N, $NAcEt_2$, $CMe_2{:}CHAc$, o-$OH{\cdot}C_6H_4{\cdot}CO_2Me$, and $CN{\cdot}CH_2{\cdot}CO_2Et$ show the rate of decomp. of C_2Ph_6 to depend relatively very little on the solvent, and a relationship between dipole moment of the medium and rate of change is not apparent. Measurements of the rate of change between —20° and 10° in $CHCl_3$ and PhMe lead to the val. 19—20±1 kg.-cal. for the energy of activation at room temp. Since the heat of dissociation of C_2Ph_6 is 10—12 kg.-cal., the compound at the moment of dissociation contains more energy than is found later in 2 mols. of normal CPh_3 and the difference may be regarded as the equiv. of a certain stabilisation of the true radical mol. primarily produced by dissociation of the ethane.

XIII. In presence of pyrogallol, CPh_3 absorbs exactly 1 mol. of O_2; the normal peroxide is not produced and the formation of $CPh_3{\cdot}O_2H$ is considered probable. A labile, primary peroxide is regarded as the carrier of chain reactions, and such a reaction is postulated for the absorption of O_2 by C_2Ph_6, which proceeds much more rapidly than accords with the dissociation of C_2Ph_6 into CPh_3. Mixtures of CPh_3 and oxidisable substances usually absorb more O_2 than both components under like conditions, as shown with NHPh·NHPh. The catalytic activity of CPh_3 is more pronounced in presence of aldehydes and unsaturated hydrocarbons, the following chain lengths varying with concn. of acceptor and radical being observed: crotonaldehyde (35), anisaldehyde (49—43), 1 : 4-dihydronaphthalene (7·5), styrene (20—16), indene (9, 51), diphenylfulvene (17, 25), dimethylfulvene (14, 35, 65). Dimethylbenzofulvene (I) is a particularly suitable acceptor without proper O_2 absorption. It appears that a "limiting chain length" exists dependent on the radical solution and hence on the concn. and also on the solvent, and therefore independent of the concn. Purification of (I) increases the chain length to 11,000 without difficulty, whilst substitution of hexahydrotoluene or CCl_4 for PhMe causes increases to 12,000—19,000 and 48,000—55,000, respectively.

XIV. The influence of pyrogallol on the absorption of O_2 in EtOBz, $CHCl_3$, and PhMe is examined in greater detail. In the case of tetraphenyldidiphenylylethane the absorption is strictly unimol. and the reaction coeff. is independent of the O_2 pressure over a certain range.

XV. The reaction between I and dichromenyls is not strictly of the first order, and the irregularities are particularly marked with di-2 : 4-diphenyl-3-benzyl-6-methylchromenyl. Since the compound absorbs O_2 abnormally in EtOBz containing pyrogallol, the irregularity is not due to an exceptional course of the changes, but is attributable to the dichromenyls. Mathematical examination of the I absorption graphs discloses the presence of a material (I) which behaves like C_2Ph_6, has a mean const. 0·0346, and a half-period of 20 min., and a substance (II) with dissociation const. 0·77 and a half-period of 0·9 min. The presence of 73% of (I) and 27% of (II) in the initial solution is calc., but the presence of a third form, not disclosed by the method of calculation, is postulated. It is not considered that chemical investigation will throw light on this type of tautomerism, but the utility of physical methods is indicated. $CH_2Ph{\cdot}CH_2{\cdot}COCl$, p-$C_6H_4Me{\cdot}OMe$, and $AlCl_3$ in CS_2 yield β-*phenylpropionyl*-p-*cresol*, m.p. 62—63°, converted by Bz_2O and PbO at 180° into 3-*benzyl*-6-*methylflavone*, m.p. 118—119°, which yields 4-*phenyl*-3-*benzyl*-6-*methylflavylium perchlorate*, decomp. 227° after softening at 218°, when treated successively with MgPhBr and $HClO_4$ and Ac_2O. H. W.

Relative stability of penta-arylethanes. II. Reactions of penta-arylethanes. W. E. Bachmann (J. Amer. Chem. Soc., 1933, 55, 3005—3010; cf. this vol., 703).—Nine compounds, $CPh_3{\cdot}CHArAr'$, dissociate when heated (usually at 85—105°) to CPh_3 and $({\cdot}CHArAr')_2$, are reduced by boiling HI–AcOH to $CHPh_3$ and CH_2ArAr', give the bromides with Br in $(CH_2Br)_2$ at 100°, are stable to 1% Na–Hg (differentiation from hexa-arylethanes), and are cleaved by Na–K. Some are stable to 40% Na–Hg. Since chemical cleavage is usually more rapid than dissociation, the effect of the five aryl groups is to weaken the C·C linking rather than break it. The order of effect is α-$C_{10}H_7$>p-C_6H_4Ph>anisyl>p-C_6H_4Me>Ph>${\cdot}C_6H_4{\cdot}C_6H_4{\cdot}$. R. S. C.

Oxidation of aromatic hydrocarbons. B. A. Buylla and J. M. Pertierra (Anal. Fís. Quím., 1933, 31, 59—64).—A yield of about 40% of phthalic anhydride is obtained by passing $C_{10}H_8$ and air over V_2O_5 on porous pot at 400—450°. o-$C_6H_4Me_2$ appears to yield the same product. R. K. C.

Constitution of some acenaphthenesulphonic acids. M. T. Bogert and R. B. Conklin (Coll. Czech. Chem. Comm., 1933, 5, 187—203).—The orientations of 3-nitroacenaphthene and its -4-sulphonic acid (B.P. 274,902; B., 1928, 293) and of acenaphthene-3-sulphonic acid are confirmed as follows. 3-Aminoacenaphthene (I) (from the product of direct nitration; cf. A., 1922, i, 1142) is converted by the diazo-reaction into *acenaphthene*-3-*sulphinic acid* (II), which is oxidised by alkaline $KMnO_4$ to the 3-sulphonic acid (III) [*Me*, m.p. 131—132°, and *Et*, m.p. 140—141° (lit. 137—139°), esters; chloride (IV), m.p. 110—111°]. (II) is more conveniently prepared by reduction of (IV) with aq. Na_2SO_3 and $NaHCO_3$. 4-Nitroacenaphthene-3-sulphonic acid (V), prepared by direct nitration of (III), is also obtained by nitration of (IV) in AcOH at 10°, reduction of the resulting 4-*nitroacenaphthene*-3-*sulphonyl chloride*, decomp. 190·3—191·3° (very rapid heating) [accompanied by the (?)5-NO_2-compound, m.p. 167·5—168·5°], to the -3-*sulphinic acid*, and oxidation of this with neutral $KMnO_4$. Other methods of conversion of the chloride into (V) or its derivatives failed. The orientation of (V) is confirmed by reduction to the 4-NH_2-compound (*Na* salt) with Zn–Cu and HCl, which gives *acenaphthenesultone*, m.p. 173°, when diazotised and boiled, and (I) when reduced in aq. solution with Na–Hg. All m.p. are corr. H. A. P.

Ring closure and radical formation. V. 9 : 10 - Tetraphenyldihydrophenanthrene and 4 : 5-dimethoxy-9 : 10-tetraphenyldihydrophenanthrene. G. WITTIG and H. PETRI (Annalen, 1933, **505**, 17—41).—Me_2 diphenate is converted by LiPh in Et_2O into *oo*′-di(diphenylhydroxymethyl)diphenyl (I), m.p. 252—253°, transformed by K in boiling dioxan into the *K* compound, which with MeI affords the *Me_1 ether* (II), m.p. 209·5—211°. (II) and K phenyl*iso*propyl give *oo*′-*di*(*diphenylmethoxymethyl*)*diphenyl* (III), m.p. 186—187·5°, converted by successive treatment with HCl in AcOH and NaOH into 9 : 9-diphenyl-5-diphenylhydroxymethylfluorene, m.p. 256°, whence 9 : 9-diphenyl-5-benzhydrylfluorene (IV), m.p. 219·5—221°. (I) is converted by HCl in hot C_6H_6 into the corresponding *anhydride*, m.p. 291—292°, also obtained from (III) and conc. H_2SO_4 and converted by K–Na in dioxan into *o*-*benzhydryl*-*o*′-*diphenylhydroxymethyldiphenyl*, m.p. 242—243°, whence (IV) by HCl in boiling AcOH. (III) is transformed by the successive action of K–Na and MeOH into *oo*′-dibenzhydryldiphenyl (V), m.p. 238—239·5°. Treatment of (III) with K–Na in dioxan followed by tetramethylethylene dibromide leads to 9 : 10-*tetraphenyldihydrophenanthrene* (VI), m.p. 339·5—341°, which resembles CPh_3 in its ready addition of K or Na [whence (V)], but is analogous to C_2Ph_4 in that it is indifferent to Br or O_2 and is converted by SO_2Cl_2 containing AcOH into *oo*′-*di*(*diphenylchloromethyl*)*diphenyl*, which passes into 9 : 9-*diphenyl*-5-*diphenylchloromethylfluorene*.

In the hope of forcing radical dissociation, compounds with substituents in the free *o*-positions of the Ph·Ph residue are investigated. *r*-*oo*′-Dimethoxydiphenic acid is converted into 2 : 2′-dimethoxy-6 : 6′ - di(diphenylhydroxymethyl)diphenyl, which, with K in dioxan, gives the K_1 compound, transformed by MeI into the *Me_1 ether* (VII), m.p. 256—257·5°. Successive action of K phenyl*iso*propyl in dioxan and MeI on (VII) yields the *Me_2 ether* (VIII), m.p. 206·5—208°, transformed by K–Na and MeOH into 2 : 2′-*dimethoxy*-6 : 6′-*dibenzhydryldiphenyl* (IX), m.p. 204·5—205·5° (*K* derivative). (VIII) treated successively with Na–K and $C_2Me_4Br_2$ gives 4 : 5-*dimethoxy*-9 : 10 - *tetraphenyldihydrophenanthrene* (X), m.p. 231·5—232°, transformed by Na–K and subsequent alcoholysis into (IX). Since (X) is stable to Br, is colourless, and shows no tendency to radical dissociation in solution, the introduction of OMe appears to cause no change in the union of the radical C atoms.

The possibility that (X) is a racemate is examined as follows. (—)-2 : 2′-Dimethoxydiphenic acid, m.p. 293·5—294·5°, $[\alpha]_D^{20}$ —116° in anhyd. $COMe_2$, is converted by CH_2N_2 into the *Me_2* ester (XI), m.p. 101—102°, $[\alpha]_D^{23}$ —160° in $COMe_2$, the racemisation consts. of which are determined in PhCl at 100° and 118·5°. (XI) is transformed into (—)-2 : 2′-*dimethoxy*-6 : 6′-*di*(*diphenylhydroxymethyl*)*diphenyl* (XII), m.p. 284°, $[\alpha]_D^{23}$ —220° in $CHCl_3$ [*anhydride* (XIII), m.p. 242·5—243°, $[\alpha]_D^{20}$ —393° in $CHCl_3$, completely racemised when heated at 315°]. (XII) is converted into its *Me_1 ether* (XIV), m.p. 238—239°, $[\alpha]_D^{23}$ —157° in $CHCl_3$, converted by HCl in C_6H_6 into (XIII), whilst the *Me_2 ether* (XV), m.p. 218—220°, $[\alpha]_D^{20}$ —150° in $CHCl_3$ [converted by conc. H_2SO_4 into (XIII)], is derived from (XII) or (XIV). (XV) with Na–K followed by MeOH gives (—)-2 : 2′-*dimethoxy*-6 : 6′-*dibenzhydryldiphenyl*, m.p. 170—170·5°, $[\alpha]_D^{20}$ —298° in $CHCl_3$, whereas the 4 : 5-dimethoxy-9 : 10-tetraphenyldihydrophenanthrene obtained from it is optically inactive. It cannot therefore be decided whether the dihydrophenanthrene derivative is plane or asymmetric in structure. H. W.

Polycyclic compounds. I. Synthesis of perylene and its mechanism. II. Four new methods of preparing perylene and their mechanisms. III. Constitution of α- and β-tetradecahydroperylenes formed by the hydrogenation of perylene under high pressure. S. UCHIDA and S. TAKATA (J. Soc. Chem. Ind. Japan, 1933, **36**, 222B, 223—224B, 224—226B).—I. A mechanism for the synthesis of perylene (I) from di-β-naphthol (II) is suggested.

II. (II) heated with H_3PO_3, H_3PO_4, $H_4P_2O_7$, or Japanese acid clay, or 2-$C_{10}H_7Cl$ (from β-$C_{10}H_7$·OH and PCl_5) heated with acid clay gives (I). Mechanisms are suggested.

III. Treatment of (I) with Pd and H_2 in decahydronaphthalene at 150° under pressure gives α-*tetradecahydroperylene*, m.p. 180—181·5° (and a little of a *substance*, m.p. 170—171·3°), a β-*isomeride*, m.p. 161—162°, being formed under similar conditions at 82°. Constitutions are suggested for these. A. A. L.

Diphenylguanidine. K. SHIMADA and T. KIMISHIMA (J. Soc. Chem. Ind. Japan, 1933, **36**, 210—211B).—Thiocarbanilide with $PbSO_4$ in EtOH–NH_3 gives pure diphenylguanidine (yield 94%). PbO, $PbCO_3$, $Pb(OAc)_2$, $Pb(NO_3)_2$, ZnO, $ZnCl_2$, HgO, and $HgCl_2$ are less effective. A. A. L.

Synthetic menthol. II. Synthesis of 2-nitro-*p*-cymene, and properties of its derivatives. H. INOUE and H. HORIGUCHI (J. Soc. Chem. Ind. Japan, 1933, **36**, 189—190B).—Improved preps. are given for 2-nitro-, b.p. 129—132°/15 mm., 2-amino-, b.p. 116—119°/15 mm. (Bz derivative, m.p. 100°; Ac derivative, m.p. 71°; benzenesulphonamide, m.p. 151°), chloronitro-, b.p. 146—148°/15 mm., and chloroamino-*p*-cymene, b.p. 156—157°/15 mm. (Bz deriv-

ative, m.p. 134°; azo-β-naphthol derivative, m.p. 162°). The last is converted into α-chlorocymene. Physical consts. of the above compounds are recorded.
A. A. L.

Four dinitrodimethyl-*p*-anisidines. H. H. Hodgson and J. H. Crook (J.C.S., 1933, 825—827).—Nitration of 3-nitrodimethyl-*p*-anisidine gives 2 : 3-, m.p. 130° [the corresponding $(NH_2)_2$-derivative condensing with benzil to *5-dimethylamino-8-methoxy-2 : 3-diphenylquinoxaline*, m.p. 233° (decomp.)], and *2 : 5-dinitrodimethyl-*p*-anisidine*, m.p. 137°, also obtained by nitration of the $2\text{-}NO_2$-compound. Dimethyl-*p*-anisidine is nitrated in H_2SO_4 and HNO_3 to the 2 : 6-$(NO_2)_2$-derivative, m.p. 151°, and in aq. H_2SO_4 and HNO_3 to a mixture of the 3 : 5-$(NO_2)_2$-derivative (I), m.p. 90°, and *3 : 5-dinitro-N-nitrosomethyl-*p*-anisidine*, m.p. 113°, which with $CO(NH_2)_2$ and H_2SO_4 forms *3 : 5-dinitromonomethyl-*p*-anisidine*, m.p. 130°. 3 : 5-Dinitro-*p*-toluenesulphonyl-*p*-anisidine after hydrolysis is converted (Sandmeyer) into *4-chloro-3 : 5-dinitroanisole*, m.p. 123°, which gives (I) with $NHMe_2$.
F. R. S.

Nitration of *o*- and *p*-aminodiphenyl derivatives. M. H. Werther (Rec. trav. chim., 1933, 52, 657—677).—Interaction of *p*-aminodiphenyl (I) and EtNCO in C_6H_6 affords *N-4-diphenylyl-N′-ethylcarbamide* (II), m.p. 208°, decomp. 290° into $(CO\cdot NHEt)_2$, and *s*-di-(4-diphenylyl)carbamide. (I) with $ClCO_2Me$ in boiling C_6H_6 containing Na_2CO_3 affords *Me diphenyl-4-carbamate* (III), m.p. 124°. (II) and abs. HNO_3 at 0° afford *N-4-(3 : 5 : 4′-trinitrodiphenylyl)-N′N′-ethylnitrocarbamide*, which is converted by boiling H_2O into *3 : 5 : 4′-trinitro-4-aminodiphenyl* (IV), m.p. 280° (*Ac* derivative, m.p. 212°), whereas boiling MeOH or EtOH affords *Me* (V), m.p. 184°, and *Et 3 : 5 : 4′-trinitrodiphenyl-4-carbamate* (VI), m.p. 180°, respectively, both of which are converted by EtOH–NH_3 into (IV). (III) and its Et analogue with abs. HNO_3 at 0° afford *Me*, m.p. 189°, and *Et 3 : 5 : 2′ : 4′-tetranitrodiphenyl-4-carbamate* (VII), m.p. 149°, respectively [also formed from (V) and (VI) with abs. HNO_3 at 0°], hydrolysed by EtOH–NH_3 to *3 : 5 : 2′ : 4′-tetranitro-4-aminodiphenyl* (VIII), m.p. 253°. 4-Bromo-3 : 2′ : 4′-trinitrodiphenyl when heated with NH_2Me in EtOH under pressure at 100° for 10 hr. affords *3 : 2′ : 4′-trinitro-4-methylaminodiphenyl* (IX), m.p. 227° (*Ac* derivative, m.p. 197°) [whereas EtOH–NH_3 affords no 3 : 2′ : 4′-trinitro-4-aminodiphenyl (*Ac* derivative, m.p. 203°)], converted by abs. HNO_3 at 0° into *3 : 5 : 2′ : 4′-tetranitro-4-methylnitroaminodiphenyl*, m.p. 172°, which with EtOH–NH_3 under pressure yields (VIII), also formed from (VII) and EtOH–NH_3. (IX) affords a 5-*Br*-derivative, m.p. 218°, whereas (IV) and (VIII) cannot be brominated similarly. The orientation of (VII) is thereby established. Reduction of 4 : 4′-dinitrodiphenyl (A., 1930, 762) affords a *by-product*, m.p. 235°, and 4-amino-4′-nitrodiphenyl, which reacts with EtNCO in C_6H_6 under pressure to give *N-4-(4′-nitrodiphenylyl)-N′-ethylcarbamide*, m.p. 248°, the NO_2-derivative of which is hydrolysed to (IV), thus establishing the orientation of (IV), (VII), and (VIII). 2-Aminodiphenyl with EtNCO in warm Et_2O during 0·5 hr. affords *N-2-diphenylyl-N′-ethylcarbamide* (X), m.p. 118°, and with $ClCO_2Me$ (or Et) in C_6H_6 containing Na_2CO_3 affords *Me* (XI), m.p. 50°, and Et diphenyl-2-carbamate (XII), b.p. 198—211° (cf. A., 1896, i, 483), respectively. (X) with excess abs. HNO_3 affords a NO_2-derivative, converted by boiling H_2O into *3 : 5 : 4′-trinitro-2-aminodiphenyl* (XIII), m.p. 227°, and by boiling MeOH or EtOH into *Me*, m.p. 77°, and *Et 3 : 5 : 4′-trinitrodiphenyl-2-carbamate*, m.p. 65°, respectively. Both urethanes are formed by nitration of (XI) and (XII), respectively, and either with EtOH–NH_3 under pressure affords (XIII). Decomp. of the diazonium derivative of (XIII) affords *3 : 5 : 4′-trinitrodiphenyl*, m.p. 170°, also obtained from the diazonium derivative of (IV). This orients the NO_2-groups in (XIII). Benzidine and EtNCO in boiling Et_2O during 6 hr. affords *4 : 4′-diethylureidodiphenyl* (XIV), decomp. at 240°, decomposed by heat into $(CO\cdot NHEt)_2$ and carbonylobenzidine. Nitration of (XIV) affords only resinous products.
J. L. D.

Mechanism of Hofmann, Curtius, and diazo-reactions. F. Bell (Chem. and Ind., 1933, 584).—An amine with the same direction of rotation is obtained from optically active 6-nitro-2-methyldiphenyl-2′-carboxylic acid by the Hofmann or Curtius reaction. The time of existence of the free radicals, therefore, is much < that of mutual rotation of the nuclei.
H. A. P.

Proof of the unsymmetrical structure of the azoxy-group. T. T. Chu and C. S. Marvel (J. Amer. Chem. Soc., 1933, 55, 2841—2850).—The compound described as 2 : 2′-azoxydiphenylethylmethane-4 : 4′-dicarboxylic acid (A., 1930, 774) is multimol. *dl*-α-Phenylbutyric acid (I) (modified prep. from the amide) gives the p-*NO_2-acid*, m.p. 118—120°, which affords a mixture of dl- (II) and meso- (III) -α-p-*azophenylbutyric acids*, $(:N\cdot C_6H_4\cdot CHEt\cdot CO_2H)_2$, m.p. 197—199° (decomp.) and 211—212° (decomp.), respectively. (I) is resolved into the d- and l-*acids*, m.p. 120—122°, $[\alpha]_D^{25}$ ±17·7° in EtOAc (*quinine* salts, m.p. 183—185° and 180—182°, $[\alpha]_D^{20}$ −42·2° and $[\alpha]_D^{25}$ −53·8° in C_5H_5N, respectively). These acids afford dl-, d-, and l-α-p-*aminophenylbutyric acids* (IV), m.p. 142—143° and 138—140°, $[\alpha]_D^{25}$ ±12·3° in EtOH, respectively, dl-α-p-*hydroxylaminophenylbutyric acid* (V), double m.p. 112—113° (decomp.) and 166—168°, the corresponding d-*acid*, $[\alpha]_D^{25}$ +38° in EtOH, and dl-α-p-*nitrosophenylbutyric acid* (VI), m.p. 182—186° (decomp.) (crude d-*acid* has $[\alpha]_D^{25}$ +42·1° in EtOH), also obtained by oxidation of (V). (VI) and (IV) give (III), which is irresolvable (*strychnine* salt, m.p. 148—150°, $[\alpha]_D^{25}$ −83·5°), but is oxidised by H_2O_2 to dl-α-p-*azoxyphenylbutyric acid*, m.p. 199—201°, resolved by *d*-$CHPhMe\cdot NH_2$ into the d-(*$CHPhMe\cdot NH_2$* salt, m.p. 192—196°, $[\alpha]_D^{25}$ +9·7° in MeOH) and l-*acids*, m.p. 206—208°, $[\alpha]_D^{25}$ +14·7° and −13·3° in MeOH. The fact that the *meso*-azo-compound gives a *dl*-azoxy-compound proves the asymmetric nature of the N_2O group. (II) is resolved by strychnine into d- and l-*azophenylbutyric acids*, m.p. 195—196° (decomp.), $[\alpha]_D^{25}$ +52·6° and −42·2° in EtOH, respectively (*strychnine* salts, m.p. 197—199° and 140—146° after softening at 130°, $[\alpha]_D^{25}$ −79·6° and −94·7° in C_5H_5N, respectively).

(II) with H_2O_2 gives a second dl-α-p-*azoxyphenylbutyric acid*, m.p. 178—180°, resolved into the d- and l-*acids*, m.p. 182—184°, $[\alpha]_D^{25}$ ±3·8° in MeOH (d-*CHPhMe·NH₂* salts, m.p. 204—206° and 201—203°, $[\alpha]_D^{25}$ +7·8° and +5·5° in MeOH, respectively).
R. S. C.

Colour and constitution from viewpoint of recent electronic theory. VI. H. H. Hodgson (J. Soc. Dyers and Col., 1933, **49**, 213—216; cf. A., 1931, 835).—Electronic explanations are offered of the substantivity (or otherwise) of benzidine derivatives, the possibility of successive coupling with the two diazonium groups in $(\cdot C_6H_4\cdot N_2X)_2$, etc., the coupling of diazonium salts with $NHPh_2$, but not with α-$C_{10}H_7\cdot NH_2$, in suspension in mineral acid, the replacement of Br by H in 4-bromo-3 : 5-dinitrobenzaldehyde, the ease of dinitration of the *p*-$C_6H_4Me\cdot SO_2\cdot$ derivatives of α-$C_{10}H_7\cdot NH_2$ and 3 : 5 : 4-$C_6H_2Me(NO_2)_2\cdot NH_2$, the separation of *m*- and *p*-xylidines by Limpach's method (cf. J.C.S., 1900, **77**, 65), and bromination of phenols in aq. as contrasted with inert solvents. It is suggested that benzidine dyes are substantive to cotton only when the two C_6 nuclei are co-planar. H. A. P.

Azo-chromophore. V. J. S. P. Blumberger (Chem. Weekblad, 1933, **30**, 538—547).—The powerful bathochromic effect of the co-ordinated *o*-hydroxy-azo-group is termed "chromophoric inversion." Usually a *p*-hydroxymonoazo-dye shows a bathochromic colour change with OH′, but with *o*-hydroxymonoazo-dyes the colour change may be absent or hypsochromic (fifty-four examples are quoted). Parallel effects are observed with aminomonoazo-dyes and H˙ (forty examples quoted), the influence of various substituents being similar in the two cases. The colour changes are satisfactorily explained on the simple electronic views developed previously (cf. A., 1932, 1243; 1927, 142). The NHNa group is suggested as a new auxochrome. It is unnecessary to assume a quinonoid structure for either type of dye. The azo-chromophore is considered to be mainly responsible for absorption in the visible part of the spectrum, the ethylenic linking contributing very little to this effect. Eighty-one absorption curves for mono-azo-dyes are illustrated. S. C.

Constitution of acyl derivatives of *o*-hydroxy-azo-compounds. A. Burawoy and I. Markowitsch (Annalen, 1933, **504**, 71—80).—The azoid structure of the compound obtained by benzoylation of β-naphthaquinone-1-phenylhydrazone follows from the difference of its absorption spectrum from that of the quinonoid lactam of β-naphthaquinone-1-phenylhydrazone-8-carboxylic acid and its close similarity to that of 1-benzeneazo-β-naphthyl Me ether. Similarly, the absorption of the benzoate of β-naphthaquinone-2-phenylhydrazone (by benzoylation of the parent material or from β-naphthaquinone and $NH_2\cdot NPhBz$) resembles that of 2-benzeneazo-α-naphthyl Me ether and differs from that of the parent, so that the derivative is azoid. The benzoate of *o*-hydroxyazobenzene resembles *o*-ethoxyazobenzene and differs from the parent compound. Contrary to Tuck, the benzoate of benzeneazo-*p*-cresol is azoid, thus differing from the parent material. H. W.

Preparation of azo-dyes from brominated β-naphthol. V. Veselý and F. Šturša (Chem. Listy, 1933, **27**, 126—128).—1 : 6-Dibromo-β-naphthol combines with diazotised *p*-$NO_2\cdot C_6H_4\cdot NH_2$ to yield 6-*bromo*-1-(4′-*nitrobenzeneazo*)-β-*naphthol*, m.p. 272°, identical with the product obtained from 6-bromo-β-naphthol. Similarly, both 1 : 4 : 6-tribromo- and 4 : 6-dibromo-β-naphthol yield 4 : 6-*dibromo*-1-(4′-*nitrobenzeneazo*)-β-*naphthol*, m.p. 221—222°. R. T.

Diethyl azobenzoate. G. Lock (J. pr. Chem., 1933, [ii], **138**, 51—54).—*o*-$C_6H_4Me\cdot NO_2$ and $SnCl_2$ give *o*-azoxytoluene, m.p. 59° (cf. A., 1911, i, 932), oxidised by $KMnO_4$ to *o*-azoxybenzoic acid (Et_2 ester, m.p. 77·5°), which is reduced by Zn dust and aq. NH_3 to the hydrazo-compound. This is oxidised by $AgNO_3$ to *o*-azobenzoic acid (Et_2 ester, m.p. 85°), also (better) obtained from *o*-$NO_2\cdot C_6H_4\cdot CHO$ or *o*-$NO_2\cdot C_6H_4\cdot CH_2\cdot OH$. *o*-Azotoluene is volatile in steam. R. S. C.

Mechanism of the oxidation of primary hydrazines. I. Reaction of primary aromatic hydrazines with salts of heavy metals. O. A. Seide, S. M. Scherlin, and G. J. Bras (J. pr. Chem., 1933, [ii], **138**, 55—68).—$NHPh\cdot NH_2$ (I) with $FeCl_3$ gives PhCl (62%), with $FeBr_3$ PhBr (50%), with $Fe(CNS)_3$ Ph_2S_2, and with $K_3Fe(CN)_6$ PhCN (10%) and Ph_2. These reactions are considered to proceed by way of the *syn*-diazonium salts. The oxidation of (I) by $Hg(OAc)_2$ to $HgPh_2$ is believed to take place by way of $NHPh\cdot NH\cdot Hg\cdot OAc$, which is oxidised to *syn*-benzenediazonium mercuriacetate; this decomposes in absence of Cu into C_6H_6, N_2, and $OH\cdot Hg\cdot OAc$, but in presence of Cu into phenylmercuriacetate (II). In conformity with this view, $Hg(OAc)_2$, $Cu(OAc)_2$, and dil. AcOH and the appropriate hydrazine give (II), m.p. 146—147°, p-*nitro*-, m.p. 202—203·5°, and p-*bromo-phenylmercuriacetate*, m.p. 194—195°, in 70, 42, and 87% yield, respectively. However, α-quinolylhydrazine (III) gives carbostyril (IV) by this reaction. (II) in hot dil. AcOH gives N_2, Hg, and $HgPh_2$, but the yield is increased by the presence of Cu, which proves the existence of an equilibrium $2HgPh\cdot OAc \rightleftharpoons HgPh_2+Hg(OAc)_2$. (I), aq. $Cu(OAc)_2$, and (III) give (IV) and $HgPh_2$. R. S. C.

Constitution of tribromophenol bromide and analogous compounds. J. Ssuknewitsch and S. Budnitzki (J. pr. Chem., 1933, [ii], **138**, 18—22).—4-Chloro-1 : 6-dibromophenol (I) and Br-H_2O give 4-*chloro*-2 : 6-*dibromophenyl hypobromite* (II), $C_6H_2ClBr_2\cdot OBr$, m.p. 94° (decomp.), which (*a*) with NH_2Ph in $CHCl_3$ gives (I) and 2 : 4 : 6-tribromoaniline, and (*b*) with hot EtOH affords (I), HBr, and paracetaldehyde. 2 : 4 : 6-Tribromophenol (III) and aq. Cl_2 give 2 : 4 : 6-*tribromophenyl hypochlorite* (IV), $C_6H_2Br_3\cdot OCl$, m.p. 115—116°, which affords similarly (*a*) (III) and 2 : 4 : 6-trichloroaniline, and (*b*) (III), Cl_2, and only traces of Br. The given structures of (II) and (IV) are proved by these differences, which refute the usually accepted (quinonoid) formula common to both substances. R. S. C.

Decomposition of iodophenols. G. H. Woollett, F. W. Vaughan, M. L. Burks, and C. O. Hinton (J. Amer. Chem. Soc., 1933, **55**, 2909—2911).—Guaiacol, I–aq. KI, and aq. NH_3 give *di-iodo-*

guaiacol, m.p. 92·4°, and resorcinol Me ether gives the I_3-compound, m.p. 123°. The Na salts of these substances and of di-iodo-*o*- and -*m*-cresol with aq. NaOH or Na_2CO_3 give red, amorphous, multimol. *compounds*, corresponding in composition to loss of 1 mol. of NaI per mol. The Na salt of di-iodo-*p*-cresol loses only a part of its NaI. Quinol Me ether is only partly iodinated under similar conditions. R. S. C.

Halogen derivatives of dehydro-β-naphthol 1-disulphide. J. A. C. McClelland and S. Smiles (J.C.S., 1933, 786—788).—Bromination of β-naphthol 1-disulphide gives 6 : 6′-*dibromo*-β-*naphthol* 1-*disulphide*, m.p. 174°, oxidised by Br and AcOH to the corresponding *dehydro*-derivative, m.p. 190°. 6-*Bromo*-2-*naphthylene* 1-*thiolcarbonate*, m.p. 167°, 3 : 3′-*dibromo*-, m.p. 176°, and its *dehydro*-derivative, m.p. 184—185°, and 3 : 3′ : 6 : 6′-*tetrabromo*-β-*naphthol* 1-*disulphide*, m.p. 221°, and its *dehydro*-derivative, m.p. 189°, are similarly obtained. F. R. S.

Laccol. G. Bertrand and G. Brooks (Bull. Soc. chim., 1933, [iv], 53, 432—443; cf. A., 1932, 943).—Laccol, b.p. about 220°/low vac. (decomp. at b.p., 280—290°/10—15 mm.) (*Ac_2* derivative, b.p. 240—250°/0·5 mm.), gives tetrahydrolaccol, b.p. 265—275°/8—10 mm., m.p. 62·6° (*Pb* salt), best purified by the Ac_2, m.p. 58·7°, or dipropionyl derivative, m.p. 34·8°. R. S. C.

Action of nitrous acid on pyrocatechol-4-sulphonic acid. J. Frejka and J. Zika (Coll. Czech. Chem. Comm., 1933, 5, 253—262).—The action of excess of HNO_2 on pyrocatechol-4-sulphonic acid (*Ba*, *Na*, and *K* salts) gives 3 : 5-*dinitroso*- [*Na_2 H* (+1·5H_2O), *K_2 H*, *Ba H* (+1·5H_2O), *Sr H* (+1·5H_2O), *Ca H* (+3H_2O), and *Ag_2 H* salts], reduced by Fe and HCl to 3 : 5-*diamino-pyrocatechol*-4-*sulphonic acid* [*dihydrochloride*; *dipicrate* (+5H_2O), decomp. 148—150°; *Ac_4* derivative]. This cannot be isolated in a pure state, since it is readily oxidised by air or by $FeCl_3$ in aq. solution to 3 : 5-*diamino*-o-*benzoquinone*-4-*sulphonic acid*. H. A. P.

Separation of two desmotropic forms of some polyhydric phenols derived from naphthalene. A. Madinaveitia and E. Olay (Anal. Fis. Quím., 1933, 31, 134—138).—Using Meyer's method of fusion and extraction of the cooled, pasty melt with $CHCl_3$, the following ketonic (β-)forms have been separated and the phenylsemicarbazones prepared (m.p. in parentheses): β-*dihydro*-2-*methyljuglone* (β-*dihydroplumbagin*), m.p. 86° (232°); β-1 : 4-*dihydroxy*-2-*methylnaphthalene*, m.p. 60° (260°) (diphenylsemicarbazide yields a *product*, m.p. 260°); β-1 : 4-*dihydroxynaphthalene*, m.p. 99° (250°) (*oxime*, m.p. 220°, darkens at 190°). Reversion to the α-form results on dissolution in NaOH containing stannite and repptn. by HCl. R. K. C.

Direct halogenation of arylaliphatic alcohols. (Mlle.) D. Sontag (Compt. rend., 1933, 197, 159—161; cf. this vol., 501).—γ-Phenylpropyl alcohol (*benzoate*, b.p. 207°/20 mm.) is brominated (in Ph group) to the *Br*-compound, b.p. 157—158°/14 mm. (*acetate*, b.p. 168—170°/17 mm.; *bromide*, b.p. 161—163°/17 mm.), and is chlorinated to a mixture of alcohols, difficult to separate [γ-*chlorophenylpropyl alcohol*, b.p. 149—150°/18 mm. (*benzoate*, b.p. 163—165°/2 mm.)]. F. R. S.

Cholesterol. XVI. I. Montignie (Bull. Soc. chim., 1933, [iv], 53, 370—372; cf. A., 1932, 381).—Cholesterol gives a *gynocardate*, m.p. 110—112° (*Br_4*-derivative, m.p. 77—78°), and *bromoacetate*, m.p. 117—118°. R. S. C.

Synthesis in sterol and sexual hormone series. W. Schlenk, O. Bergmann, and E. Bergmann (J.S.C.I., 1933, 52, 209—210T).—An attempt to prepare the hydrocarbon $C_{17}H_{14}$ (? or $C_{18}H_{16}$), previously obtained by dehydrogenation of cholesteryl chloride or cholic acid, by dehydrogenation with Se of 1-*allyl*-3 : 4-*dihydrophenanthrene* (I), m.p. 129—130·5°, gave 1 : 2-*cyclo*pentenophenanthrene (?) (cf. this vol., 710), m.p. 118—120·5° (picrate, m.p. 134—136°). α-$C_{10}H_7$·MgBr and CH_2Cl·CH_2·OH in presence of MgEtBr give β-1-*naphthylethyl alcohol*, m.p. 61°, b.p. 174—176°/14 mm., converted by $SOCl_2$ into its *chloride*, b.p. 165—166°/16 mm., which with $CHNa(CO_2Et)_2$ gives *Et* γ-1-*naphthylpropane*-αα-*dicarboxylate*, b.p. 234—236°/15 mm.; the corresponding free *acid*, m.p. 150—150·5°, is readily decarboxylated by heat to γ-1-naphthylbutyric acid. Interaction of 1-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene with Mg allyl bromide gives 1-*hydroxy*-1-*allyl*-1 : 2 : 3 : 4-*tetrahydrophenanthrene*, m.p. 102—104°, dehydrated by 85% H_2SO_4 at 100° to (I). The crude dehydration product with Se at 300—340° gives a further *hydrocarbon*, $C_{17}H_{14}$, m.p. 164—168° (clear and mobile at 205—207°), b.p. 178—183°/0·1—0·3 mm. H. A. P.

β-Ergostenol. II. F. W. Heyl, M. C. Hart, and H. Emerson (J. Amer. Chem. Soc., 1933, 55, 2870—2871; cf. A., 1932, 511).—β-Ergostenol gives a *propionate*, m.p. 110°, *phthalate*, m.p. 152—154°, *benzoate*, m.p. 158°, (22·5°), p- and m-*nitro*- and 3 : 5-*dinitro-benzoate*, m.p. 180°, 148°, and 164° (25·0°, 21·5°, and 15·0°), respectively, and a *phenylurethane*, m.p. 146—147° (16·1°), the figures in parentheses being $[\alpha]_{5461}$. α-*Ergostenol* 3 : 5-*dinitrobenzoate* and *phthalate* have m.p. 197° (−2·8°) and 185° (1·45°), respectively. R. S. C.

Increase in reaction velocity of tertiary acids by the presence of a carbonyl group in the γ-position. H. Appel.—See this vol., 911.

Racemisation of chaulmoogric and hydnocarpic acids. W. S. Hinegardner (J. Amer. Chem. Soc., 1933, 55, 2831—2834).—*d*-Chaulmoogramide (I), $[\alpha]_D^{25}$ +57·1°, when distilled with P_2O_5 at 3—4 mm., gives dl-*chaulmoogronitrile*, b.p. 155—158°/2·5 mm., hydrolysed to dl-*chaulmoogric acid*, m.p. 68·5° (dl-*amide*, m.p. 105—106°). The *dl*-amide and -acid do not depress the m.p. of the *d*-compounds. (I) and $SOCl_2$ in C_6H_6 give d-*chaulmoogronitrile*, $[\alpha]_D^{25}$ +55·2° in $CHCl_3$, hydrolysed to the *d*-acid (II), $[\alpha]_D^{25}$ +61·4° in $CHCl_3$, and racemised by distillation with P_2O_5. (II) is not racemised by PCl_3 or $POCl_3$ at 100° or PCl_5 at 150°, and is decomposed by distillation with P_2O_5 in vac. *d*-Hydrocarpamide, $[\alpha]_D^{25}$ +69·4°, gives similarly the dl-*nitrile*, b.p. 155—156°/2—3 mm., hydrolysed to the dl-*acid*, m.p. 58·5—59°, alone or mixed with the *d*-acid. R. S. C.

Alkyl and alkylamine esters of *p*-aminothiobenzoic acid and related compounds. H. L. Hansen and L. S. Fosdick (J. Amer. Chem. Soc., 1933, **55**, 2872—2874).—*p*-Nitrothiobenzoic acid (modified prep.) affords the *Me*, m.p. 96—97°, *Et*, m.p. 67—68°, *Pr*, m.p. 30—31°, *Bu*, m.p. 13—15°, and β-*chloroethyl*, m.p. 91—92°, esters, whence were obtained *Me*, m.p. 113—114°, *Et*, m.p. 79—79·5°, *Pr*, m.p. 60—61°, *Bu*, m.p. 37—38°, β-*chloroethyl*, m.p. 99—101°, and p-β-*diethylaminoethyl*, m.p. 52—52·5° (*hydrochloride*, m.p. 177·6—178°) p-*aminothiobenzoate*. These compounds have strong anæsthetic properties, the last-named (thiocaine) being very rapid in action and having a low toxicity. R. S. C.

Preparation of some alkyl-substituted phenylacetonitriles in liquid ammonia. L. H. Baldinger and J. A. Nieuwland (J. Amer. Chem. Soc., 1933, **55**, 2851—2853).—Na and $CH_2Ph\cdot CN$ in liquid NH_3 give the Na derivative, which with alkyl halides (best, chlorides) give 35—50% yields of α-*phenyl*-n-*propio*-, b.p. 118—120°/19 mm., -n-*butyro*-, b.p. 126—129°/19 mm., -n-*valero*-, b.p. 120—123°/7 mm., -n-*hexo*-, b.p. 152—155°/20 mm., and -n-*heptonitrile*, b.p. 165—168°/22·5 mm. Some PhMe is also formed. R. S. C.

Stereoisomeric phenylmethylethyl and phenylmethylpropyl betaines. (Mme.) Guaisnet-Pilaud (Compt. rend., 1933, **197**, 156—157).—The betaine monohydrate from Et phenylmethylethyliodoaminoacetate (cf. this vol., 387) when heated gives *Et phenylmethylaminoacetate*, b.p. 137—138°/14 mm. (with NH_3, *phenylmethylaminoacetamide*, m.p. 162°, formed), and the dihydrate yields *Me phenylethylaminoacetate*, b.p. 147—148°/15 mm. (*phenylethylaminoacetamide*, m.p. 108°). Ag_2O and methylpropylaniline iodoacetate afford a *monohydrate*, m.p. 172°, and a *dihydrate*, m.p. 81·5°, with elimination of I, which give similar results when heated. F. R. S.

Synthesis of α-naphthylacetic acid. DeW. T. Keach (J. Amer. Chem. Soc., 1933, **55**, 2974—2975).—1-Allylnaphthalene and $KMnO_4$ in EtOH–H_2O give a 43% yield of α-naphthylacetic acid, m.p. 106° (lit. 131°), and a little αβ-*dihydroxy*-γ-1-*naphthylpropane*, m.p. 110°. R. S. C.

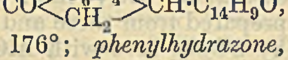
Synthesis of some alkylphenanthrenes and alkylphenanthrene-10-carboxylic acids by the Pschorr reaction. M. G. Bogert and G. S. Stamatoff (Rec. trav. chim., 1933, **52**, 584—592).—Interaction of *p*-ethyl-, 2 : 4-dimethyl-, and 2-methyl-5-*iso*propyl-benzyl chloride (A., 1923, i, 549) with KCN in boiling EtOH–H_2O affords p-*ethyl*- (I), b.p. 123·5—125·5°/12 mm. (hydrolysed to the *acid*, m.p. 88·5—89·5°), 2 : 4-*dimethyl*- (II), b.p. 140°/11 mm., and 2-*methyl*-5-iso*propyl-phenylacetonitrile* (III), b.p. 144°/14 mm., respectively. The *K* salts of the acids from (I), (II), and (III) with *o*-$NO_2\cdot C_6H_4\cdot CHO$ and Ac_2O during many hr. at 100° afford α-(p-*ethylphenyl*)-, m.p. 172·8—173·2°, α-(2 : 4-*dimethylphenyl*)-, m.p. 187—188°, and α-(2-*methyl*-5-iso*propylphenyl*)-o-*nitrocinnamic acid*, m.p. 183—184°, respectively, reduced by boiling aq. $FeSO_4$–NH_3 to *NH_2*-compounds, m.p. 200—201° (IV) (*Ac* derivative, m.p. 256—257°), 217·5—218° (V) (*hydrochloride*), and a tar (VI) which cannot be purified, respectively. (IV), (V), and (VI) in HCl at 0° with amyl nitrite, followed by Cu powder, afford 3-*ethyl*-, m.p. 195—196° (*picrate*, m.p. 166—167°), 1 : 3-*dimethyl*-, m.p. 188—189°, and 1-*methyl*-4-iso*propyl-phenanthrene*-10-*carboxylic acid*, m.p. 201—202°, respectively, which are decarboxylated to 3-*ethyl*-, an oil (*picrate*, m.p. 119·5—120·5°; *quinone*, m.p. 168·2—169°), 1 : 3-*dimethyl*-, m.p. 76—77° (*picrate*, m.p. 153—155°; *quinone*, m.p. 218—219°), and 1-*methyl*-4-iso*propyl-phenanthrene*, m.p. 68—68·5° (*picrate*, m.p. 113·6—114·1°), which is different from retene. J. L. D.

Phenolic acids. III. Esters of aspirin. P. P. T. Sah, T. S. Ma, and H. H. Lei (Sci. Rep. Nat. Tsing Hua Univ., 1933, **2**, 13—17).—*Ac* derivatives of the following salicylates are described: Me, m.p. 48—49°, Et, b.p. 155—158°/15 mm., 281—283°/760 mm., Pr^{α}, b.p. 162—164°/10 mm., 291—293°/760 mm., Bu^{β}, b.p. 165—168°/10 mm., 293—295°/760 mm., Bu^{α}, b.p. 175—178°/10 mm., 303—305°/760 mm., and *iso*amyl, b.p. 175—178°/10 mm., 301—303°/760 mm. Pr^{β} salicylate did not acetylate, and acetylsalicyl chloride with $Pr^{\beta}OH$ gives $Pr^{\beta}OAc$ and Pr^{β} salicylate. Nitration of the above esters gives 3 : 5-$(NO_2)_2$-derivatives of the deacetylated esters (A., 1932, 1246). A. A. L.

Amino-acids and related compounds. V. Electrolytic oxidation of tyrosine and phenylalanine. Y. Takayama (Bull. Chem. Soc. Japan, 1933, **8**, 178—188; cf this vol., 940).—More energy is absorbed in the electrolytic oxidation of phenylalanine than of tyrosine. In both cases NH_3 is produced rather less rapidly than is accounted for by the disappearance of N as NH_2, due it is suggested to the formation of melanine. The same products are obtained in both cases, viz., CO_2, NH_3, AcOH, succinic acid, *p*-$OH\cdot C_6H_4\cdot CH_2\cdot CO_2H$, quinol, benzoquinone, and melanine. H. A. P.

Emetics derived from mandelic and malic acids. Volmar and Betz (Compt. rend., 1933, **197**, 414—416).—A mixture of equiv. concns. of mandelic acid and Na mandelate fixes the max. amount of Sb_2O_3. *Na antimonyl mandelate* is isolated cryst. having the composition
$Sb(OH)(\cdot O\cdot CHPh\cdot CO_2H)(\cdot O\cdot CHPh\cdot CO_2Na)$. Max. fixation by *l*-malic acid occurs with a mixture of 2 mols. of acid and 1 mol. of neutral Na salt, yielding *Na antimonyl* l-*malate*,
$Sb(OH)[\cdot O\cdot CH(CH_2\cdot CO_2Na)(CO_2H)]_2+$
$Sb(OH)[\cdot O\cdot CH(CH_2\cdot CO_2H)(CO_2H)]_2$?, $[\alpha]_D$ +83·4°. These compounds are more stable to H_2O than the corresponding lactic acid derivative (this vol., 376). A. C.

Synthesis of phenolic long-chain fatty acids. J. B. Niederl and C. Liotta (J. Amer. Chem. Soc., 1933, **55**, 3025—3026).—Oleic acid (I), *m*-cresol, and H_2SO_4–AcOH give ι-m-*tolyloxystearic acid*, b.p. 280°/23—24 mm., rearranged to ι-3-*hydroxy*-p-*tolylstearic acid*, m.p. 37° (II). (I) and HBr give ι-bromostearic acid, the structure of which is proved by its reaction with *m*-$C_6H_4Me\cdot OK$ and subsequent rearrangement to (II). R. S. C.

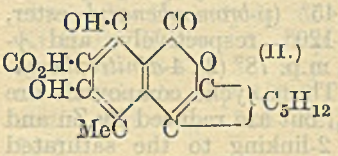
β-Anthronyl-β-phenylpropionic acid and its derivatives. Synthesis of 3-(9-anthronyl)hydrindone. P. E. Gagnon and L. Gravel (Canad. J. Res., 1933, 8, 600—615).—*Et_2 benzylidene-*, b.p. 176—177°/5 mm., and o-*chlorobenzylidene-malonate*, b.p. 182—183°/5 mm., m.p. about 30°, and *Me_2 o-chlorobenzylidenemalonate*, b.p. 175°/3 mm., m.p. 58—59°, with anthrone and piperidine in MeOH give *Et_2 β-9-anthronyl-β-phenyl-*, m.p. 104—105°, and *-β-o-chlorophenyl-ethane-αα-dicarboxylate*, m.p. 119—120° (corresponding *Me_2* ester, m.p. 148—149°), $C_{10}H_9O{\cdot}CHAr{\cdot}CH(CO_2Et)_2$, which afford *β-anthronyl-β-phenyl-* (I), m.p. 196—197° (*Ag* salt), and *-β-o-chlorophenyl-propionic acid*, m.p. 159—161°. (I) and PCl_5 give the *chloride* (II), m.p. 115—116°, whence were obtained the *Me*, m.p. 111—112°, and *Et* ester, m.p. 88—89°, *amide*, m.p. 181—182°, and *anilide*, m.p. 168—169°, and β-9-anthronyl-β-phenylpropiophenone, m.p. 115—116°. (I) and H_2SO_4, or (II) and $AlCl_3$, best in CS_2, give 3-(9-*anthronyl)hydrindone*, enolic *form*, m.p. 188°, and ketonic *form*,  $CO{<}^{C_6H_4}_{CH_2}{>}CH{\cdot}C_{14}H_9O$, m.p. 162° (*hydrazone*, m.p. 176°; *phenylhydrazone*, m.p. 224—225°; *semicarbazone*, m.p. 243°; *oxime*, m.p. 181—184°), both giving the same 2-*Br*-derivative, m.p. 169—171° (by Br–Et_2O), and oxidised by HNO_3 (*d* 1·2) quantitatively to phthalic acid and anthraquinone, whereby the alternative constitution, 13-hydroxy-11-phenylbenzanthrone, is excluded.

R. S. C.

Biochemistry of micro-organisms. XXIX. 2 : 5-Dihydroxybenzoic acid (gentisic acid), a new product of the metabolism of glucose by *Penicillium griseo-fulvum*, Dierckx. H. Raistrick and P. Simonart. **XXX, XXXI. Molecular constitution of the metabolic products of *Penicillium brevi-compactum*, Dierckx, and related species. (I) Acids $C_{10}H_{10}O_5$, $C_{10}H_{10}O_6$, and $C_{10}H_{10}O_7$.** A. E. Oxford and H. Raistrick. **(II) Mycophenolic acid.** P. W. Clutterbuck and H. Raistrick (Biochem. J., 1933, 27, 628—633, 634—653, 654—667).—XXIX. The metabolic products from the growth of *P. griseo-fulvum*, on Czapek–Dox medium containing 8% glucose and 0·25% $NaNO_3$, at 30° gives 2-hydroxy-6-methylbenzoic acid (cf. A., 1931, 524), mannitol, fumaric and gentisic acids (2 : 5-dihydroxybenzoic acid).

XXX. The three acid metabolic products (cf. A., 1932, 1289), $C_{10}H_{10}O_5$ (I), $C_{10}H_{10}O_6$ (II), and $C_{10}H_{10}O_7$ (III), are 3 : 5-dihydroxy-2-carboxylbenzyl Me ketone, -2-carboxyphenylacetylcarbinol (or a mixture of its tautomerides), and a hydrated form of -2-carboxybenzoyl Me ketone, respectively. A *substance*, $C_{11}H_{12}O_5$, m.p. 173—175°, has also been isolated. (I) is converted into $C_{10}H_8O_4$ (IV) by dehydrating agents. (I) forms a *mono*-2 : 4-*dinitrophenylhydrazone*, m.p. 224—226° (decomp.), (II) gives the *mono*-2 : 4-*dinitrophenylhydrazone* of $C_{10}H_8O_5$, m.p. 232° (decomp.), and (III) the *mono*-2 : 4-*dinitrophenylhydrazone* of $C_{10}H_8O_6$, m.p. 216° (decomp.); (II) and (III) form the same *monophenylhydrazone*, m.p. 214° (decomp.). (III) yields a supposed *quinoxaline* ($+H_2O$), m.p. 210° (decomp.), which is abnormal. (I) affords the *Ac_2* derivative of (IV), m.p. 123—124°; (II) forms (?) *Ac_3* derivative of $C_{10}H_8O_5$, m.p. 172—174°. Methylation of (I) by CH_2N_2 gives the *Me ether* of the *Me* ester, m.p. 88—91°, which is converted by MeI–K_2CO_3 into the *Me_2 ether* of (IV), m.p. 149—151°, hydrolysed to the *Me_2 ether* of (I), m.p. 139—141°. Methylation of (IV) by CH_2N_2 yields the *Me ether* of $C_{11}H_{10}O_4$, m.p. 124—125°, whilst (II) similarly gives the *Me ether* of the *Me* ester, m.p. 82°. (III) is reduced (Pd–H_2) to (II), and the Na salt of (II) is oxidised by $CuSO_4$ to (III), whilst both (II) and (III) are reduced (Zn–H_2SO_4) to (I), and (III) and (I) reduced (Zn–Hg) to (IV). Oxidation of (III) by H_2O_2 affords 3 : 5-dihydroxyphthalic acid, and of the Me_2 ether of (IV) by $KMnO_4$ gives 3 : 5-dimethoxyphthalic acid. The Me_2 ether of (I) when heated gives a ketone, oxidised ($KMnO_4$) to 3 : 5-dimethoxybenzoic acid and when treated with I–NaOH yields CHI_3 (side-chain must be $CH_2{\cdot}COMe$). The Me_2 ether of (IV) and EtOH–NH_3 form 6 : 8-dimethoxy-3-methyl*iso*carbostyril.

XXXI. Mycophenolic acid (I), $C_{17}H_{20}O_6$, m.p. 141° (*Ac* derivative, m.p. 158—160°), contains one OMe and is demethylated to *normycophenolic acid* (II), m.p. 184°. By titration, (I) is shown to contain one CO_2H and a lactonic ring, the OH of which is not phenolic. (I) and CH_2N_2 give the *Me* ester of the *Me ether*, m.p. 58°, hydrolysed to the *Me ether* of the acid, m.p. 112°, which is oxidised ($KMnO_4$) to a dilactonic acid, $C_{16}H_{14}O_6(OMe)_2$, m.p. 153°, and subsequently to the anhydride of 1 : 5-dimethoxybenzene-2 : 3 : 4 : 6-tetracarboxylic acid, m.p. 220°. Reduction (Pd–H_2) of (I) gives *dihydromycophenolic acid*, m.p. 139°. Fusion of (I) with KOH affords 3 : 5-dihydroxy-*o*-xylene (*bis*-p-*bromobenzoate*, m.p. 144—145°) and oxidation with HNO_3 gives a lactonic *acid*, $C_7H_{10}O_4$ (*Me* ester, b.p. 100°/0·1 mm.), isomerised by NaOH to a dibasic acid, m.p. 163°, and resistant to oxidation by $KMnO_4$. The annexed formula is suggested for (II), the position of the Me group in (I) being unknown.



(II.)

F. R. S.

γ-Iodopropyl chloride as a synthetic reagent. Synthesis of α-phenyl-dibasic acids. F. H. Case (J. Amer. Chem. Soc., 1933, 55, 2927—2932).—$CH_2Cl{\cdot}CH_2{\cdot}CH_2{\cdot}OH$, red P, and I give γ-iodopropyl chloride (I), b.p. 169—173° (58·3% yield), which with KCN gives *γ-iodobutyronitrile* (II), b.p. 113—116°/7 mm. Hydrogenation (PtO_2) of β-chloropropiophenone in AcOH gives *γ-chloro-α-phenylpropyl alcohol*, b.p. 130—132°/8 mm. (p-*nitrobenzoate*, m.p. 62—63°). $CNaPh(CO_2Et)_2$ (III) and (II) in PhMe give an ester, hydrolysed to *α-phenyladipic acid*, m.p. 132—133°. $CHNa(CO_2Et)_2$, NaI, and (I) in EtOH give *Et_2 γ-iodopropylmalonate*, b.p. 164—168°/8 mm., which with (III) affords esters, hydrolysed to $CH_2Ph{\cdot}CO_2H$ and *cyclo*butane-1 : 1-dicarboxylic acid, and with $CHNaPh{\cdot}CN$ (IV) gives esters, hydrolysed to yield a little *α-phenylpimelic acid*, m.p. 92—93°. (IV) and (I) in Et_2O give a nitrile, hydrolysed to an *acid*, $C_{11}H_{12}O_2$, m.p. 106—107°, probably 1-*phenyl*cyclo*butane*-1-*carboxylic acid* (since it resists hydrogenation), also obtained from (III) and (I) in EtOH, and from $CNa_2Ph{\cdot}CN$ and $CH_2(CH_2I)_2$ in Et_2O. $CNaEt(CO_2Et)_2$ and (I) in EtOH give impure *Et_2*

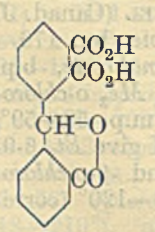
γ-iodopropylethylmalonate, b.p. 162—167°/9 mm., which with (III) in PhMe affords *α-phenyl-α′-ethylpimelic acid,* α-, m.p. 138—139°, and β-, m.p. 149—150°, forms. *Et κ-bromoundecoate,* b.p. 175—179°/6 mm., and (III) in PhMe afford an ester, hydrolysed to *α-phenylundecane-αα′-dicarboxylic acid,* m.p. 87—88°. (III) and $(CH_2I)_2$ in EtOH give esters, yielding $CH_2Ph{\cdot}CO_2H$ and αβ- (α- or β-form) -diphenylsuccinic acid; $(CH_2Br)_2$ gives similarly only $CH_2Ph{\cdot}CO_2H$; $CH_2(CH_2I)_2$ gives $CH_2Ph{\cdot}CO_2H$ and an oily acid.

R. S. C.

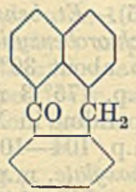
Additive reactions of phenyl vinyl ketone. III. Methyl malonate. C. F. H. Allen and H. W. J. Cressman (J. Amer. Chem. Soc., 1933, **55**, 2953—2960; cf. A., 1932, 385).—β-Chloropropiophenone, NaOAc, and an excess of pure $CH_2(CO_2Me)_2$ in MeOH give *Me₂ β-benzoylethylmalonate* (I), m.p. 42°, b.p. 165—176°/5—6 mm. (decomp.) (*Et₂* ester, an oil; 2 : 4-*dinitrophenylhydrazone,* m.p. 139°), hydrolysed by 10% aq. KOH to the corresponding *acid,* m.p. 168—170°, which at 175—180° gives CO_2 and γ-benzoylbutyric acid. Under other conditions the condensation affords *Me₂ di-(β-benzoylethyl)malonate,* m.p. 132°. (I) and Br give mixtures, whence by KOAc–MeOAc *Me₂ 2-benzoyl*cyclo*propane-*1 : 1-*dicarboxylate* (II), m.p. 74°, b.p. 185—190°/4 mm. (2 : 4-*dinitrophenylhydrazone,* m.p. 169°), was obtained. This is stable to dry NaOMe–MeOH or $Mg(OMe)_2$, but with NaOMe and a trace of H_2O gives an oil, whence aq. KOH forms 2-*benzoyl*cyclo*propane*-1 : 1-*dicarboxylic acid* (III), m.p. 170—172°, which loses CO_2 to give cis- and trans-2-*benzoyl*cyclo*propane*-1-*carboxylic acid,* m.p. 145° (p-*bromophenacyl* ester, m.p. 122°), and 118—120°, respectively, and γ-*benzoylbutyrolactone* (IV), m.p. 78° (2 : 4-*dinitrophenylhydrazone,* m.p. 174°). These cyclic compounds are all stable to conc. H_2SO_4, but are reduced by Zn and 80% AcOH at the 1 : 2-linking to the saturated aliphatic compounds. (III) and HBr–AcOH at 100° gives an oil, containing Br, which slowly passes into *α-carboxy-γ-benzoylbutyrolactone,* m.p. 122° (decomp. 125—130°); this at 150—155° or in hot KOAc–MeOH gives (IV). (II) gives similarly a halogenated oil, whence (II) is regenerated by KOAc–MeOAc. *Me γ-benzoylbutyrate,* m.p. —2°, b.p. 147—148°/8 mm. (2 : 4-*dinitrophenylhydrazone,* m.p. 149°), with Br in CCl_4 gives an oil, which with KOAc–MeOAc forms *Me γ-benzoyl-γ-acetoxybutyrate* (V), m.p. 60° (2 : 4-*dinitrophenylhydrazone,* m.p. 158°), and with NaOMe gives (IV), also obtained from (V) by alkaline or, better, acid hydrolysis, and by bromination of γ-benzoylbutyric acid followed by treatment with cold, aq. Na_2CO_3. In all these reactions fission occurred at the 1 : 2-linking.

R. S. C.

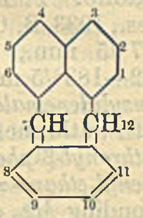
Synthesis of phthaloylnaphthol. L. F. Fieser and (Mrs.) M. Fieser (J. Amer. Chem. Soc., 1933, **55**, 3010—3018).—The oxidation product of phthaloyl-β-naphthol, benzhydrol-2 : 3 : 2′-tricarboxylic acid lactone (A., 1931, 1292) (I) (modified prep.) (*imide,* m.p. 303—304°) titrates as a lactonic dicarboxylic acid, and with KOH at 180° (with or without HCO_2K) is reduced to *diphenylmethane*-2 : 3 : 2′-*tricarboxylic acid,* $+1{\cdot}5H_2O$, m.p. about 145° (decomp.) and 200° (anhydride) (*Me₃* ester, m.p. 79°; *anhydride,* m.p. 202°), which with conc. H_2SO_4 at 150° or $AlCl_3$–NaCl at 150° gives anthrone-1 : 5-dicarboxylic acid, oxidised to anthraquinone-1 : 5-dicarboxylic acid. 2-(2′-Methoxy-1′-naphthoyl)benzoic acid, m.p. 196° (modified prep.), with Zn dust and aq. NaOH gives the *lactone,* m.p. 139°, of *phenyl-2′-methoxy-1′-naphthylcarbinol-2-carboxylic acid,* further reduced by the same reagents to the methanecarboxylic acid. Similarly were prepared: phenyl-2′ : 3′-, m.p. 254°, 2′ : 6′-, m.p. 218°, and -2′ : 7′-*dimethyl-1′-naphthylmethane-2-carboxylic acid,* m.p. 211°. The acid chlorides, prepared from these and similar acids (finely divided) by $SOCl_2$, give with $AlCl_3$ in $PhNO_2$ (less well with conc. H_2SO_4) the following derivatives of 7-*pleiadone* (II) (derived from the hypothetical *pleiadene* (III)): 1-*MeO*- (IV), m.p. 160°; 1-*Me*- (V), m.p. 128°; 1 : 2-, m.p. 195°, 1 : 5-, m.p. 159°, and 1 : 6-*Me₂*-, m.p. 172°. (IV) with $AlCl_3$ in hot C_6H_6 gives 1-*hydroxy*-7-*pleiadone,* m.p. 232° (*Ac* derivative, m.p. 195°), and with MgPhBr gives (probably) 7-*hydroxy*-1-*methoxy*-7-*phenyl*-7 : 12-*dihydropleiadene,* m.p. 186°. (V), however, gives a *hydrocarbon,* m.p. 237°. The pleiadones with CrO_3 in hot AcOH give 1-*methyl*-, m.p. 183°, 1 : 2-, m.p. 175°, 1 : 5-, m.p. 179°, and 1 : 6-*dimethyl*-, m.p. 241°, and 1-methoxy- (VI) -7 : 12-*pleiadenedione.* (VI) is identical with phthaloyl-β-naphthol Me ether; with MgPhBr it gives a *compound,* $C_{31}H_{22}O_2$, m.p. 183—184° (*acetate,* m.p. 212°). Reiche's formula for phthaloyl-β-naphthol (A., 1931, 1060) and Fieser's for (I) (*loc. cit.*) are thus confirmed, but the mechanism of the oxidation of the former to the latter remains obscure.



(I.)



(II.)



(III.)

R. S. C.

Colour and chemical constitution. Effect of auxochromic groups on phthalophenone (lactone of triphenylcarbinol-o-carboxylic acid). N. Ghatak (Bull. Acad. Sci. U.P., Allahabad, 1933, **2**, 253—258).—Condensation with H_2SO_4 of p-hydroxybenzoylbenzoic acid with the appropriate phenol has given the following: 4 : 4′-*di*-, m.p. 252°, 4 : 4′ : 5′-*tri*-, m.p. 148—149°, 4 : 4′ : 6′-*tri*-, m.p. 164°, 4 : 3′ : 6′-*tri*-, m.p. 153—155°, 4 : 3′ : 4′ : 5′-*tetra*- m.p. 147—148°, and 4 : 2′ : 4′ : 6′-*tetra-hydroxy*-, m.p. 256°; 4 : 4′-*dihydroxy*-5′-*methyl*-, m.p. 117°, -6′-*methyl*-, m.p. 131°, -6′-*methyl*-3′-iso*propyl*-, m.p. 231—232°, and -3′-*methyl*-6′-iso*propyl*-, m.p. 178—179°, 4 : 6′-*dihydroxy*-3′-*methyl*-, m.p. 135°, -4′-*dimethylamino*-, m.p. 142°, and -4′-*diethylamino-phthalophenone,* m.p. 93°; also 4-*hydroxydiphenyl*-4′-*hydroxy*-α-*naphthyl*-, m.p. 171°, -2′-*hydroxy*-α-*naphthyl*-, m.p. 153°, and -2′ : 7′-dihydroxy-α-naphthyl-, m.p. 261°, -*carbinol*-2″-*carboxylic lactone.* The substances afford reddish-violet solutions in aq. NaOH, blue in the case of the α-naphthol derivative. Absorption max. are given.

F. R. S.

Aminoguanidine derivatives. (Miss) V. A. Conard and R. L. Shriner (J. Amer. Chem. Soc., 1933, 55, 2867—2870).—Aminoguanidine (modified prep.) and p-$NMe_2\cdot C_6H_4\cdot CHO$ give *ωω-di(guanidinamino)dimethyl-p-toluidine*, p-$NMe_2\cdot C_6H_4\cdot CH[NH\cdot NH\cdot C(:NH)\cdot NH_2]_2$, $+H_2O$, m.p. 178—179° (*hydrochloride*), and *p-dimethylaminobenzylideneaminoguanidine*, $+2H_2O$ (lost at 105°), m.p. 149° [*hydrochloride*, $+2H_2O$, m.p. 210° (decomp.); *dihydrochloride*, m.p. 221—227° (decomp.)]. The salts have no hypoglycæmic action. R. S. C.

Phenanthrene series. III. Hydroxy-aldehydes and -ketones. E. Mosettig and A. Burger. **IV. Phenanthrene-2-, -3-, and -9-aldehydes.** E. Mosettig and J. van de Kamp (J. Amer. Chem. Soc., 1933, 55, 2981—2989, 2995—2999; cf. A., 1932, 1029).—III. The structures of 2-hydroxyphenanthrene-1-aldehyde, m.p. 172—173° (*Schiff's base*, m.p. 160—161°), and 9-hydroxyphenanthrene-10-aldehyde, m.p. 133—134° (*Schiff's base*, m.p. 160—161°), are confirmed by oxidation (Dakin–Barger and H_2O_2–O_2, respectively) to 1 : 2-dihydroxyphenanthrene and phenanthraquinone, respectively. 3-Acetoxyphenanthrene is decomposed by $AlCl_3$ or $AlBr_3$, but with $AlCl_3$ and AcCl (1 mol.) in $PhNO_2$ gives a 30% yield of *3-acetoxy-(? 6- or 7-)-acetylphenanthrene*, m.p. 155° (*semicarbazone*, m.p. 218°; *-9 : 10-quinone*, m.p. 206—208°), also obtained from 3-hydroxyphenanthrene, AcCl (2 mols.), and $AlCl_3$, leading to a *3-hydroxyacetylphenanthrene*, m.p. 180—181° [*Me ether*, m.p. 106—107° (*semicarbazone*, m.p. 203—205°)], and a *3-methoxyphenanthrenecarboxylic acid* (this and all the acids prepared from ketones are obtained by NaOCl), m.p. 238—239° (*Me* ester, m.p. 125—126°). Arguments are presented confirming the structure assigned to 3-hydroxyphenanthrene-2-carboxylic acid. 3-Methoxyphenanthrene gives (Friedel–Crafts) a *3-methoxyacetylphenanthrene*, m.p. 98—99° (*semicarbazone*, m.p. 217—219°), affording a *3-methoxyphenanthrenecarboxylic acid*, m.p. 200° (*Me* ester, m.p. 81·5—82·5°). Fries rearrangement of 2-acetoxyphenanthrene (I) and the Friedel–Crafts reaction with 2-hydroxy- or 2-methoxy-phenanthrene (*A*) give *2-methoxy-1-acetylphenanthrene*, m.p. 175—176°, oxidised to *2-methoxyphenanthrene-1-carboxylic acid*, m.p. 244—246° (decomp.) [*Me* ester, m.p. 145—146°, also obtained from *2-methoxyphenanthrene-1-aldehyde*, m.p. 160° (*semicarbazone*, m.p. 300—315°)], identical with Werner's "2-hydroxyphenanthrene-3-carboxylic acid" (A., 1903, i, 173). However, the Friedel–Crafts reaction with 2-acetoxyphenanthrene gives a *2-acetoxyacetylphenanthrene*, m.p. 120—122·5° [*-9 : 10-quinone*, m.p. 238—240° (decomp.)], leading to a *2-hydroxyacetylphenanthrene*, m.p. 186° [*Me ether*, m.p. 117° (*semicarbazone*, m.p. 241—242°)], and a *2-methoxyphenanthrenecarboxylic acid*, m.p. 251—252° (*Me* ester, m.p. 79—80°). Reaction *A* leads also to a little *2-methoxyacetylphenanthrene*, m.p. 132—133° (*semicarbazone*, m.p. 223°). The Fries rearrangement of 9-acetoxyphenanthrene (II) and the Friedel–Crafts reaction with 9-hydroxyphenanthrene (III), m.p. 155°, give *9-hydroxy-10-acetylphenanthrene*, m.p. 96° [rearranges to a second *form*, m.p. 101·5—102°, when melted; *Me ether*, an oil (*picrate*)], oxidised by CrO_3 to 9 : 10-phenanthraquinone. (II) and (III) with 1 and 2 mols., respectively, of AcCl give, however, *9-hydroxy-10 : 3-(or : 6-)-diacetylphenanthrene*, m.p. 175·5—176·5° (*Me ether*, m.p. 111·5—112·5°), oxidised to 3-acetyl-9 : 10-phenanthraquinone. The following are also described: *3-methoxy-*, m.p. 80° [*semicarbazone*, m.p. 237—239° (decomp.)], and *3-acetoxy-phenanthrene-4-aldehyde*, m.p. 98—99°; *9-methoxyphenanthrene-10-aldehyde*, m.p. 79—81° (*semicarbazone*, m.p. 211°); *3-methoxyphenanthrene-4-carboxylic acid*, m.p. 153—154° (decomp.) (*Me* ester, m.p. 122°), prepared from the aldehyde; *3-hydroxyphenanthrene-4-carboxylic acid*, m.p. 125° (decomp.) (loses CO_2 quantitatively at 130° [*Ac* derivative, $+H_2O$ (lost at 95° in vac.), m.p. 105—115°, anhyd., m.p. 162—163° (decomp.); *Me ether* of *Me* ester, m.p. 133—133·5°]; and *9-methoxyphenanthrene-10-carboxylic acid*, m.p. 113°, prepared from the aldehyde.

IV. Hydrogenation (Pd–$BaSO_4$ in decahydronaphthalene) of *phenanthroyl-2-*, m.p. 101—101·5°, -3-, and -4-*chlorides* gives *phenanthrene-2-*, m.p. 59—59·5°, -3-, m.p. 79·5—80°, and -4-*aldehyde*, m.p. 100·5—101° (*oximes*, m.p. 194—195°, 145—145·5°, and 157—157·5°; *semicarbazones*, m.p. 281—282°, 274—275°, and 221—222°, respectively), reduced (PtO_2 in EtOH) to 2-, m.p. 125—125·5°, 3-, m.p. 103—103·5° (*benzoate*, m.p. 84·5—85°), and *4-phenanthrylmethyl alcohol*, m.p. 149—149·5°, whence the corresponding *bromides*, m.p. 111—111·5°, 114·5—115°, and 103—103·5°, and *cyanides*, m.p. 106—106·5°, 84·5—85°, and 96·5—97°, respectively, were obtained. Hydrolysis of the cyanides by 25% KOH–EtOH gives 2-, m.p. 183·5—184·5° (*Me* ester, m.p. 78—78·5°), 3-, m.p. 177—177·5° [*Me* ester, an oil (*picrate*, m.p. 103·5—104°)], and *4-phenanthrylacetic acid*, m.p. 220—221° (*Me* ester, m.p. 75—75·5°). R. S. C.

Poly-membered ring systems. I. Synthesis of polymethylene ketones with more than six-membered rings. K. Ziegler, H. Eberle, and H. Ohlinger (Annalen, 1933, 504, 94—130).—Successive addition of $NHEt_2$ and MeCN to 1·06*N*-LiPh in Et_2O at −10° and decomp. of the product with H_2O affords $CH_2Ac\cdot CN$ in 86% yield. Similarly Pr^aCN and $LiNEt_2$ afford *α-butyrylbutyronitrile* (I), b.p. 96°/11 mm., in 71·5% yield, hydrolysed by 70% H_2SO_4 to $COPr^a_2$ (semicarbazone, m.p. 133°). (I) is obtained in 90% yield from Pr^aCN and LiNPhEt (from LiBu and NHPhEt) in Et_2O. Sebaconitrile (II) and $LiNEt_2$ in conc. solution give a 13% yield of *cyano*cyclo*heptanone* (III), b.p. 140—141°/12 mm. (*semicarbazone*, m.p. 162°), hydrolysed by conc. H_2SO_4 or 48% HBr to suberone in poor yield. In more dil. solution and with apparatus to ensure the invariable ratio 1 : 1 of reactants, the yield rises to 71%. (III) is unusually readily hydrolysed by NaOH to the *Na* salt of sebacoheminitrile. A 90% yield of (III) is obtained from (II) and LiNPhEt. In special apparatus, azelaodinitrile is transformed into *cyano*cyclo*octanone*, b.p. 158—160°/13 mm., m.p. 55—56° (*semicarbazone*, m.p. 161°), readily hydrolysed by 48% HBr to cyclooctanone (semicarbazone, m.p. 167—168°) and *2 : 9-dicyano-1 : 8-diketo*cyclo*hexadec-*

ane, m.p. 171°, hydrolysed to 1 : 8-diketo*cyclo*hexadecane, m.p. 83—84° (dioxime, m.p. 185—186°). Treatment of αζ-dicyanotetradecane with $LiNEt_2$ and subsequently with H_2O and 20% H_3PO_4 leads to *dicyanodi-iminocyclotriacontane* (hydrolysed to *cyclo*triacontanedione) and *cyanocyclopentadecanone-imine*, m.p. 142° (yield 30—40%), hydrolysed by boiling dil. H_2SO_4 to *cyclo*pentadecanone, b.p. 120°/0·1 mm. In like manner are prepared *cyanocycloheptadecanoneimine*, m.p. 108—109° [hydrolysed by 70% H_2SO_4 to *cyclo*heptadecanone (dihydrocivetone)], and *tetratriacontane-ατ-dione*, m.p. 84°. H. W.

Beckmann change. I. Spontaneous rearrangement of oxime picryl ethers. A. W. Chapman and C. C. Howis (J.C.S., 1933, 806—811).—*Benzophenoneoxime benzoate*, m.p. 99°, gives on heating dibenzanilide; *benzophenoneoxime* o-*nitrobenzoate*, m.p. 185—188°, chars. *Benzophenoneoxime picryl ether*, m.p. 103—105°, rearranges to benz-*N*-picrylanilide on heating alone or in a solvent. *Acetophenoneoxime picryl ether*, m.p. 112°, rearranges to *acet*-N-*picrylanilide*, m.p. 198°; p-*chlorobenzophenone-α-oxime picryl ether*, m.p. 117°, forms p-*chlorobenz*-N-*picrylanilide*, m.p. 223—224°, whilst the -β-*oxime*, m.p. 109—110°, yields *benz*-N-*picryl*-p-*chloroanilide*, m.p. 208—210°. Similar rearrangements have been obtained: *benzophenoneoxime* 2 : 4 : 6-*trinitro*-m-*tolyl ether*, m.p. 127° [*benz*-2 : 4 : 6-*trinitro*-m-*tolylanilide*, m.p. 255° (decomp.)]; *di*-p-*tolylketoxime picryl ether*, m.p. 106—107° (p-*toluo*-N-*picryl*-p-*toluidide*, m.p. 166—169°), and 2 : 4 : 6-*trinitro*-m-*tolyl ether*, m.p. 114° (p-*toluo*-2 : 4 : 6-*trinitro*-m-*tolyl*-p-*toluidide*, m.p. 144° and 168—170°); *di*-p-*chlorophenylketoxime picryl ether*, m.p. 129° (p-*chlorobenz*-N-*picryl*-p-*chloroanilide*, m.p. 194—195°), and 2 : 4 : 6-*trinitro*-m-*tolyl ether*, m.p. 129° (p-*chlorobenz*-2 : 4 : 6-*trinitro*-m-*tolyl*-p-*chloroanilide*, m.p. 166—168°); and p-*chloroacetophenoneoxime picryl ether*, m.p. 133° (p-*chloro*-N-*picrylacetanilide*, m.p. 191°). The velocity of the rearrangements changes with the solvent, indicating that the rearrangements are probably intramol. F. R. S.

Reaction of aromatic ketones with sodium. II. Reactions of sodium pinacolates. W. E. Bachmann (J. Amer. Chem. Soc., 1933, 55, 2827—2830; cf. this vol., 505).—Na_2 pinacolates (prepared from Na and $COPh_2$, *p*-$C_6H_4Ph\cdot COPh$, or fluorenone) in Et_2O–C_6H_6 with MgX_2 or MgRX (X=halogen) give red solutions of the MgX-derivatives of the pinacols, which with H_2O afford 80—90% yields of pinacols. $(\cdot CHPh_2\cdot ONa)_2$ does not react with NaPh. The preps. of $HgPh_2$ and NaPh are modified. R. S. C.

Grignard reaction in the synthesis of ketones. III. Preparation and characterisation of a series of mono- and di-chlorodeoxybenzoins. S. S. Jenkins (J. Amer. Chem. Soc., 1933, 55, 2896—2899; cf. this vol., 610).—The benzyl Grignard reagents (3 mols.) and appropriate amides afford *Ph* m-*chlorobenzyl ketone*, m.p. 43° (101—102°), m-*chlorophenyl benzyl*, m.p. 62° (120°), m-, o-, and p-*chlorobenzyl*, m.p. 65°, 71°, and 74·5° (103—104°, 130·5—131·5°, and 100°), respectively, *ketones*, o-*chlorophenyl* m-*chlorobenzyl ketone*, b.p. 185—190°/6 mm. (86—87°), and p-*chlorophenyl* m-*chlorobenzyl ketone*, m.p. 75·5° (127—128°), the m.p. in parentheses being those of the anti-(benzyl)-*oximes*, which rearrange to the following anilides, also prepared from the appropriate acid and basic components: m-*chlorophenylacetanilide*, m.p. 130°, *phenylaceto*-m-*chloroanilide*, m.p. 95°, m-*chlorophenylaceto*-m-, -o-, and -p-*chloroanilide*, m.p. 120°, 120°, and 150·5°, respectively, and o- and p-*chlorophenylaceto*-m-*chloroanilide*, m.p. 154° and 137·5°, respectively. *m*-$C_6H_4Cl\cdot CH_2Br$, b.p. 103—105°/8 mm., m.p. 15—15·5°, is prepared from *m*-C_6H_4ClMe and Br in CCl_4 at 60—80° in light, and m-*chlorophenylacetic acid*, m.p. 77·5—78·5°, from *m*-$C_6H_4Cl\cdot CH_2\cdot MgBr$. All m.p. are corr. R. S. C.

True nature of a so-called dihydropyrocatechol. G. Dupont and E. Urion (Compt. rend., 1933, 197, 158—159).—The "dihydropyrocatechol," obtained from the sol. tar of pine (B., 1931, 467), has been identified as 3-methyl*cyclo*pentane-1 : 2-dione in its enolic form. F. R. S.

Strainless monocyclic rings. M. Qudrat-i-Khuda (Nature, 1933, 132, 210).—Direct reduction (Clemmensen) of dimethyldihydroresorcinol gives a second isomeric ketone (semicarbazone, m.p. 162°), supporting the view of a strain-free configuration of the substituted *cyclo*hexane ring. L. S. T.

Syntheses of ketones by means of mixtures of acids and acid anhydrides. I. F. Unger (Annalen, 1933, 504, 267—286).—Examination of the action of various acids and anhydrides on PhOMe (I) and PhOEt (II) shows that org. acids resemble certain metallic halides and inorg. acids in their ability to activate the condensation of other org. acids with unsaturated compounds with production of ketones; one or both org. acids must be in the form of anhydride. If both acids are free, aromatic compounds do not react, whereas aliphatic and hydroaromatic unsaturated substances pass into the corresponding saturated esters. Production of ketones depends on the temp., particularly on the strength of the activating acid and the character of the unsaturated compound. An exact parallelism between the activation and the dissociation const. of the activating acid cannot be drawn. No generalisation can be made between the relative strengths of the activating and reacting acids and the rate of reaction, nor can it be foretold which acid will react, although in most cases the acyl of the acid with the smaller dissociation const. is introduced. The reverse is the case when *o*-substituted or inorg. acids are used.

In general, (I) or (II) is heated with acid and anhydride (mol. ratio 1 : 1 : 2) at 170—180°. The following p-*anisyl ketones* are described: *Me*, b.p. 133—134°/10 mm., 256—258°/755 mm., m.p. 38·5° (*semicarbazone*, m.p. 196·5°; p-*nitrophenylhydrazone*, m.p. 195—195·5°); *Et*, b.p. 148—149°/15 mm., m.p. 27° (*semicarbazone*, m.p. 172°; p-*nitrophenylhydrazone*, m.p. 149—150°); Pr^β, b.p. 152·5—153°/16 mm.; Bu^β, b.p. 158·5—159·5°/12 mm. (*semicarbazone*, m.p. 203·5°); CH_2Ph, b.p. 221—222°/11 mm., m.p. 77—78° (p-*nitrophenylhydrazone*, m.p. 157·5°); Pr^α, b.p. 152—153°/12 mm. (*semicarbazone*, m.p. 173·5°); n-*amyl*, b.p. 172—174°/14 mm. (*semicarbazone*, m.p. 142·5°); α-*ethylpropyl*, b.p. 168—170°/14 mm., and *α-propyl*-n-*butyl*, b.p. 183—186°/13 mm., which do not react with $NH_2\cdot CO\cdot NH\cdot NH_2$ or *p*-$NO_2\cdot C_6H_4\cdot NH\cdot NH_2$; *pentadecyl*, m.p. 75°; Δ^{η}-*heptadecenyl*, m.p. 43°; *benzhydryl*, m.p. 130°, from (I), $CHPh_2\cdot CO_2H$, and $(CH_2Cl\cdot CO)_2O$ or (I), $CPh_2{:}CO$, and $CH_2Cl\cdot CO_2H$; *CPh_3*, m.p. 200·5°; Ph, m.p. 61—62° (p-*nitrophenylhydrazone*, m.p. 198—199°); o-*C_6H_4Me*, b.p. 202—204°/13 mm.; p-*$C_6H_4\cdot OMe$*, m.p. 146°; o-*C_6H_4Br*, b.p. 226—229°/10 mm., m.p. 96°; p-*C_6H_4Br*, m.p. 160—161°; o-*C_6H_4Cl*, b.p. 209—211°/9 mm., m.p. 84·5°; α-*$C_{10}H_7$*, m.p. 101·5—102°; 2 : 4 : 6-*$C_6H_2Br_3$*, m.p. 149—150°. (II), $CH_2(CO_2H)_2$, and Ac_2O at 120° and then at 150—160° afford p-*ethoxyphenyl Me ketone*, b.p. 145·4—145·8°/13 mm., 268—269°/758 mm., m.p. 37—38° (*semicarbazone*, m.p. 181·5°; p-*nitrophenylhydrazone*, m.p. 211°). (I), β-phenylpropionic acid, and $(CH_2Cl\cdot CO)_2O$ at 170° yield 1-hydrindone, b.p. 127—129°/20 mm., m.p. 41—42°, whilst βββ-triphenylpropionic acid similarly affords *p*-anisyl CH_2Cl ketone and 3 : 3-*diphenyl*-1-*hydrindone*, m.p. 121° (p-*nitrophenylhydrazone*, m.p. 234°). (I), PhCHO, and $CH_2Cl\cdot CO_2H$ at 160° yield 4 : 4′-*dimethoxytriphenylmethane*, b.p. 242—246°/11 mm., m.p. 101·5°, whereas (I), benzhydrol, and $CH_2Cl\cdot CO_2H$ at 170—180° give 4-methoxytriphenylmethane, b.p. 235—236°/16 mm., m.p. 63°, and a *substance* $C_{38}H_{28}O$, m.p. 147—148°. H. W.

Synthesis of hydroxyphenyl α-bromoethyl ketones. C. Torres and J. Amargós (Anal. Fís. Quím., 1933, **31**, 37—47).—By heating the product obtained by fusing phenol and $AlCl_3$, with EtCOCl at 125—130°, and treatment with dil. HCl, a mixture of *o*- and *p*-hydroxypropiophenones (2 : 4-*dinitrophenylhydrazones*, m.p. 229° and 189°, respectively; *semicarbazone* of *o*-derivative, m.p. 221°) is obtained. Analogously, with $CHMeBr\cdot COBr$, there are obtained o-, m.p. 32°, b.p. 143—147°/18 mm. (2 : 4-*dinitrophenylhydrazone*, m.p. 143—144°), and p-*hydroxyphenyl α-bromoethyl ketone*, m.p. 81° [2 : 4-*dinitrophenylhydrazone*, m.p. 147° (decomp.); *benzoate*, m.p. 87°]. Interaction of pyrocatechol, $POCl_3$, and $CHMeCl\cdot CO_2H$ or $CHMeBr\cdot CO_2H$ yields only small amounts of the α-halogenated 3 : 4-dihydroxypropiophenones. Pyrocatechol dipropionate, m.p. 25—26°, yields with Br in AcOH the di-α-bromopropionate, m.p. 62°, b.p. 220—227°/18 mm. An attempt to convert the latter into the α-bromoethyl ketone by treatment with $AlCl_3$ and pyrocatechol in $PhNO_2$ resulted in the formation of only a trace af ketone. 3 : 4 - Dihydroxypropiophenone (2 : 4 - *dinitrophenylhydrazone*, m.p. 226°) yields with Br in AcOH the α-Br-compound. R. K. C.

Reformatsky reaction with anisil. J. W. Cook and W. Lawson (J.C.S., 1933, 827—829).—Anisil, $CH_2Br\cdot CO_2Et$, and Zn give *Et* ββ′-*dihydroxy*-ββ′-*dianisyladipate*, m.p. 153—154°, which on reduction (Hg–Zn) forms an *acid*, $C_{20}H_{22}O_6$, m.p. 248—249° (*Me* ester, m.p. 108—109°), and an *acid*, $C_{19}H_{22}O_4$, m.p. 160·5—161·5° (*Me* ester, m.p. 99—100°). The reaction also yields a resin, reduced to an *acid*, $C_{18}H_{20}O_4$, m.p. 167—168° (*Me* ester, m.p. 63—64°), due to the condensation of one CO group only of anisil. F. R. S.

Synthesis of isomeric unsymmetrical benzoins. S. S. Jenkins (J. Amer. Chem. Soc., 1933, **55**, 3048).—Ph *p*-methoxybenzyl ketone and Br in CCl_4 in light give desyl bromide, which with NaOEt yields *Ph α-hydroxy*-p-*methoxybenzyl ketone* (*anisbenzoin*), m.p. 89°, rearranged by KCN–EtOH to benzanisoin. R. S. C.

Preparation of ninhydrin (triketohydrindene hydrate). W. O. Teeters and R. L. Shriner (J. Amer. Chem. Soc., 1933, **55**, 3026—3028).—1 : 3-Diketohydrindene (I) (modified prep. from Et_2 phthalate and EtOAc) and SeO_2 in aq. dioxan give a 31—35% yield of ninhydrin (II). Aq. $Ce(SO_4)_2$ and (I) gave a resin. (I) with HNO_2 gives *triketohydrindene-2-oxime*, m.p. 200—201° (decomp.), resistant to hydrolysis, and condenses with *p*-$NO\cdot C_6H_4\cdot NMe_2$ to a product, whence (II) could not be obtained. R. S. C.

Resorcinol ketones and *C*-alkylresorcinols. K. W. Rosenmund, R. Buchwald, and T. Deligiannis (Arch. Pharm., 1933, **271**, 342—352).—5-Ethylresacetophenone, m.p. 117—118° (lit. 115°), is obtained from 4-ethylresorcinol diacetate (I) and $AlCl_3$ (slightly > 2 mols.) at 40—50° (47% yield) or from (I), 4-ethylresorcinol (II), and $AlCl_3$ in $PhNO_2$ first at room temp. and then at 50—60° (method *A*) (nearly quant. yield). 2 : 6-*Diacetyl-4-ethylresorcinol*, m.p. 74°, is prepared from (I) and $AlCl_3$ alone at 110° or in $PhNO_2$ at 60—70° (50% yield). Similarly are prepared 6-*propionyl*-, m.p. 67·5° (*phenylhydrazone*, m.p. 170°), -*butyryl*-, m.p. 100° (*phenylhydrazone*, m.p. 142·5°), -*valeryl*-, m.p. 92°, b.p. 220°/9 mm. (*phenylhydrazone*, m.p. 125—126°), -*hexoyl*-, b.p. 220—225°/10 mm., m.p. 93—94° (*phenylhydrazone*, an oil), -*benzoyl*-, m.p. about 63—64°, and 2 : 6-*dipropionyl*-, m.p. 81°, -4-*ethylresorcinol*, and 6-*acetyl*-, m.p. 108—109°, -*propionyl*-, m.p. 73—74°, b.p. 190—195°/9·5 mm. (*phenylhydrazone*, m.p. 143—144°), -*butyryl*-, m.p. 64°, b.p. 190°/9 mm. (*phenylhydrazone*, m.p. 139—140°), -*valeryl*-, b.p. 205°/9·5 mm., m.p. 85° (*phenylhydrazone*, an oil), -*hexoyl*-, m.p. 53°, b.p. 225—230°/9 mm. (*phenylhydrazone*, an oil), -*benzoyl*-, m.p. 138—140°, b.p. 240—245°/9 mm., and 2 : 6-*diacetyl*-, m.p. 64—65°, -4-*propylresorcinol*. Thence by Clemmensen or catalytic (Pd–$BaSO_4$) reduction are obtained : 4 : 6-diethylresorcinol; 4-*ethyl*-6-*propyl*-, m.p. 65°, b.p. 170—175°/11 mm., -6-*butyl*-, b.p. 220°/9 mm., -6-*amyl*-, b.p. 220°/11 mm., -6-*hexyl*-, b.p. 215°/11 mm., -2 : 6-*dipropyl*-, b.p. 195°/9 mm., 6-*benzyl*-4-*propyl-resorcinol*, b.p. 220°/9 mm.; 2 : 6-*diethyl*-4-*propyl*-, b.p. 195°/11 mm., 4-*propyl*-6-*butyl*-, b.p. 200°/13 mm., -6-*amyl*-, b.p. 195—200°/14 mm., -6-*hexyl*-, b.p. 210—215°/14 mm., and 6-*benzyl*-4-*ethyl*-, b.p. 230—235°/9 mm., -*resorcinol*. The appropriate diacylresorcinols and slightly > 2 mols. of $AlCl_3$ at 70—130° (not higher) give 2 : 4-*diacetyl*- (III), m.p. 88—89°, b.p. 170—172°/26 mm., -*dipropionyl*- (IV), m.p. 78—79°, b.p. 184—185°/24 mm., -*dibutyryl*-, b.p. 190°/20 mm., and -*divaleryl*-, b.p. 196°/20 mm., -*resorcinol*. Method *A* is generally better than the usual modification, in accordance with the view that the rearrangement is a bimol. process. Clemmensen reduction of (III) gives (II); catalytic reduction (Pd in AcOH at 3 atm.) gives

2-*acetyl*-4-*ethylresorcinol*, m.p. 127° (*phenylhydrazone*, m.p. 147), giving (II) by Clemmensen reduction. (IV) affords similarly 4-propylresorcinol and 2-*propionyl*-4-*propylresorcinol*, m.p. 92° (*phenylhydrazone*, m.p. 124°). R. S. C.

Constituents of *Filix mas*. I. Aspidinol. A. Robertson and W. F. Sandrock (J.C.S., 1933, 819—823).—2 : 6-*Dinitro*-4-*ethoxytoluene*, m.p. 108—109°, prepared by ethylation of 2 : 6-dinitro-*p*-cresol, is reduced ($SnCl_2$–HCl) to 6-*nitro*-4-*ethoxy*-o-*toluidine*, m.p. 89—90° (*Ac* derivative, m.p. 192—193°), which gives the corresponding -*cresol*, m.p. 117—118°, ethylated to 2-*nitro*-4 : 6-*diethoxytoluene*, m.p. 103°. This is reduced (Na_2S) to 4 : 6-*diethoxy*-o-*toluidine* (*Ac* derivative, m.p. 134—135°), the sulphate of which with $NaNO_2$–H_2SO_4 forms C-*methylphloroglucinol* α-*Et₂ ether*, m.p. 64—65°. The ether and *n*-butyronitrile condense to 2-*hydroxy*-4 : 6-*diethoxy*- (I), m.p. 103·5—104·5° (*acetate*, m.p. 82—83°), and 4-*hydroxy*-2 : 6-*diethoxy*-3-*methyl*-n-*butyrophenone*, m.p. 68°. (I) is identical with monoethylaspidinol, and with Ac_2O and NaOAc forms 5 : 7-*diethoxy*-2 : 8-*dimethyl*-3-*ethylchromone*, m.p. 140—141°.

Methylation of 6-nitro-4-ethoxy-*o*-cresol gives the *Me ether*, m.p. 89—90°, reduced to 6-*methoxy*-4-*ethoxy*-o-*toluidine* (*Ac* derivative, m.p. 132—133°), which forms the -*cresol* (+H_2O), m.p. 52°. The cresol condenses with *n*-butyronitrile to 2-*hydroxy*-4-*methoxy*-, m.p. 114—115° (*acetate*, m.p. 72—73°), and 4-*hydroxy*-2-*methoxy*-6-*ethoxy*-3-*methyl*-n-*butyrophenone*, m.p. 59°, the former giving 7-*methoxy*-5-*ethoxy*-2 : 8-*dimethyl*-3-*ethylchromone*, m.p. 132—133°, with Ac_2O and NaOAc. Aspidinol (2 : 6-dihydroxy-4-methoxy-3-methylbutyrophenone), m.p. 143° (*diacetate*, m.p. 68°), is obtained by condensation of methylphloroglucinol β-Me ether and *n*-butyronitrile, identical with a natural specimen. Methylation of *C*-methylphloro-*n*-butyrophenone with MeI–K_2CO_3 or CH_2N_2 gives 2-*hydroxy*-4 : 6-*dimethoxy*-3-*methyl*-n-*butyrophenone*, m.p. 111—112° (*acetate*, m.p. 61—62°), which cyclises to 5 : 7-*dimethoxy*-2 : 8-*dimethyl*-3-*ethylchromone*, m.p. 171—172°. F. R. S.

Anthraquinone derivatives. II. Chloroaminoanthraquinones. M. Hayashi and A. Nakayama (J. Soc. Chem. Ind. Japan, 1933, 36, 202—204B).—Comparison of absorption spectra with those of 4- and 5-amino-2-benzoylbenzoic acids indicates that the NH_2-compounds, m.p. 192° and 225·5—226° (this vol., 612), are the 5- and 4-NH_2-derivatives, respectively. The corresponding 5-, m.p. 198°, and 4-NO_2-derivatives, m.p. 194—194·5°, are also obtained from the chloride (I) of 1-Me 4-nitrophthalate with PhCl and $AlCl_3$, together with (?) *nitro*-3 : 4-*di*-p-*chlorobenzoylbenzene*, m.p. 177·5—178·5°. (I) with conc. NH_3 gives 4-nitrophthaldiamide. A. A. L.

Scission of aloin. E. Léger (J. Pharm. Chim., 1933, [viii], 18, 25—26).—A discussion (cf. Rosenthaler, A., 1932, 516). W. O. K.

Mechanism of the formation of α-terpineol from linalool. R. Horiuchi (J. Soc. Chem. Ind. Japan, 1933, 36, 191—193B).—A study of the products of reaction of AcOH–H_2O, AcOH, and Ac_2O under various conditions with linalool, geraniol, and nerol leads to the conclusion that the first products in the above rearrangements are geraniol and nerol, the latter then forming terpineol. A. A. L.

Raman effect in terpenes. IV. Terpinenes and terpinolene. G. Dupont, J. Lévy, and (Mlle.) Marot (Bull. Soc. chim., 1933, [iv], 53, 393—406; cf. this vol., 337).—Terpineol and aq. $H_2C_2O_4$ (I) at 100° give cineole (II) (40%), dipentene (III), α- (IV), and γ- (V) -terpinene, terpinolene (VI), and constituents *T* and *U* (obtained also from pinene). With Al_2O_3 it gives (VI), (IV), limonene (VII), and (II) (trace), and with 80% HCO_2H (II) (40%), (VI), (III), (IV), *T*, and *Z*. Terpin and anhyd. (I) give (II) (11%), (IV), (III), *T*, and *Z*. α-Terpenyl acetate at 80—90° gives (IV), (VII), and possibly (VI). Dipentene hydrochloride and NH_2Ph give pure (III); terpinene dihydrochloride (VIII) gives (II) and nearly pure (IV). (VIII), from commercial terpinolene, gives (III), (IV), and traces of (VI). (II) and aq. (I) give slowly (IV), (V), and a little *T*. R. S. C.

Terpenes, sesquiterpenes, and related compounds. I. Silicon compounds of menthol and the refractivity of silicon. S. Uchida and T. Kondō (J. Soc. Chem. Ind. Japan, 1933, 36, 190—191B).—$SiCl_4$ with the calc. amounts of menthol gives *monomenthoxysilicon trichloride*, b.p. 112—113°/9 mm., *dimenthoxysilicon dichloride*, b.p. 193°/8 mm., *trimenthoxysilicon monochloride*, b.p. 244—245°/10 mm., and *tetramenthoxysilicon*, m.p. 93°, b.p. 264°/7 mm. The at. refractivity of Si found from the three first of these is 5·114. A. A. L.

Picrocrocin, the terpene-glucoside of saffron, and the biogenesis of carotenoid carboxylic acids. R. Kuhn and A. Winterstein (Naturwiss., 1933, 28, 527).—Picrocrocin (I), $C_{16}H_{26}O_7$, $[\alpha]_D$ −58° in H_2O [*Ac₄* derivative, $C_{24}H_{34}O_{11}$, m.p. 143° (*semicarbazone*, $C_{25}H_{37}O_{11}N_3$, m.p. 105°)], is decomposed by acids or alkalis without addition of H_2O to glucose (1 mol.) and *safranal* (II), $C_9H_{13}\cdot CHO$ (1 mol.). (II) is monocyclic, with two double linkings; it is oxidised by $KMnO_4$ to $[\cdot CHMe\cdot CO_2H]_2$ and AcOH and by controlled catalytic hydrogenation yields β-*cyclo*citral. Autoxidation produces β-*cyclo*geranic acid. (II) is therefore a *dihydro*-β-cyclo*citral* ($\Delta^{1:5}$-m-*terpadien*-2-*al*). (I), which gives no CH_2O with $Pb(OAc)_4$, is considered to be 5-β-*glucosido*-Δ-1-m-*terpen*-2-*al*. As (I) is regarded as an oxidative degradation product of carotenoid carboxylic acids, the above ring structure is assumed to be present in the latter. R. N. C.

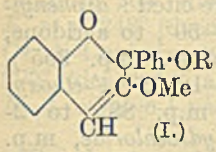
Stability of the tetrahydrofuran ring. I. Fission of the oxide linking in tetrahydrofurfuryl alcohol. Derivatives of αβε-trihydroxypentane. R. Paul (Bull. Soc. chim., 1933, [iv], 53, 417—426).—Partly a detailed account of work already published (this vol., 397). Tetrahydrofurfuryl bromide and powdered KOH give 2-*methylenetetrahydrofuran*, b.p. 82—83°, immediately hydrolysed by 2*N*-H_2SO_4 to $OH\cdot[CH_2]_3\cdot COMe$, b.p. 115—117°/29 mm. (*semicarbazone*, m.p. 155—157°). R. S. C.

Orientation in the furan nucleus. VI. β-Substituted furans. H. Gilman and R. R. Burtner (J. Amer. Chem. Soc., 1933, 55, 2903—2909; cf.

this vol., 505).—The prep. of Me coumalate, Me bromocoumalate, and furan-2 : 4-dicarboxylic acid (I) is described. (I) with Cu-bronze at 285° gives 3-furoic acid (II), identical with the natural product [*acid chloride* (III), b.p. 65°/47 mm., m.p. 29°; *amide*, m.p. 169°], the *Et* ester, b.p. 65—67°/14 mm., of which is nitrated (here, as below, by fuming HNO_3 in Ac_2O at —15°) to *Et 2-nitro-4-furoate*, m.p. 56°, hydrolysed to the corresponding *acid*, m.p. 138°, also obtained by nitration of (II). (II) and Br in $CHCl_3$ give *2-bromo-4-furoic acid*, m.p. 130°, also obtained from (I) by way of the HgCl-compound. The Me_2 ester of (I) with Br at 160° gives an ester, hydrolysed to *5-bromofuran-2 : 4-dicarboxylic acid*, m.p. 250°, reduced to (I) by Zn dust and hot, aq. NH_3, and giving by way of the HgCl-compound *2-bromo-3-furoic acid*, m.p. 158°. Hydrogenation of (III) yields *3-furfuraldehyde* (IV), b.p. 70—72°/43 mm., 144°/732 mm. (*phenylhydrazone*, m.p. 149·5°), nitrated to *2-nitro-4-furfurylidene diacetate*, m.p. 87°. Nitration of the *diacetate*, m.p. 50°, b.p. 130°/15 mm., of (IV) gives an oil, hydrolysed by acid to *2-nitro-4-furfuraldehyde*, m.p. 76°, the *hydrazone*, m.p. 122° (decomp.), of which affords (Wolff–Kishner) 3-methylfuran (2-*HgCl*-compound, m.p. 142°), nitrated to 2-nitro-3-methylfuran. These reactions allow formulation of the following rules for the substitution of β-substituted furans: if the group in the β-position is *o*-*p*-directing in the C_6H_6 series, the substituent enters the contiguous α-position; if it is *m*-directing, the more remote α-position is substituted.

R. S. C.

Pyrenium salts. XX. Oxidation of pyrenium salts. W. Dilthey and W. Höschen (J. pr. Chem., 1933, [ii], **138**, 42—50; cf. A., 1931, 1305).—3-*Methoxyflavenium perchlorate*, m.p. 195—196° [from the chloride (modified prep.)], gives with MeOH or EtOH the *ethers* (I), R=*Me*, m.p. 117—118°, and *Et*, m.p. 126°, and with H_2O_2 in AcOH affords o-*benzoyloxyphenylacetic acid*, m.p. 142°, slightly bitter, hydrolysed to BzOH and *o*-hydroxyphenylacetic acid, bitter, and obtained also by oxidation of 3-*hydroxyflavenium perchlorate*, m.p. 226—227° (decomp.), which is prepared from *o*-$OH{\cdot}C_6H_4{\cdot}CHO$, $CH_2Bz{\cdot}OMe$, and HCl. 7-*Hydroxy-3-methoxyflavenium perchlorate*, m.p. 245—246°, gives, when oxidised, 4-*hydroxy-2-benzoyloxyphenylacetic acid*, m.p. 186—187°, but 7-*hydroxy-3 : 4′-dimethoxyflavenium picrate*, m.p. 249°, affords *Me 4-hydroxy-2-anisoyloxyphenylacetate*, m.p. 112—113°, hydrolysed to anisic acid. In the above oxidations H_2O_2 attacks first the 2-position. This and the results of nitration show that the charge on the pyrenium cation is isolated, if at all, on the 2-C atom.



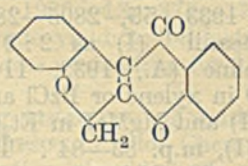
(I.)

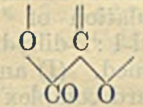
R. S. C.

Rotenone. XXV. Synthesis of tetrahydrotubanol and tetrahydrotubaic acid. H. L. Haller. **XXVI. Synthesis of the parent substances of some characteristic rotenone derivatives.** F. B. La Forge (J. Amer. Chem. Soc., 1933, **55**, 3032—3035, 3040—3048; cf. this vol., 163).—XXV. $MgBu^{\beta}Br$ and 2 : 6-dimethoxybenzonitrile (modified prep.) in Et_2O–PhMe give 2 : 6-*dimethoxyphenyl Bu*$^{\beta}$ *ketone*, b.p. 136°/1 mm. (does not give an oxime or a semicarbazone), reduced (Clemmensen) to a *substance*, (?) δε-*di*-(2 : 6-*dimethoxyphenyl*)-βη-*dimethyloctane*, m.p. 188°, and 2 : 6-*dimethoxy*iso*amylbenzene*, b.p. 102°/1 mm., demethylated by HI, or, better, $AlCl_3$ in PhMe, to tetrahydrotubanol.

XXVI. 2 : 2′-Dimethoxybenzoin and $SOCl_2$ give 2 : 2′-*dimethoxydesyl chloride*, m.p. 87°, reduced by Zn dust and KOH–EtOH–H_2O to 2 : 2′-*dimethoxydeoxybenzoin*, m.p. 57° (also obtained by a similar reduction of 2 : 2′-dimethoxybenzoin), which with HI and a little PhOH gives 2 : 2′-*dihydroxydeoxybenzoin anhydride* (I), m.p. 95—98°. Salicylaldehyde $OMe{\cdot}CH_2$ ether (modified prep.), b.p. 128—130°/11 mm., and KCN in aq. EtOH give 2 : 2′-*dimethoxybenzoin Me ether*, b.p. 200—210°/1 mm., hydrolysed to 2 : 2′-*dihydroxybenzoin*, m.p. 142—149°, which is reduced to 2 : 2′-*dihydroxydeoxybenzoin* (II), m.p. 104° [anhydride = (I)]. (I), NaOEt, and $CH_2Br{\cdot}CO_2Et$ give *anhydro-2-hydroxy-2′-carbomethoxydeoxybenzoin*, m.p. 170°; this is also obtained similarly from (II), but longer heating gives also α-*benzopyrano*-γ-*benzopyrone* (III), reduced (Zn dust, KOH) to 2′-*hydroxy-2-carbomethoxydeoxybenzoin*, m.p. 129°, which with hot KOH–H_2O_2 gives 2-carbomethoxyphenylacetic acid. (II) and $COCl{\cdot}CO_2Et$ in C_5H_5N give α-*benzopyrono*-γ-*benzopyrone* (IV), m.p. about 240° (decomp.), colourless. *Ethylene ethers* of the following were prepared: *disalicylaldehyde*, m.p. 130° (*oxime*, m.p. 170°), 2 : 2′-*dihydroxybenzoin*, m.p. 165° (5-*Ac* derivative, m.p. 165°), 2 : 2′-*dihydroxybenzil*, m.p. 200°, and 2 : 2′-*dihydroxydesyl chloride*, m.p. 105°.

(III.)





(IV.)

R. S. C.

Calorimetric determination of simple and polynuclear derivatives of pyrrole. A. Stern and G. Klebs (Annalen, 1933, **504**, 287—297).—The heats of combustion of mono- and di-nuclear pyrroles can be calc. from the characteristics of the individual at. linkings. This is true for di-derivatives when the nuclei are formed in the 1- or 2-position as pyrromethanes, directly as in the diphenyl type or as pyrromethenes. Tetrapyrranes behave similarly. The thermochemical characteristics of $CH_2{\cdot}CN$ (β), C⋮N (β), $\cdot CH_2{\cdot}CH(CO_2Et)_2$ (β), C·O·H (β), $:N{\cdot}NH_2$, CO·NH·C:O, C·NH·C (in ring), C·N:C (in ring), CO·O·CO, and C:N·OH (α) are 297·1, 30·0, 995·7, 4·7, 159·3, 77·0, 94·0, 90·0, 11·2, and 69·2 kg.-cal., respectively.

H. W.

Action of Grignard's reagent on *N*-methylpyrrolidone. Synthesis of substituted pyrrolines. R. Lukeš (Chem. Listy, 1933, **27**, 97—100, 121—126).—1-Methylpyrrolid-2-one yields with MgRBr (R=alkyl) a mixture of dialkylpyrrolidine and alkylpyrroline, whilst with MgR′Br (R′=aryl) only pyrroline derivatives are obtained. The following compounds have been prepared by this reaction: 1 : 2-dimethyl-$\Delta^{2:3}$-pyrroline (*perchlorate*, m.p. 238°); 1 : 2 : 2-*trimethylpyrrolidine*, b.p. 130—135° [*picrate*, m.p. 250° (decomp.)]; 1-*methyl-2-ethyl*-$\Delta^{2:3}$-*pyrroline*, b.p. 40—41°/10 mm. (*perchlorate*, m.p. 209°; *chloroaurate*, m.p. 115—117°); 1-*methyl*-2 : 2-*diethylpyrrolidine*, b.p. 168° [*picrate*, m.p. 233° (decomp.); *chloroaurate*, m.p. 159—163°]; 1-*methyl*-2-n-*propyl*-$\Delta^{2:3}$-*pyrroline*, b.p. 82°/30 mm.; 1-*methyl*-2 : 2-*di*-n-*propylpyrrolidine*, b.p. 206°/738 mm. (*picrate*, m.p. 130°); 2-*phenyl*-1-*methyl*-$\Delta^{2:3}$-*pyrroline*, b.p. 112°/13 mm. (*hydrochloride*, $+H_2O$, m.p. 96°; *perchlorate*, m.p. 117—118°; *chloroaurate*, m.p. 95—97°; *chloroplatinate*, m.p. 140—141°). R. T.

Cleavage of carbonyl compounds by alkalis. IX. Phenacylpyridinium salts. S. H. Babcock and R. C. Fuson (J. Amer. Chem. Soc., 1933, **55**, 2946—2948; cf. this vol., 74).—Phenacylpyridinium chloride with 20% NaOH gives BzOH and a solution, whence by alkaline $K_3Fe(CN)_6$, followed by Br, 3 : 5-dibromo-1-methylpyridone is obtained. p-*Bromo*-α-*methylphenacylpyridinium bromide*, m.p. 232—233° (from C_5H_5N and α : *p*-dibromopropiophenone), leads to *p*-$C_6H_4Br{\cdot}CO_2H$ and *N*-ethylpyridone, b.p. 124°/9 mm. (3 : 5-Br_2-compound, m.p. 109°), also prepared from C_5H_5N and Et_2SO_4. R. S. C.

Alleged formation of aliphatic keto-anils. J. T. Murray, W. F. Short, and R. Stansfield (J. Amer. Chem. Soc., 1933, **55**, 2805—2806).—Formulation of "acetoneanil" (I) as 2 : 2 : 4-trimethyl-1 : 2-dihydroquinoline (A., 1932, 1142) is confirmed. (I) and Bz_2O in xylene or BzCl and the Grignard complex from (I) and MgMeI in Et_2O give the N-*Bz* derivative of (I), m.p. 83—84°. The Ac derivative, m.p. 54°, b.p. 163—164°/15 mm., of (I) gives (I) on hydrolysis and 2 : 4-dimethylquinoline with dry HCl at 180°. The supposed benzyl derivative (A., 1930, 1571) is impure (I). R. S. C.

Derivatives of 8-aminoquinoline as antimalarials. I. Effect of alkyl [groups] in position 6 on the chemotherapeutic properties. O. J. Magidson and I. T. Strukov (Arch. Pharm., 1933, **271**, 359—369).—8-Nitro-6-methoxy- and -6-ethoxyquinoline (I) are prepared from *m*-nitro-*p*-acetanisidide and -phenetidide in 56·5 and 71% yield, respectively. These are reduced by $(NH_4)_2S$ in EtOH (79% yield) or other reagents to 8-amino-6-methoxy- and 8-*amino*-6-*ethoxy-quinoline* (II), b.p. 172—176°/2 mm., m.p. 60° [*picrate*, m.p. 195—196° (decomp.); *benzylidene* and *Ac* (III) derivatives, m.p. 113—114° and 144°, respectively]. (II) with NaOEt at 150—160°, followed by *iso*amyl bromide at 130—140°, gives 8-iso*amylamino*-6-*ethoxyquinoline* (IV), b.p. 207—210°/8 mm. (*hydrochloride*). 8-Aminoquinoline and $CH_2Cl{\cdot}CH_2{\cdot}NEt_2$,HCl at 120° give 8-β-(diethylamino)ethylaminoquinoline (V), b.p. 163—164°/4 mm. (II) gives similarly 8-β-(*diethylamino*)-*ethylamino*-6-*ethoxyquinoline* (VI), b.p. 235—238°/8—9 mm. [dihydrochloride, m.p. 210—212° (decomp.); *NO*-derivative, m.p. 127°]. (I) and H_2SO_4 (65% by wt.) at 120—140° give 8-*nitro*-6-*hydroxyquinoline* (VII), m.p. 230° (decomp.). (VI) and HBr at 145—155° give 8-β-(*diethylamino*)*ethylamino*-6-*hydroxyquinoline hydrobromide*, $+2H_2O$, m.p. 108—114°. The Na or K salt of (VI) with the appropriate alkyl halide at 100° gives the following *ethers* of (VII): Pr^{β}, m.p. 70°; Pr^{α}, m.p. 89°; Bu^{α}, m.p. 90°; iso*amyl*, m.p. 83°; n-*octyl*, m.p. 61°; and *allyl*, m.p. 114·5°. These are reduced by $(NH_4)_2S$ in EtOH to the following 8-*amino*-6-*hydroxyquinoline ethers*: Pr^{β} (*dihydrochloride*); Pr^{α}, b.p. 188—189°/3·5 mm.; Bu^{α}, b.p. 197—202°/5 mm.; iso*amyl*, b.p. 195—197°/2—3 mm., m.p. 53°; n-*octyl*, b.p. 212—217°/1 mm. (*dihydrochloride*); and *allyl* (*dihydrochloride*). Thence were prepared the following 8-β-(*diethylamino*)*ethylamino*-6-*hydroxyquinoline ethers*: Pr^{β}, b.p. 205—208°/2 mm. (*dihydrochloride*, hygroscopic); Pr^{α}, b.p. 210—211°/2 mm. (*dihydrochloride*); Bu^{α}, b.p. 210—213°/ ? mm. (*dihydrochloride*); iso*amyl*, b.p. 238—245°/2—3 mm.; n-*octyl*, b.p. 255—262°/1 mm.; and *allyl* (*meconate*). The val. of the OR-derivatives of (VI) as antimalarials (canary tests) falls as R changes from H through Me to higher alkyl groups, being very low if R is Pr or Bu, and 0 if R is *n*-octyl or allyl. 8-Amino-6-methoxyquinoline and *N*-*iso*amyl and -di*iso*amyl derivatives are inactive. R. S. C.

Synthesis of quinoline derivatives. III. K. Dziewoński and J. Mayer (Rocz. Chem., 1933, **13**, 370—374).—$COPhPr^{\alpha}$ when heated at 240° for 4 hr. with PhNCS yields 4-*anilino*-2-*phenyl*-3-*methylquinoline*, m.p. 158° [*sulphate*, m.p. 180° (decomp.); *picrate*, m.p. 240° (decomp.); 4-N-*NO*-, m.p. 120°, 4-N-*Ac*, m.p. 170°, and 6-NO_2-derivative, m.p. 240° (*sulphate*, m.p. 296° decomp.)], converted by fusion with NaOH into the corresponding 4-OH-derivative. R. T.

Simplified preparation of acridones and 9-chloroacridines. W. Dirscherl and M. Thron (Annalen, 1933, **504**, 297—304).—Diphenylamine-*o*-carboxylic acids are converted by PCl_5 into the corresponding chlorides, which when heated alone or in solution pass into acridone hydrochlorides, from which HCl is removed at a higher temp. or by KOH–EtOH, yielding acridones. If the chloride is heated with the chlorides of P (mainly $POCl_3$), 9-chloroacridines result, 1 mol. of PCl_5 sufficing for the whole change. The following examples are cited: *diphenylamino*-o-*carboxyl chloride*, m.p. 48—50°, to acridone, m.p. 355° (*hydrochloride monohydrate*, m.p. 355°), and 9-chloroacridine, m.p. 119—120⁰; 4′-*ethoxydiphenylamine*-o-*carboxyl chloride*, m.p. 88°, to 2-*ethoxyacridone*, m.p. 258—259° [*hydrochloride*, m.p. 190° (decomp.), and its *monohydrate*, m.p. 225—226°], and 9-*chloro*-2-*ethoxyacridine*, m.p. 147—148°; 4′-*methyldiphenylamine*-o-*carboxyl chloride*, m.p. 66° (decomp.), to 2-*methylacridone*, m.p. 345° (*hydrochloride* and its *monohydrate*, m.p. 320°), and 9-*chloro*-2-*methylacridine*, m.p. 121—122°; 4-*nitro*-4′-*ethoxydiphenylamine*-2-*carboxylic acid*, m.p. 195°, to the *chloride*, m.p. 118—120°, decomp. 125—130°, and thence to 7-*nitro*-2-*ethoxyacridone*, m.p. 365° (*hydrochloride*), and 9-*chloro*-7-*nitro*-2-*ethoxyacridine*, m.p. 196°; 2-methyldiphenylamine-*o*-carboxylic acid to 4-*methylacridone hydrochloride* and 4-methylacridone, m.p. 343°. H. W.

Mechanism of the formation of acridones by condensation of *o*-nitrobenzaldehydes with aromatic hydrocarbons. III. I. Tanasescu and (Mme.) M. Macarovici. **IV. Reply to Lehmstedt.** I. Tanasescu (Bull. Soc. chim., 1933, [iv], **53**, 372—

380, 381—384; cf. A., 1932, 169).—III. 2 : 4-CHO·$C_6H_3(NO_2)_2$, PhMe, and H_2SO_4 give the substance, m.p. 105° (*A*), and 3-*nitro-6-methylacridone*, m.p. > 300°, which with $POCl_3$ and $NPhMe_2$ gives (probably) impure 3-*nitro*-9-p-*dimethylanilino*-6-*methylacridine*, m.p. 200° after softening at 170°. PhCl gives similarly (*A*) and 6-*chloro*-3-*nitroacridone*, m.p. > 300°, which gives similarly 6-*chloro*-3-*nitro*-9-p-*dimethylanilinoacridine*, m.p. 235° after softening at 230°. Similarly were obtained 6-*bromo*-3-*nitro*-, m.p. > 300°, and 2-*chloro*-6-*methyl-acridone*, decomp. 200°, and 2-*chloro*-9-p-*dimethylanilino*-6-*methylacridine*, m.p. 261°. 5-Chloro-2-nitrobenzaldehyde, PhMe, and H_2SO_4 give 2-*chloro*-N-*oxy*-p-*tolylanthranil*, m.p. > 300°, a yellow *substance*, and (*A*).

IV. Polemical (cf. A., 1932, 754). R. S. C.

Heterocyclic ketones. I. β-Aminoketones and related pyrazolines derived from benzylidene- and furfurylidene-acetone. H. B. NISBET and C. G. GRAY (J.C.S., 1933, 839—840; cf. A., 1928, 301).—Furfurylideneacetone, $NHMe_2$,HCl and paraformaldehyde in EtOH give *α-dimethylamino-ε-furyl-Δ^{α}-penten-γ-one hydrochloride*, m.p. 170° (*phenylhydrazone*, m.p. 185°). The following are similarly obtained: *α-diethylamino-*, m.p. 125°, and *α-piperidino-ε-furyl-Δ^{α}-penten-γ-one hydrochloride*, m.p. 192° (darkens) [*phenylhydrazone* (I), m.p. 182°]. The phenylhydrazone of α-diethylamino-ε-phenyl-Δ^{α}-penten-γ-one is not a pyrazoline, since it gives NH_2Ph on reduction. The phenylhydrazone of the corresponding piperidino-compound in hot AcOH gives the *pyrazoline*, m.p. 60°. The *pyrazoline hydrochloride*, m.p. 158°, is similarly obtained from (I). A. A. L.

Co-ordination compounds of oximes. III. Compounds of 4-oximino-1-phenyl-3-methyl-5-pyrazolone with the alkali metals, nickel, and thallium. O. L. BRADY and (MISS) M. D. PORTER (J.C.S., 1933, 840—842).—The prep. is described of *Li*, m.p. 203° (decomp.), *Na*, m.p. 230° (decomp.), *K*, m.p. 248° (decomp.), *Rb*, m.p. 233° (decomp.), and *Cs di-4-oximino-1-phenyl-3-methyl-5-pyrazolone*, m.p. 209° (decomp.), and *Tl*, m.p. 219° (decomp.), and *Ni 4-oximino-1-phenyl-3-methyl-5-pyrazolone*. A. A. L.

Synthesis of 5-α-naphthyl-5-ethylhydantoin. DE W. T. KEACH (J. Amer. Chem. Soc., 1933, 55, 2979—2981).—α-$C_{10}H_7$·COEt, anhyd. HCN, and NH_3 in EtOH give *α-amino-α-1-naphthyl*-n-*butyronitrile* (*hydrochloride*), which with KCNO in AcOH gives *α-carbamido-α-1-naphthyl*-n-*butyronitrile*, m.p. 201—202°, hydrolysed by hot HCl to *5-α-naphthyl-5-ethylhydantoin*, not hypnotic, m.p. 222—223°. R. S. C.

Brazilin and hæmatoxylin. XIII. Phenoxycitramalic acids. P. PFEIFFER and H. HOYER (J. pr. Chem., 1933, [ii], 138, 69—80; cf. this vol., 832).—Et *m*-anisoxyacetylcyanoacetate, KCN, $(NH_4)_2CO_3$, and CO_2 (pressure) in EtOH at 80—90° give m-*anisoxyacetamide*, m.p. 110°. *Et* γ-m-*anisoxyacetoacetate*, b.p. 170—180°/0·5 mm. (*Cu* salt, m.p. 121°) (best obtained from Et *m*-anisoxyacetate, $CH_2Cl·CO_2Et$, and Zn filings), similarly gives *Et* 5-m-*anisoxymethylhydantoin-5-acetate*, m.p. 133—134°, hydrolysed by cold aq. NH_3 to 5-m-*anisoxyhydantoin-5-acetamide*, m.p. 203—204°, and slowly by hot 25% KOH to α-m-*anisoxymethylasparagine*, m.p. about 170° (decomp.) (sinters from 153°) (*Ba* salt, $+H_2O$), which with HNO_2 gives γ-m-*anisoxycitramalic acid*, an oil (*Ba* salt, $+H_2O$). OPh·CH_2·CO_2Et, $CH_2Br·CO_2Et$, and Zn give Et γ-phenoxyacetoacetate (not isolated pure), whence were prepared *Et 5-phenoxymethylhydantoin-5-acetate*, $+H_2O$ (lost at 120°), m.p. (anhyd.) 157—158°, the corresponding *acid*, m.p. 238—239°, *α-phenoxymethylasparagine*, m.p. 230—240° (decomp.) (*Ba* salt, $+H_2O$), and *γ-phenoxycitramalic acid*, m.p. 173—174° (*Me_2* ester, m.p. 67—68°). R. S. C.

Amino-acids and related compounds. VI. Electrolytic oxidation of glyoxalinylpropionic acid. Y. TAKAYAMA (Bull. Chem. Soc. Japan, 1933, 8, 189—195; cf. this vol., 720).—Electrolytic oxidation of glyoxalinylpropionic acid in 2*N*-H_2SO_4 gives succinic acid (> 30·4%), the semi-aldehyde thereof, NH_3, and NH_2-compounds (12·5%), including carbamide (1·3%). R. S. C.

2 : 5-Dihydroxy-3 : 4 : 5 : 6-tetrahydropyrimidine. J. S. TURSKI and P. KAŹMIERCZAK (Rocz. Chem., 1933, 13, 375—378).—Dichlorohydrin and carbamide yield 2 : 5-*dihydroxy*-3 : 4 : 5 : 6-*tetrahydropyrimidine* on heating for 1 hr. at 135° in C_5H_5N. R. T.

Ring structure of uridine. P. A. LEVENE and R. S. TIPSON (J. Biol. Chem., 1933, 101, 529—534).—Acetylation of uridine (I) affords *triacetyluridine* (cf. A., 1911, i, 96), catalytically reduced to triacetyldihydrouridine, the Me derivative of which on simultaneous hydrolysis and oxidation (Br–HBr) yields a mixture of trimethylribonolactone and its Me ester. The rotation of the lactone during hydrolysis indicates a γ-lactone, confirmed by formation of *dl*-dimethoxysuccinic acid on oxidation with HNO_3 under conditions which give trimethoxyglutaric acid from trimethyl-δ-ribonolactone (A., 1931, 1399). Hence (I) is a ribofuranoside. F. O. H.

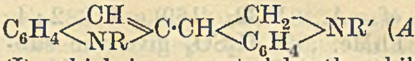
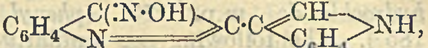
Pyrimidines. CXXXIII. Reactions and derivatives of ethyl 2-keto-4-phenyl-6-methyl-1 : 2 : 3 : 4-tetrahydropyrimidine-5-carboxylate. K. FOLKERS and T. B. JOHNSON (J. Amer. Chem. Soc., 1933, 55, 2886—2893; cf. this vol., 616).—Thiocarbamide, $CH_2Ac·CO_2Et$, PhCHO, and a little HCl in EtOH give *Et 2-thio-4-phenyl-6-methyl-1 : 2 : 3 : 4-tetrahydropyrimidine-5-carboxylate* (I), m.p. 207—208°. Methylcarbamide affords similarly *Et 2-keto-4-phenyl-1 : 6-dimethyl-1 : 2 : 3 : 4-tetrahydropyrimidine-5-carboxylate*, m.p. 176—178°. MeNCO and Et β-aminocrotonate give α-(*N*-methylcarbamyl)-β-iminobutyrate. (I) with Br in $CHCl_3$ at 5° gives the 5 : 6-*Br_2-compound*, m.p. 180—181°, and with $POCl_3$ at 100° gives *Et 2-chloro-4-phenyl-6-methyl-1 : 4-dihydropyrimidine-5-carboxylate*, readily hydrolysed. This with cold NaOMe–MeOH–C_6H_6 gives *Et 2-keto-4-phenyl-3 : 6-dimethyl-1 : 2 : 3 : 4-tetrahydropyrimidine-5-carboxylate*, m.p. 159—160° (unchanged by HCl–EtOH), and with NH_3 affords *Et 2-imino-4-phenyl-6-methyl-1 : 2 : 3 : 4-tetrahydropyrimidine-5-carboxylate*, m.p. 85—87°, decomposed slowly by cold, and rapidly by hot, dil. HCl. All m.p. are corr. R. S. C.

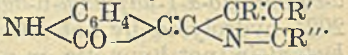
Mechanism of the narcosis induced by hypnotics. I. Synthesis of coloured derivatives of phenobarbital. (MISS) M. RISING, J. H. SHROYER, and J. STIEGLITZ (J. Amer. Chem. Soc., 1933, **55**, 2817—2820).—Phenobarbital (5-phenyl-5-ethylbarbituric acid) gives the 5-m-*nitrophenyl*, m.p. 279—280°, and thence by hydrogenation (PtO_2) the 5-m-*aminophenyl*, m.p. 207·5—208·5°, derivatives. The diazotised base, coupled with β-naphthol, resorcinol, salicylic acid, and tyrosine, gives *dyes*, approx. m.p. 302°, 248—250°, 250—251°, and 200° (decomp. 216—222°), respectively, which are pharmacologically inactive. All m.p. are corr. R. S. C.

Spatial structure of the platinum–tetrammine salts. F. ROSENBLATT and A. SCHLEEDE (Annalen, 1933, **505**, 51—58).—The optical activity observed by Reihlen is due to asymmetry of the substituents, and does not establish the tetrahedral configuration. Asymmetry of the complex salts is commensurate with the plane arrangement of the atoms united to Pt. Thus if the N atoms of $C_2H_4(NH_2)_2$ lie in the same plane as Pt, four arrangements are possible, viz. (i) with both $\cdot C_2H_4\cdot$ groups in the plane of Pt; (ii) with one above and one below the plane; (iii) with both above the plane; (iv) with one above and one in the plane of the Pt. If, as in Reihlen's compounds, the group $\cdot C_2H_4\cdot$ is unsymmetrically substituted, each of these types renders possible *cis*- and *trans*-isomerism and four of the eight sterically possible forms are asymmetric.

K_2PtCl_6 and 2 : 2′-dipyridyl (I) yield the *compound* $Pt(C_{10}H_8N_2)Cl_2$, into which NH_3, C_5H_5N, or a further mol. of (I) could not be introduced. The *salt* [Pb dip en]Cl_2 is converted into the corresponding bromocamphorsulphonate (II), which is not resolved by crystallisation from H_2O. (II) is converted into the *compounds* [Pt dip en]I_2,H_2O and Pt dip$(CN)_2$. H. W.

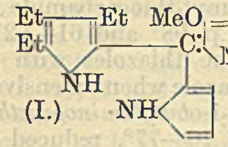
The viologen indicators. L. MICHAELIS and E. S. HILL (J. Gen. Physiol., 1933, **16**, 859—873).—Various viologen indicators (quaternary bases derived from 4 : 4′-dipyridyl) have been prepared and their oxidation–reduction (I) properties studied. They differ from other indicators of this type in that the colour is exhibited by the reduced form and also in that the (I) potential of these substances is independent of p_H. The (I) potential of a solution which causes coloration to the extent of A% of the max. colour is $E_0 - 0{\cdot}06 \log A/(100-A)$, where E_0 is the normal potential of the viologen used. Vals. for E_0 (at 30°) for methyl-, ethyl-, betaine-, and benzyl-viologens are given. Some properties of the last three compounds (NN′-*diethyl*-, NN′-*dibetaine*-, and NN′-*dibenzyl*-4 : 4′-*dipyridylium dichloride*, respectively) are recorded. A. W.

Constitution of dimeric indoles. O. SCHMITZ-DUMONT, K. HAMANN, and K. H. GELLER (Annalen, 1933, **504**, 1—19).—The quant. depolymerisation of di-indole (I) to indole, the presence in it of two active H, and the observation that only 1 NH can be acylated or caused to react with PhNCO indicate the structure  $C_6H_4{<}\begin{matrix}CH\\NR\end{matrix}{>}C\cdot CH{<}\begin{matrix}CH_2\\C_6H_4\end{matrix}{>}NR'$ (*A*; R=R′=H) for (I), which is supported by the ability of skatole and 1- and the inability of 2-methylindole to dimerise. (I) is transformed by $NaNO_2$ and AcOH into *dinitrosodi-indole* (II), m.p. 160—162° (decomp.), converted by boiling EtOH into *nitrosodi-indole* (*A*; R=H, R′=NO), m.p. 121—122° after softening at 117°. *Nitrosoacetyldi-indole* (II) (*A*; R=NO, R′=Ac), m.p. 126—128° (decomp.), and *nitrosobenzoyldi-indole*, m.p. 150—151° (decomp.), are derived from the acyldi-indoles and $NaNO_2$ in AcOH. There are prepared analogously *dinitroso*- (III), m.p. 127—129° (decomp.), *nitroso*-, m.p. 170° (decomp.), and *nitrosoacetyl*-, m.p. 127—129° (decomp.), *-di-7-methylindole, dinitroso*-, m.p. 134° (decomp.), *nitroso*-, m.p. 145—146° (decomp.), and *nitrosoacetyl*-, m.p. 67—69° (decomp.), *-diskatole*. (IV) is converted by KOH–EtOH under N_2 at room temp. mainly into 2 : 3-*di-indolyl*, m.p. 206° (slight decomp.) after softening at 204°, the constitution of which follows from its transformation by $NaNO_2$ in AcOH–HCl into *oximino*-2 : 3-*di-indolyl* (V),  $C_6H_4{<}\begin{matrix}C(:N\cdot OH)\\N\end{matrix}{>}C\cdot C{<}\begin{matrix}CH\\C_6H_4\end{matrix}{>}NH$, m.p. 242—243° (decomp.) (obtained also as a secondary product of the above reaction) [*Ac_2 derivative*, m.p. 214—215° (decomp.), converted by conc. HCl into (VI); *Bz_2 compound*, m.p. 228—229° (decomp.)]. (V) is also obtained by oximation of indoxyl-red, into which it is converted by reduction by $Na_2S_2O_4$ to 3-*amino*-2 : 3-*di-indolyl*, not molten below 250°, and treatment of the *Ac* derivative, m.p. 200—201°, with $NaNO_2$. (II) and KOH–EtOH yield acetyldi-indole, m.p. 157—158°, and (V), whilst (III) and NaOEt afford 2 : 3-*di-7-methylindolyl*, m.p. 204—205° (decomp.), and *oximino*-2 : 3-*di-7-methylindolyl*, m.p. 244—245° (decomp.). H. W.

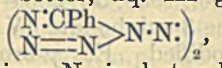
Isatin condensation products of pyrroles (pyrrole-blue). P. PRATESI (Annalen, 1933, **504**, 258—266).—Condensation does not occur between isatin (I) and 1-methyl-, 1-phenyl-, 1-ethyl-, 1-acetyl-, 2 : 5-dimethyl-, or 2 : 4 : 5-trimethyl-3-ethyl-pyrrole in AcOH or H_2SO_4. (I) condenses with 2 : 3-dimethyl-, 3-methyl-4-ethyl-, and 2 : 4-dimethyl-3-ethyl-pyrrole with loss of 1 H_2O and formation of the *substances* $C_{14}H_{12}ON_2$, $C_{15}H_{14}ON_2$, and $C_{16}H_{16}ON_2$, respectively, the mol. wt. of which could not be determined in PhOH, $PhNO_2$, or veratrole. The dyes could not be caused to react with Ac_2O and NaOAc or AcCl. Their absorption spectra are closely similar. They are therefore formulated  $NH{<}\begin{matrix}C_6H_4\\CO\end{matrix}{>}C{:}C{<}\begin{matrix}CR{:}CR'\\N{=}CR''\end{matrix}$. H. W.

Catalytic oxidation of cysteine with copper. K. A. C. ELLIOTT (Biochem. Z., 1933, **263**, 230).—Andresen and Nielsen (this vol., 793) used an unsuitable respiration vessel and failed to prevent irregular diffusion of O_2. Hence their criticism of the author's work (A., 1930, 869) cannot be maintained. W. McC.

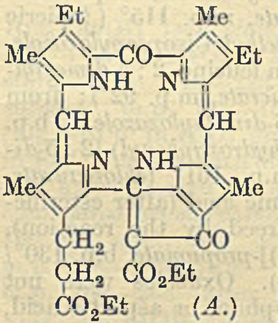
Constitution of prodigiosin. H. RAUDNITZ (Naturwiss., 1933, **21**, 518).—In opposition to the views of Wrede (A., 1932, 1043) prodigiosin is formulated as 2 : 3 : 4-triethylpyrryl-(5)-3′-methoxy-(2′)-pyrryl-(2″)-pyrrylmethane (I).


(I.)

W. O. K.

Derivatives of 1-aminotetrazole. R. Stollé [with A. Netz, O. Kramer, S. Rothschild, H. Erbe, and O. Schick] (J. pr. Chem., 1933, [ii], **138**, 1—17).—Benzylidenebenzhydrazide chloride, CClPh:N·N:CHPh, and NaN_3, when heated in EtOH for 1 hr. only, give benzylidenebenzhydrazide azide, N_3·CPh:N·N:CHPh. 1-Amino-5-phenyltetrazole (*Ac_2* derivative, m.p. 90°) gives with $COMe_2$ slowly the iso*propylidene* compound, m.p. 66°, and with Cl_2 and aq. $NaHCO_3$, or fresh aq. Cl_2, the N-*Cl_2*-derivative, highly explosive, which in HOCl or, better, aq. KI gives 1 : 1′-*azo*-(5-*phenyltetrazole*),  $\left(\begin{matrix}N{:}CPh\\N{=}{=}N\end{matrix}{>}N\cdot N{:}\right)_2$, deflagrates at 141°, explosive (gives N_2 in hot solvents). *p*-Tolylaldazine and Cl_2 in dry CCl_4 at 35° give p-*tolylidene*-p-*tolylhydrazide chloride*, m.p. 96°, which with NaN_3 yields 1-p-*tolylideneamino*-5-p-*tolyltetrazole*, m.p. 176°, whence by HCl 1-*amino*-5-p-*tolyltetrazole*, m.p. 141°, is obtained. This gives with HNO_2 5-*p*-tolyltetrazole and with HOCl the N-*Cl_2*-derivative, very unstable, whence 1 : 1′-*azo*-(5-p-*tolyltetrazole*), explosive (gives *p*-tolyltetrazole in hot AcOH), is obtained by KI. Similarly were prepared o-*chlorobenzylidene*-o-*chlorobenzhydrazide chloride*, m.p. 77°, 1-o-*chlorobenzylideneamino*-5-o-*chlorophenyltetrazole*, m.p. 140°, 1-*amino*-5-o-*chlorophenyltetrazole*, m.p. 173° (*Ac_2* derivative, m.p. 106°; N-*Cl_2*-derivative), 1 : 1′-*azo*-(5-o-*chlorophenyltetrazole*), m.p. 112° (decomp.), 5-o-*chlorophenyltetrazole*, m.p. 177° (decomp.), p-*nitrobenzylidene*-p-*nitrobenzhydrazide chloride* (I) (prepared from the azine by Cl_2–I in C_2HCl_5), m.p. 164°, and *azide* (II), m.p. 244° (decomp.), 1-p-*nitrobenzylideneamino*-5-p-*nitrophenyltetrazole* [from (II) in hot AcOH or (I) and NaN_3 in hot xylene], m.p. 261° (decomp.), 1-*amino*-5-p-*nitrophenyltetrazole*, m.p. 154°, 5-p-*nitrophenyltetrazole*, m.p. 222° (*benzylidene* derivative, m.p. 240°), m-*nitrobenzylidene*-m-*nitrobenzhydrazide chloride*, m.p. 144°, and *azide*, m.p. 134° (decomp.), 1-m-*nitrobenzylideneamino* - 5 - m - *nitrophenyltetrazole*, m.p. 185° (decomp.), and *anisylideneanishydrazide chloride* (III), m.p. 150°. (III) with N_2H_4,H_2O gives *anisylideneanishydrazone hydrazide*, $OMe\cdot C_6H_4\cdot C(NH\cdot NH_2){:}N\cdot N{:}CH\cdot C_6H_4\cdot OMe$, m.p. 190—200° (decomp.), which with $OMe\cdot C_6H_4\cdot CHO$ in hot EtOH forms *dianisylideneanishydrazone hydrazide*, m.p. 149°. Benzanilideimide chloride and N_2H_4 in cold ligroin give triphenyltriazole and a little *benzanilideimide hydrazide*, m.p. 90°, which with HNO_2 give diphenyltetrazole. Benzoylphenylhydrazide chloride and N_2H_4 give anilinodiphenylpyrrodiazole. *p*-Tolylidine-*p*-toluoylhydrazide and Cl_2 give di-*p*-tolylfurodiazole. R. S. C.

***iso*Phæoporphyrin *a_6*.** H. Fischer and J. Riedmair (Annalen, 1933, **505**, 87—102).—Reduction of native phæophorbide *a* or methylphæophorbide *a* with AcOH–HI at low temp. leads to iso*phæoporphyrin* a_6 (I) (previously considered to be *iso*phæoporphyrin a_5, which should be deleted from the lit.). Phæophorbide Sandoz gives a much smaller yield, since phylloerythrin, neophæoporphyrin a_6, and phæoporphyrin a_7 are also produced. Reduction in N_2 gives almost exclusively phæoporphyrin a_5 (II), whereas the highest yields of (I) are obtained in O_2, so that (I) is a secondary product. (I) is characterised by the *Me_2* ester (II), m.p. 276°, which yields a *dioxime*, hydrolysed by 20% HCl to (III). (I) is unusually stable towards reducing agents, but is very readily oxidised. Energetic degradation with KOH–MeOH leads to the known porphyrins of energetic chlorophyll degradation, indicating the same skeleton in (I) and (II) and the probable position of the second CO between two pyrrole nuclei. The presence in (I) of the isocyclic ring characteristic of chlorophyll is established by hydrolysis to a *chloroporphyrin* e, the *Me_3* ester, m.p. 270°, of which exhibits oxime displacement, does not add HCN, and is hydrolysed to (I), which is therefore *A*. (I) gives a *Bz* derivative, probably a mixed anhydride of (I) and BzOH. H. W.


(*A*.)

Constitution of cytochrome. II. K. Zeile and P. Piutti (Z. physiol. Chem., 1933, **218**, 52—64; cf. A., 1932, 627).—Treatment of hæmatoporphyrin hydrochloride with HBr–AcOH and digestion of the product with C_5H_5N gives 6 : 7-*di*-(β-*carboxyethyl*)-2(or 4)-α-*hydroxyethyl*-4(or 2)-α-*pyridinium hydrobromide*-1 : 3 : 5 : 8-*tetramethyl*-*ethylporphin* (I). By introduction of Fe and treatment with HBr–AcOH, hæmatoporphyrin is obtained. Protoporphyrin (II) forms a compound similar to (I) with 1 mol. of histidine Me ester. A series of compounds with *N* bases was obtained from the acid chlorides of porphyrins by combining the $\cdot CH_2\cdot CH_2\cdot CO_2H$ group with NH_2-acid esters as in peptide synthesis : *mesoporphyrindiamide* ; 6 : 7-*di*(*propionyl*-N-*glycine Me ester*)-1 : 3 : 5 : 8 - *tetramethyl* - 2 : 4 - *diethylporphin*, m.p. 261° (corr.) [Fe salt, m.p. 274° (corr.)]; dl-6 : 7-*di*(*propionyl* - N - *alanine Me ester*) - 1 : 3 : 5 : 8 - *tetramethyl*-2 : 5-*diethylporphin*, m.p. 276° (corr.); 6 : 7-*di*(*propionyl*-N-*glycine Me ester*)-1 : 3 : 5 : 8-*tetramethylporphin*, m.p. 289° (corr.); dl-6 : 7-*di*(*propionyl*-N-*leucine Me ester*)-1 : 3 : 5 : 8-*tetramethylporphin*, m.p. 285° (corr.) (free *acid*). All show spectra identical with that of the parent porphyrin. Hydrolysis of the HBr additive product of (II) gives *ethylhæmatoporphyrin*. With mesochlorohæmin ester in $CHCl_3$ glyoxaline affords *glyoxalinemesoesterhæmin*. Saturation of histidine in MeOH with NH_3 and treatment of the residue on evaporation with aq. HCl and $COMe_2$ gave *histidineamide dihydrochloride*, m.p. 259° (corr.). J. H. B.

Fluorescence of the porphyrins. I. H. Fink and W. Hoerburger (Z. physiol. Chem., 1933, **218**, 181—201).—The influence of various factors (concn., presence of salts, solubility) on the fluorescence of the porphyrins was studied. The p_H–fluorescence curves are plotted for four isomeric copro- and three uro-porphyrins. They are reproducible and offer a suitable means of characterisation. J. H. B.

Preparation of oxazoles from α-amino-acids. F. Wrede and G. Feuerriegel (Z. physiol. Chem., 1933, **218**, 129—141).—Oxazoles are produced by heating α-NH_2-acids with AcCl and AcOH, but better yields are obtained by addition of PCl_5 to the NH_2-acid after acetylation with Ac_2O and NaOAc. The following were prepared by this method: from glycine, 2 : 5-dimethyloxazole [*chloroaurate*, m.p. 152°; *chloroplatinate*; picrate, m.p. 124° (? picric acid)]; from alanine, 2 : 4 : 5-*trimethyloxazole*, b.p. 134° [*chloroaurate*, m.p. 93°; *picrate*, m.p. 115° (? picric acid)]; from valine, 2 : 5-*dimethyl*-4-iso*propyloxazole*, b.p. about 150° (*picrate*); from leucine, 2 : 5-*dimethyl*-4-iso*butyloxazole*, b.p. 180° (*picrate*, m.p. 92°); from phenylalanine, 4-*benzyl*-2 : 5-*dimethyloxazole*, b.p. 267°; from tyrosine, (4-*hydroxyphenyl*)-[2 : 5-*dimethyloxazolyl*-(4)]-*methane*, m.p. 161° (*chloroaurate*, m.p. 103—104°); from glutamic acid (after esterification of the CO_2H groups freed by the reaction), *Me* β-[2 : 5-*dimethyloxazolyl*-(4)]-*propionate*, b.p. 130°/12 mm. (*picrate*, m.p. 118°). Oxazoles were not obtained from cystine, tryptophan, or aspartic acid, although the last gave a *compound* $C_8H_{13}O_4N$, b.p. 205°/1 mm. J. H. B.

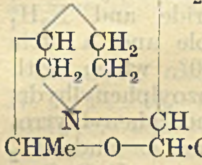
Local anæsthetics containing the morpholine ring. II. J. H. Gardner, (Miss) D. V. Clarke, and J. Semb (J. Amer. Chem. Soc., 1933, **55**, 2999—3000; cf. A., 1931, 1075).—The following are prepared: the *hydrochlorides* of β-4-*morpholinepropyl cinnamate*, m.p. 189·6° (powdered) or 178° (large crystals), *phenylurethane*, m.p. 186·8°, and α-*naphthylurethane*, m.p. 170·7°, and of β-4-*morpholine-ethyl cinnamate*, m.p. 215·2°, and *phenylurethane*, m.p. 232·3°; β-4-*morpholine-ethyl* α-*naphthylurethane*, m.p. 96·5° (*hydrochloride*, hygroscopic). All are local anæsthetics of low toxicity. R. S. C.

Formation and stability of polybromide derivatives of heterocyclic compounds. II. Polybromide ion derivatives of alkylaminobenzthiazoles obtained from *s*-phenylalkylthiocarbamides and bromine, and a comparison of the ease of nuclear substitution by bromine in 1-alkylaminobenzthiazolium and 1-imino-2-alkyl-1 : 2-dihydrobenzthiazolium ions. M. O. Farooq, R. F. Hunter, and S. T. H. Jaffery (J. Indian Chem. Soc., 1933, **10**, 189—196).—NHPh·CS·NHEt with excess of Br in hot $CHCl_3$ affords 1-*ethylaminobenzthiazole hydrotetrabromide*, m.p. 90°, which contains a $Br_4^{\ominus}$ ion [also obtained from 1-*ethylaminobenzthiazole hydrobromide*, m.p. 219—220° (prepared from the base and HBr) and excess of Br in warm $CHCl_3$], converted by H_2SO_3 into 1-ethylaminobenzthiazole, m.p. 93—94° (lit., 87—88°), and by boiling EtOH–H_2O into 5-bromo-1-ethylaminobenzthiazole as a result of the high reactivity of the *p*-position to the ring N atom in the thiazolium ion (cf. A., 1930, 483). Similarly, NHPh·CS·NHPr$^{\alpha}$ (I) affords 1-n-*propylaminobenzthiazole hydropentabromide*, m.p. 57—59°, which loses Br over KOH to give the *hydrotribromide*, m.p. 57° [also obtained from (I) and a lower concn. of Br], further reduced by H_2SO_3 to the base. *s*-Phenyl-*iso*butyl- and -*iso*amyl-thiocarbamide and Br afford *hydrotribromides*, m.p. 98° and 61—62°, respectively, both reduced to the thiazoles with H_2SO_3. 1-*iso*-Butylaminobenzthiazole when extensively brominated affords 5-*bromo*-1-iso*butylaminobenzthiazole hydropentabromide*, m.p. 76—77°, reduced to 5-bromo-1-*iso*butylaminobenzthiazole (A., 1927, 263). *s*-Phenyl-*n*-hexylthiocarbamide, m.p. 110° (lit., 103—104°), affords an unstable *hydropentabromide*, m.p. 66—67°, reduced (H_2SO_3) to 1-*n*-hexylaminobenzthiazole, m.p. 67—68° (lit., 57°). The -*n*-heptylthiocarbamide, m.p. 78° (lit., 70—71°), gives an indefinite Br-additive *compound*, m.p. 73—74°, reduced to 1-*n*-heptylaminobenzthiazole, m.p. 61—62° (lit., 55°). J. L. D.

Synthesis of nornicotine and nicotine. L. C. Craig (J. Amer. Chem. Soc., 1933, **55**, 2854—2857).—The prep. of Na pyridine-3-sulphonate (V catalyst; 35—40% yield) is modified. Et γ-bromopropyl ether forms a Grignard reagent normally, which with β-picolinonitrile gives 3-*pyridyl* γ-*ethoxypropyl ketone*, b.p. 141—143°/5 mm., the oily oxime of which is reduced (EtOH–Fe–AcOH–Zn dust) to δ-3-*pyridyl*-δ-*amino*-n-*butyl alcohol*, b.p. 151—152°/5 mm. (*picrate* and *phenylthiourethane*, oils; *oxalate*, m.p. 155°), also obtained in poor yield from the oily phenylhydrazone by Zn and AcOH. This base with 48% HBr at 150—155° gives nornicotine, b.p. 139—140°/12 mm., and thence nicotine. R. S. C.

Polarimetric determination of quinine and its salts. C. Lapp (Ann. Chim. Analyt., 1933, [ii], **15**, 289—301).—[α] of quinine and some of its salts shows changes at p_H 4·5 and 6·5, being const. between these two vals., and corresponding with successive dissociation at the N atoms; the results are independent of the nature of the acid. The amount of quinine either alone or as the salt may be determined by measuring [α] between p_H 4·5 and 6·5. F. R. S.

Analogies between β-*iso*cinchonine (cinchonigine) and β-*iso*quinidine. A. Konopnicki, R. Ludwiczakówna, and J. Suszko (Rocz. Chem., 1933, **13**, 360—369).—β-*iso*Cinchonine [regarded as (I) (*methiodide*, m.p. 252°; *benzyliodide*, m.p. 216°; *oxide*, m.p. 192—193°)] yields when heated at 100° for 30 hr. with 25% AcOH β-*iso*cinchonicine [*hydriodide*, m.p. 149—150°; N-*Ac*, m.p. 121°, N-*NO*-, $+H_2O$, m.p. 101—103°, *Br*-, m.p. 60°, N-*Me*, m.p. 86° (*methiodide*, m.p. 231—232°; *hydriodide*, m.p. 282°; *Br*-derivative, m.p. 178—179°), N-*Et*, m.p. 85—86° (*hydriodide*, m.p. 232°), and N-*benzyl* derivative, an oil]. The behaviour of (I) towards various reagents is in every way analogous to that of β-*iso*quinidine (II) under similar conditions, and the [α] of the above compounds vary similarly to those of the corresponding derivatives of (II). R. T.



(I.)

Attempts to prepare antimalarials. IV. Derivatives of cotarnine. G. S. Ahluwalia, K. N. Kaul, and J. N. Rây (J. Indian Chem. Soc., 1933,

10, 197—201; cf. A., 1932, 1047).—Cotarnine (I) and o-$NO_2·C_6H_4·CHO$ in hot EtOH afford 1-*cotarnino*-o-*nitrophenyl ketone*, m.p. 154°, reduced ($SnCl_2$–HCl) during 10 hr. to the *amine*, m.p. 121°, which affords with $COMe_2$ in EtOH, *anhydrocotarnino-4-quinoline*, m.p. 133°. Similarly, (I) and 3 : 4-dimethoxy-6-nitrobenzaldehyde afford 1-*cotarnino*-(3′ : 4′-*dimethoxy*-6′-*nitrophenyl*) *ketone*, m.p. 165° (decomp.), which cannot be reduced to the amine. *Me* β-2 : 4-*dinitrophenylpropionate*, m.p. 40°, with (I) in MeOH containing piperidine affords a *compound*, m.p. 112—113°, not reduced to an anhydrocotarninoquinoline. Nitration of β-3 : 4-methylenedioxyphenylpropionic acid in AcOH at 0° affords the 6-NO_2-derivative, m.p. 152° (*Me* ester, m.p. 72°). Similarly, β-piperonylpropionamide affords the 6-NO_2-derivative, m.p. 186°. (I) with $COPh·CH_2Br$ or $COPh·CH_2·OMe$ in boiling EtOH affords ω-*ethoxy*-ω-*cotarninoacetophenone*, m.p. 120°. (I) in hot EtOH with ω-anilino-, ω-p-toluidino-, and ω-*m*-toluidino-acetophenone affords *anhydrocotarnino-anilino-*, m.p. 130° (decomp.), -p-*toluidino-*, m.p. 134°, and -m-*toluidino-acetophenone*, m.p. 116°, none of which can be cyclised to an indole. (I) in hot EtOH with β-aceto-α-naphthol, resacetophenone, and phenylcarbamide affords *products*, m.p. 146°, 191° (isolated as the hydrochloride), and 155°, respectively. J. L. D.

Preparation of hydrastinine from narcotine. K. Toptschiev (J. Appl. Chem. Russ., 1933, 6, 529—535).—In large-scale repetition of Pyman and Remfry's synthesis (J.C.S., 1912, **101**, 1595) 53 kg. of narcotine yielded on oxidation 26 kg. of cotarnine, which with Zn and H_2SO_4 gave 20 kg. of hydrocotarnine, and this with Na in $C_5H_{11}·OH$ yielded 8·17 kg. of hydrohydrastinine, which on oxidation with I gave 4 kg. of hydrastinine hydrochloride. R. T.

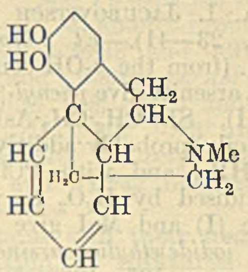
Camphorcarboxylates of the alkaloids. J. Bouillot and M. Leulier (J. Pharm. Chim., 1933, [viii], **18**, 49—59).—Camphorcarboxylic acid (I) (cf. A., 1903, i, 4) when anhyd. has m.p. 119°, $[\alpha]_D$ +10·82° in EtOH. (I) in hot $CHCl_3$ with strychnine and brucine affords *strychnine* (+4H_2O, m.p. 128°), and *brucine camphorcarboxylate*, m.p. 90°, $[\alpha]_D$ +6·65° in EtOH, respectively. (I) (Ba salt) and sparteine sulphate in H_2O afford the *neutral salt*, $[\alpha]_D$ +39·5° in H_2O, and the basic salt (+3H_2O, $[\alpha]_D$ +12·5° in H_2O). The camphorcarboxylates are easily hydrolysed or decomposed by heat. J. L. D.

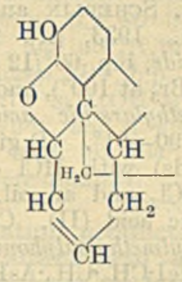
Alkaloids of *Berberis heteropoda*. A. Orekhov (Arch. Pharm., 1933, **271**, 323—327).—This plant contains oxyacanthine+berbamine (2·7), berberine (3·85), palmatine (0·20), and jatrorrhizine + columbamine (0·25%). R. S. C.

M.p. and crystal forms of morphine. L. Kofler and A. Kofler (Arch. Pharm., 1933, **271**, 387—392).—Anhyd. morphine is obtained in stable, micro-m.p. 240° or 248° (decomp.) according to the rate of heating, and metastable, m.p. 197°, forms. Crystallographic data and photomicrographs of these and the hydrated form are given. R. S. C.

Deoxymorphines. L. F. Small and D. E. Morris (J. Amer. Chem. Soc., 1933, **55**, 2874—2885).—Deoxycodeine-*A* cannot be demethylated. α-Chloromorphide is resinified by Na and EtOH, or Zn dust and EtOH, but, when reduced electrolytically, gives *deoxymorphine*-A (I), m.p. 260—262°, $[\alpha]_D^{28}$ +106° in 10% AcOH [*salicylate*, m.p. 248—251° (decomp.), $[\alpha]_D^{26}$ +85° in MeOH; *benzoate*, m.p. 240—245° after sintering at 215—223°, $[\alpha]_D^{31}$ +82° in EtOH; *H sulphate*, m.p. 145—151° after softening at 130°, $[\alpha]_D^{32}$ +61·6° in H_2O], giving (as benzoate) with CH_2N_2 in Et_2O (but not with other reagents) deoxycodeine-*A*, and hydrogenated (as salicylate) (PtO_2) in EtOH to *tetrahydrodeoxymorphine* (II), unstable, sublimes at 150°/0·3 mm., $[\alpha]_D^{24}$ −77±5° in MeOAc [*salicylate*, m.p. 238—240°, $[\alpha]_D^{23}$ −31° in MeOH; *hydrochloride*, m.p. 260—262° after softening at 255—260°, $[\alpha]_D^{24}$ −47° in EtOH; *hydriodide*, m.p. 268—271°, $[\alpha]_D^{24}$ −32·7° in H_2O; *methiodide*, m.p. 269—271° (decomp.), $[\alpha]_D^{31}$ −31° in MeOH], also obtained from tetrahydrodeoxycodeine (IV) by HI and giving this base when treated as hydrochloride with an excess of CH_2N_2 in MeOH. Dihydromorphine hydrate, double m.p. 132° and 204—206°, and $SOCl_2$ give chlorodihydromorphide, m.p. 228—229° after sintering at 155°, $[\alpha]_D^{30}$ −145° in EtOH (*hydrochloride*, m.p. 323—326°, $[\alpha]_D^{28}$ −131° in H_2O), which is not reduced electrolytically or catalytically, with CH_2N_2 gives chlorodihydrocodide, and with Na and pure MeOH at 140° affords *deoxymorphine*-C (III), +0·5H_2O, m.p. 189—190° (slight sintering at 130°), $[\alpha]_D^{31}$ −155·7° in EtOH [*hydrochloride*, +1·5H_2O, decomp. 240—245° when fresh and 291—294° when kept, $[\alpha]_D^{30}$ −147° in H_2O; *hydriodide*, m.p. 292—294°, $[\alpha]_D^{32}$ −111° in H_2O; *methiodide*, softens at 155—160°, m.p. 260—264° (decomp. 265°), $[\alpha]_D^{32}$ −98° in MeOH], giving with CH_2N_2 in MeOH–Et_2O deoxycodeine-*C* [*tartrate*, m.p. about 161—165° (decomp. 170°)] and obtained therefrom by NaOMe–MeOH at 140°, and hydrogenated as hydrochloride in H_2O to (II) and in AcOH to a mixture of (II) and *dihydrodeoxymorphine*-D. The last base, when methylated, gives dihydrodeoxycodeine-*D*, m.p. 103—105° (*H tartrate*, +2H_2O, m.p. 124—125°, $[\alpha]_D^{18}$ −29·9° in H_2O, anhyd., m.p. 154—154·5°), and is also obtained by hydrogenation of deoxycodeine-*C* in AcOH. Tetrahydrodeoxycodeine exists in two anhyd. *forms*, m.p. 124—125° (unstable) and 156—157·5° (stable). The substance termed "deoxycodeine-*B*" (A., 1931, 1077) was deoxycodeine-*A*, anhyd. m.p. 159—161°, and +H_2O, two forms, m.p. 151—152° (decomp. 153°) and about 122—126°, respectively (both lose H_2O in the air), $[\alpha]_D$ −118·8° in EtOH (*salicylate*, m.p. 220·5—221°, $[\alpha]_D$ +104·4°; methiodide obtained cryst., m.p. 219—221°, $[\alpha]_D$ +95·7°), mixed with a tenaciously retained *substance*, m.p. about 115°, $[\alpha]_D^{26}$ +6·6° in 10% AcOH, which is hydrogenated to (IV). R. S. C.

(I.)





(III.)

Arsenic derivatives of organic sulphides. I. *sec.*-Phenyl-β-sulphidoalkylarsinic acids of the type, SR·C_2H_4·AsR′O·OH, and their derivatives. S. M. Scherlin and A. I. Jacubovitsch (J. pr. Chem., 1933, [ii], **138**, 23—41).—*Et β-bromoethyl sulphide*, b.p. 60°/12 mm. (from the β-OH-compound by PBr_3 at 100°), and Na arsenite give *phenyl*-β-(*ethylthiol*)*ethylarsinic acid* (I), SEt·CH_2·CH_2·$AsPhO_2H$, m.p. 90—91°. (I) gives oils (probably additive compounds) with HCl or HBr, and with PCl_3 gives $AsPhCl_2$ and an oil, oxidised by H_2O_2 to phenylarsinic acid (II). Crude (I) and MeI give *phenyl*-β-(*ethylmethylsulphonium iodide*)*ethyliodoarsine* (III), SEtMeI·CH_2·CH_2·AsPhI, m.p. 105—106°, but pure (I) gives *phenyl*-β-(*ethylsulphonium iodide*)*ethylarsinic acid*, m.p. 97—100°, which with HCl liberates I and with HI gives (III). (I) with Br, followed by NaOH, gives (II), and with 1·5 or 3% H_2O_2 affords *phenyl*-β-(*ethylsulphone*)*ethylarsinic acid*, SO_2Et·CH_2·CH_2·$AsPhO_2H$, m.p. 177°, which with HCl, H_2S, and a little I gives *phenyl*-β-(*ethylsulphone*)-*ethylchloroarsine*, SO_2Et·CH_2·CH_2·AsPhCl, m.p. 66°. C_5H_{11}·SK and CH_2Cl·CH_2·OH give iso*amyl β-hydroxyethyl sulphide*, b.p. 110—111°/13 mm., whence iso*amyl β-bromoethyl sulphide*, b.p. 102°/13 mm., and the crude *iso*amyl analogue of (I) were obtained; the last with H_2O_2 gives *phenyl*-β-(iso*amylsulphone*)-*ethylarsinic acid*, m.p. 139·5—140·5°. Similarly were obtained *ethyl*-β-(*ethylsulphone*)*ethylarsinic acid*, m.p. 164—165°, *Ph β-bromoethyl sulphide* (from the β-OH-compound and PBr_3), *phenyl*-β-(*phenylsulphone*)*ethylarsinic acid* (IV), m.p. 192—193° (decomp.), and *phenyl*-β-(*phenylthiol*)*ethylarsinic acid* (V), m.p. 85—86° (*Ca* salt). (V) gives an oil with HCl and with PCl_3 an oily chloride which decomposes when distilled to $AsPhCl_2$. (IV) and PCl_3 give *phenyl*-β-(*phenylsulphonyl*)*ethylchloroarsine*, m.p. 90—91°. The C·As‴ linking is weakened by the SR group, and the ease of oxidation of the S atom is greatly increased by the presence of As in the mol. R. S. C.

Hydrochlorides and perchlorates of *p*-aminophenylarsinic acid. J. Prat (Compt. rend., 1933, **197**, 67—69).—The *dihydrochloride* (+1H_2O) (I), and the *perchlorates* NH_2·C_6H_4·AsO_3H_2,$HClO_4$ and $2NH_2$·C_6H_4·AsO_3H_2,$HClO_4$ are described. At 100° in dry air (I) loses 1 H_2O and 1 HCl, but the hydrochloride of the Ac derivative is stable, whence it is concluded that the residue after heating (I) is the arsonium chloride. H. A. P.

Tetra-arylarsonium halides. F. F. Blicke and C. Marzano (J. Amer. Chem. Soc., 1933, **55**, 3056).—Addition of halogen acid to the product of reaction of MgPhBr and $AsPh_3O$ gives *tetraphenylarsonium chloride*, m.p. 272—274°, *bromide*, m.p. 273—275°, and *iodide*, m.p. 292—293°, the halogen of which is fairly stable to NaOH–EtOH and Ag. R. S. C.

Phosphorus derivatives of triphenylmethane. H. H. Hatt (J.C.S., 1933, 776—786).—Triphenylmethylhydrogenphosphinic acid (I), m.p. 245—248° (decomp. 255—260°) [improved prep.; *Ag* salt; *Me* ester, m.p. 163—164°; *Et* ester, m.p. 118—121·5°. (I) is regenerated from the esters with I-free HI in AcOH], with I in AcOH, or alkaline $KMnO_4$, gives triphenylmethylphosphinic acid (II) [Me ester, m.p. 154·5—155·5° (no second form; cf. A., 1924, 832); additive *compound* with $POCl_3$], and with PCl_3 in presence of N_2 gives *triphenylmethyldichlorophosphine* (III), m.p. 138—140° (decomp. 240°). (III) is converted by NaOH into (I), by NaOEt–EtOH into $CHPh_3$ (IV), by H_2SO_4 into CPh_3·OH (V), by O_2 in Et_2O or C_6H_6 into PhOH, $COPh_2$, [CPh_3·O·]$_2$ (VI), and triphenylmethylphosphinyl dichloride (VII), and by I in $NaHCO_3$ in $CHCl_3$ into (V) and (VI). (VII) is also obtained from CPh_3·OK with PCl_3, is stable to Cl_2, Br, or I in $CHCl_3$, and is converted by EtOH-free NaOEt according to the conditions mainly into the Et (VIII), or Et H (IX) ester of (II), or into Et triphenylmethylchlorophosphinate (X), m.p. 140—141°, which is converted by H_2SO_4 into (V), and by HI in AcOH into triphenylmethylchlorophosphinic acid (XI), m.p. 229—230°. (XI) is also obtained from (II) with PCl_5 in C_6H_6, whilst PCl_5 alone with (XI) or (VII) gives CPh_3Cl. PCl_5 in C_6H_6 converts (IX) into (X) [isolated as (XI)], and a little (II) and (IV). (V) with PCl_2·OEt gives (X) and a little (XI). (XI) with Et_2SO_4 and K_2CO_3 in xylene gives (X) and *Et triphenylmethylchloropyrophosphinate*, m.p. 221—222·5°, also obtained by the action of Et_2SO_4 in xylene on a mixture of (VII) and (XI), and converted by H_2SO_4 into (V). The mechanism of the formation of the pyro-ester is discussed. (VIII) with PCl_5 in C_6H_6 gives *Et triphenylmethylpyrophosphinate* (mixture of stereoisomerides, α-, m.p. 222—223°, and β-, m.p. 228—231°), hydrolysed by HI in AcOH, or by HCl at 195—200° to the *acid*, m.p. 267—270° (decomp. 280°) [mixture of *Me* esters, m.p. 227—233°, similarly obtained from the Me ester of (II), and not separated; *Ag* salt], which is an individual giving the same mixtures on re-esterification. The asymmetry of the pyro-acid is considered to be destroyed by ionisation or tautomeric shift of the H atoms of the OH groups. The constitutions of (VII) and related compounds are discussed and reasons are given for preferring its formulation as a phosphinyl dichloride rather than as triphenylmethoxyphosphorus dichloride (cf. A., 1929, 1470). A. A. L.

Decomposition and reactions of carbamide. III. Reactions of carbamide with amines and amino-acids. J. M. Das-Gupta (J. Indian Chem. Soc., 1933, **10**, 169—175).—Interaction of aromatic amines and varying proportions of $CO(NH_2)_2$ give results substantially in agreement with previous work (cf. A., 1923, i, 902) and indicate the probable absence of *s*-diphenylcarbamide-4 : 4-distibinic acid (A., 1931, 751) in "urea stibamine" (I). Alkaline hydrolysis of (I) affords no carbamide derivative, but *p*-stibanilic acid, which appears to be the principal constituent of (I). J. L. D.

Interaction of the boron sextet with adjacent groups. D. L. Yabroff, G. E. K. Branch, and H. J. Almquist (J. Amer. Chem. Soc., 1933, **55**, 2935—2941).—Combination formulæ for $B(OH)_3$ involving the tautomeric effect are in better accord than other formulæ with the nature of its additive compounds, the substitution of aromatic B compounds, and the fact that it is a weaker acid than phenylboric acid ($\alpha = 1{\cdot}9 \times 10^{-9}$ at 20°). R. S. C.

Mercury derivatives of camphor. I. Constitution of Reychler's acid. J. D. Loudon (J.C.S., 1933, 823—825).—Camphor-10-sulphinic acid (I) with $HgCl_2$ in EtOH gives *camphor*-10-*mercurichloride* (II), m.p. 166°, converted by alkaline $SnCl_2$ into *biscamphor*-10-*mercury* (III), m.p. 255—256° [reconverted into (I) by $HgCl_2$], and by Br in KBr at room temp. into *camphor*-10-*mercuribromide*, m.p. 156° [also obtained from (I) and (III) with $HgBr_2$, or from (III) together with 10-bromocamphor by bromination], or at 70° into 10-bromocamphor (*oxime*, m.p. 156°), which is identical with β-bromocamphor. Similar reactions are described for *camphor*-10-*mercuri-iodide*, m.p. 146°, and for 10-*iodocamphor*, m.p. 75° (*oxime*, m.p. 158°) [best prepared by the action of I in C_6H_6 on (II)]. (III) with $(SCN)_2$ in $CHCl_3$ gives camphor-10-thiocyanate (not isolated), reduced to camphor-10-thiol (and a little camphor), which is also obtained from (I), or from camphorchlorosulphoxide. The composition of the above compounds, and hence of Reychler's acid, follows from the known 10-position of the S atom in the last-named compound. A. A. L.

Abnormal reactions of magnesium benzyl chloride. II. Mechanism of the *o*-tolyl rearrangement. J. R. Johnson (J. Amer. Chem. Soc., 1933, **55**, 3029—3032; cf. A., 1932, 385).—The abnormal reactions of $CH_2Ph\cdot MgBr$ are explained, without assuming rearrangement of free CH_2Ph ions or radicals, on the assumption of the formation of primary additive complexes leading, through chelation and ring opening, to abnormal products.

R. S. C.

Reactions of magnesium triphenylmethyl bromide. II. W. E. Bachmann and R. F. Cockerill (J. Amer. Chem. Soc., 1933, **55**, 2932—2934; cf. A., 1931, 1058).—$CPh_3\cdot MgBr$ with dry air gives after decomp. by dil. acid $(CPh_3\cdot O\cdot)_2$ (10%) and $CPh_3\cdot OH$ (54%). With the reagents stated (first name) it gives the following products in $> 66\%$ yield: MeI, CPh_3Me; EtBr, CPh_3Et; $Pr^{a}Br$, CPh_3Pr^{a} (41% yield); $Bu^{\gamma}Br$, $CHPh_3$; allyl bromide, δδδ-*triphenyl*-Δ^{a}-*butene*, m.p. 69·5—70·5° (hydrogenated to ααα-triphenylbutane); CH_2PhCl, $CPh_3\cdot CH_2Ph$; $ClCO_2Me$ (or Et), $CPh_3\cdot CO_2Me$ (or Et); $CH_2Cl\cdot OMe$, $CPh_3\cdot CH_2\cdot OMe$; $HgBr_2$, CPh_3; S, $CPh_3\cdot SH$; PhOBz, CPh_3Bz (46% yield); PhNCS, $CPh_3\cdot CS\cdot NHPh$. R. S. C.

Organic lead compounds. V. Asymmetric derivatives. P. R. Austin (J. Amer. Chem. Soc., 1933, **55**, 2948—2953; cf. A., 1932, 1148).—Attempts to resolve asymmetric Pb compounds containing four covalent linkings failed. $PbPh_3Cl$ and $MgPr^{a}Br$ in Et_2O–C_6H_6 give *Pb triphenyl* n-*propyl*, m.p. 69—70°, which with HCl gives *Pb diphenyl* n-*propyl chloride*, m.p. 141° (decomp.), or *Pb phenyl* n-*propyl dichloride* (I), m.p. 123° (decomp.), according to the conditions. (I) with *o*-$C_6H_4Me\cdot MgBr$ or Pb di-*o*-tolyl chloride with $MgPr^{a}Br$ affords *Pb di*-o-*tolyl phenyl* n-*propyl*, m.p. 49—50°, which with HCl gives *Pb* o-*tolyl phenyl* n-*propyl chloride* (II), m.p. variable, max. 122—123° (decomp.); this with d- or l-p-*lithiumphenyl* sec.-*octyl ether* (III) gives *Pb phenyl* p-sec.-*octyloxyphenyl* o-*tolyl* n-*propyl*, $C_6H_{13}\cdot CHMe\cdot O\cdot C_6H_4\cdot PbPhPr^{a}\cdot C_6H_4Me$, an oil, $[\alpha]_D^{25}$ +2·4° or −3·2° in $CHCl_3$, which could not be separated into isomerides and gave (II) with HCl. Similarly were prepared: *Pb triphenyl* n-*amyl*, m.p. 16—17°; and *Pb diphenyl* n-*amyl chloride*, m.p. 123° (decomp.). *d*- and *l*-β-Bromo-octane, b.p. 80—81°/18 mm., $[\alpha]_D$ +36·36° and −37·46°, and *p*-$C_6H_4Br\cdot ONa$ give d- and l-p-*bromophenyl* sec.-*octyl ether*, b.p. 141—144°/2 mm., $[\alpha]_D^{25}$ +8·10° and −7·72° in EtOH, whence d- and l-(III), $[\alpha]_D^{25}$ +8·3° and −9·8°, and d- and l-p-*carboxyphenyl* sec.-*octyl ether*, m.p. 63—64°, $[\alpha]_D^{25}$ +9·64° and −10·42° in EtOH, were obtained.

R. S. C.

Proteins and their degradation products. I. Liberation of mixtures of amino-acid esters from mixtures of their hydrochlorides. S. Uchida and S. Ai (J. Soc. Chem. Ind. Japan, 1933, **36**, 221—222B).—The use of Ag_2O in Et_2O–EtOH is recommended. A. A. L.

Clupein. VII. K. Felix, R. Hirohata, and K. Dirr (Z. physiol. Chem., 1933, **218**, 269—279; cf. this vol., 80).—After hydrolysis of clupein Me ester hydrochloride (I) with 2*N*-HCl for 16 hr. the N pptd. by phosphotungstic acid corresponds with the arginine (II) content and the N not pptd. with the NH_2-acid content. Thus the linkings between mono-NH_2-acid (III) and (II) are completely hydrolysed. (II) and arginylarginine (IV) (*dipicrolonate*, decomp. 290°) were obtained from the reaction products. After 8 hr. hydrolysis of (I) with *N*-HCl the product gave the biuret reaction. In addition to (II) a protone (*picrolonate*, m.p. 190°, decomp 220°) containing 2 mols. of (II) and 1 mol. of (III) (having 5 C atoms, not identified) was isolated, also *triarginylarginine* (V) (*picrolonate*, decomp. 190°, blackens 230°; *picrate*, sinters 190°, decomp. 220°). The clupein mol. yields two kinds of protone differing only in the linking of (III), which is attached in the one case through CO_2H, and in the other through NH_2 to (IV). These protones are arranged alternately in the chain and can thus give rise to (V). J. H. B.

Simultaneous determination of nitrogen and the halogens in organic substances. D. Buttescu (Bul. Chim. Soc. Române, 1933, **34**, 105—110).—The substance is mixed with Ag powder (made by reducing Ag_2O with H_2) and heated gently in a current of H_2, the gases evolved and the H_2 passing over Ni-quartz to convert the N in the substance into NH_3, which is absorbed in H_2SO_4 and determined volumetrically. The halogen is retained by the Ag in the boat and the Ag halide is extracted from this mixture by treatment with aq. NH_3 (for Cl or Br) or $Na_2S_2O_3$ (for I) and converted into AgCl for weighing. A. R. P.

Analysis of propylene and *cyclo*propane in mixtures containing both. S. Z. Roginski and F. H. Rathmann (J. Amer. Chem. Soc., 1933, **55**, 2800—2805).—Mixtures of propylene (I) and *cyclo*propane (II) may be analysed by aq. I–Br, which reacts very rapidly with (I), but very slowly with (II). Other methods are inaccurate or tedious. The reagent also removes traces of (I) from nearly pure (II). The small amount of I used acts catalytically for the reaction of (I) with Br only. (II) reacts more rapidly with conc. H_2SO_4 than does (I), and is rapidly attacked by cold aq. $KMnO_4$. Preliminary experiments on the isomerisation of (II) to (I) by Pt–asbestos at 600—650° are described. R. S. C.

Reactions of organic sulphur compounds. L. Bermejo and J. J. Herrera (Anal. Fís. Quím., 1933, **31**, 48—49).—Me, Et, Pr, Bu, and amyl sulphides give violet colorations with Na nitroprusside in feebly alkaline solution, but Ph_2S, PhSH, and $(CH_2Ph)_2S$ do not. R. K. C.

Identification of organic compounds. XII. Carboxylic acid principle and its importance for the detection of organic acids. L. Rosenthaler (Arch. Pharm., 1933, **271**, 328—337).—Org. acids give reactions similar to the substances derived formally from them by loss of CO_2, *e.g.*, $CCl_3{\cdot}CO_2H$ resembles $CHCl_3$ rather than AcOH; when isomerism exists, the resemblance is the greater the easier is the loss of CO_2. This is called the "carboxylic acid principle." Examples are quoted. R. S. C.

Determination of oxalacetic acid. P. Ostern (Z. physiol. Chem., 1933, **218**, 160—163).—The CO_2 quantitatively developed with NH_2Ph by Wohl's reaction (A., 1901, i, 365) is measured manometrically. $CH_2Ac{\cdot}CO_2H$ interferes, but as it reacts much more slowly than oxalacetic acid, the correct val. for the latter may be found by extrapolation. J. H. B.

Identification of the acyl group in certain esters. C. F. Koelsch and D. Tenenbaum (J. Amer. Chem. Soc., 1933, **55**, 3049—3050).—MgEtBr and p-$C_6H_4Me{\cdot}NH_2$ in Et_2O give $C_6H_4Me{\cdot}NH{\cdot}MgBr$, which reacts with a no. of esters to give the *p*-toluidides. Et β-chlorolactate gives β-*chlorolacto*-p-*toluidide*, m.p. 164—165°, and the p-*toluidide*, m.p. 168—169°, of *N*-*p*-tolylserine. The method fails with esters of several dibasic acids. R. S. C.

Hydrazines. II. *p*-Tolylhydrazine as a reagent for the identification of aldehydes and ketones. P. P. T. Sah and H. H. Lei. **III. *p*-Chlorophenylhydrazine as a reagent for the identification of aldehydes and ketones.** P. P. T. Sah, H. H. Lei, and T. Shen (Sci. Rep. Nat. Tsing Hua Univ., 1933, **2**, 1—5, 7—12).—II. *p*-Tolylhydrazine (improved prep.) gives p-*tolylhydrazones* of the following: *m*-, m.p. 154—155°, and *p*-nitrobenzaldehyde, m.p. 164—165°, furfuraldehyde, m.p. 105—106°, 2-furfurylideneacetone, m.p. 187—188° (sinters 181°), COPhMe, m.p. 126—127°, $COPh_2$, m.p. 84—85°, $CH_2Ac{\cdot}CO_2Et$, m.p. 87—88°, Et lævulate, m.p. 117—119°, Et oxalacetate, m.p. 105—106°, benzylideneacetone, m.p. 179—180° (sinters 171°).

III. *p*-Chlorophenylhydrazone (improved prep.) gives the following: *acetaldehyde*-, m.p. 98—99°, benzaldehyde-, m.p. 134—135°, salicylaldehyde-, m.p. 177—178°, *cinnamaldehyde*-, m.p. 138—139°, m-, m.p. 158—159°, and p-*nitrobenzaldehyde*-, m.p. 162—163°, *furfuraldehyde*-, m.p. 97—98°, *furfurylideneacetone*-, m.p. 179—180°, *acetophenone*-, m.p. 108—109°, *benzophenone*-, m.p. 121—122°, *Et acetoacetate*-, m.p. 115—116°, *Et lævulate*-, m.p. 112—113° *Et oxalacetate*-, m.p. 119—120°, *benzylideneacetone*-, m.p. 179—180°, and p-*nitrobenzylideneacetone*-p-*chlorophenylhydrazone*, m.p. 218—219°. All m.p. are corr. A. A. L.

2 : 4-Dinitrophenylhydrazine in determination of carbonyl compounds. C. Torres and S Brosa (Anal. Fís. Quím., 1933, **31**, 34—36; cf. A., 1932, 411).—Δ^6-*m*-Menthen-5-one (Δ^6-1-methyl-3-*iso*propyl*cyclo*hexen-5-one, "hexetone") forms a 2 : 4-*dinitrophenylhydrazone*, m.p. 104°, which is pptd. quantitatively from aq.-alcoholic H_2SO_4. R. K. C.

Cuprometric determination of sugars in the presence of ammonia. L. Bey, R. Bey, and G. Valensi (Bull. Soc. chim., 1933, [iv], **53**, 407—416).—Directions are given for the determination of glucose, fructose, invert sugar, lactose, and maltose by ammoniacal Cu tartrate. The effects of various factors are studied. R. S. C.

Shaffer–Somogyi reagent [for determination of sugar]. V. J. Harding and C. E. Downs (J. Biol. Chem., 1933, **101**, 487—492).—The Somogyi reagent (A., 1927, 69) is made up in two parts which are kept separate until used. The influence of varying p_H on the reduction vals. of different sugars is studied, the results providing a method of sugar differentiation. The presence of NH_3 influences the determination of sugars; it is removed by MgO and KH_2PO_4. H. D.

Microchemical reaction for cholesterol. C. van Zyp (Pharm. Weekblad, 1933, **70**, 775—776).—Cholesterol (I) gives characteristic bluish-black, strongly dichroic crystals when treated in the dark with vapours of conc. HI containing I. The reaction fails with ergosterol and phytosterol (II) or with mixtures of (I) containing 5% of (II). Animal fats which have been adulterated with vegetable fats also fail to give the reaction. The latter should be useful in examining cod-liver oil. S. C.

Polarographic studies with the dropping mercury cathode. XXXIII. Micro-determination of cysteine and cystine in the hydrolysates of proteins, and the course of protein decomposition. R. Brdička (Coll. Czech. Chem. Comm., 1933, **5**, 238—252).—Cystine (I) (and cysteine) is determined in the products of hydrolysis of proteins (II) by comparison of the polarographic curves in the presence of $CoCl_2$ with those of solutions of (I) of known concn., the optimum concn. being 1·2—24 mg. per litre (this vol., 619, 681). The method is accurate to about 5%. The hydrolysis products from glutathione give high results. Albumins contain approx. twice as much (I) as globulins. A similar method using $Co[NH_3]_6Cl_3$ is applied to (II), and an equation derived which is shown to describe approx. the course of hydrolysis of (II). A. A. L.

Compounds which give a Beilstein reaction yet contain no halogen. J. van Alphen (Rec. trav. chim., 1933, **52**, 567—568).—Many derivatives of 1 : 3 : 4 : 6-Δ^2-trimidine, which contain no halogen, give a positive Beilstein test. J. L. D.

Reactions of purine bases with copper sulphate and alkali. R. Klimek and J. K. Parnas (Z. physiol. Chem., 1933, **218**, 30—32).—The purine bases unsubstituted in position 7 (adenine, guanine, hypoxanthine, xanthine, trichloropurine, theophylline) give alkali-sol. complexes with $Cu^{\cdot\cdot}$; 7-methyladenine, theobromine, caffeine, and 2 : 6-dichloro-7-methylpurine give no such complex. The alkali-sol. Cu complex given by one of the adenine nucleotides is a property of the carbohydrate group, not of the glyoxaline ring. J. A. B.

Erythroquinine reaction : its realisation, technique, and specificity. M. R. Monnet (J. Pharm. Chim., 1933, [viii], **18**, 59—65).—Factors influencing the reaction are investigated. J. L. D.

Selenium in the determination of phosphorus and nitrogen in phospholipins. F. E. Kurtz (Ind. Eng. Chem. [Anal.], 1933, **5**, 260).—Using Se as catalyst, digestion is more rapid than with Cu or Hg, and is more convenient than using a H_2SO_4–HNO_3 mixture. N and P can be determined in the same digest. E. S. H.

Biochemistry.

Apparatus for maintaining artificial respiration in laboratory animals. W. R. Bond Science, 1933, **77**, 515—516). L. S. T.

Oxidation of hæmocyanin. J. B. Conant, B. F. Chow, and E. B. Schoenbach (J. Biol. Chem., 1933, **101**, 463—473).—Hæmocyanin from *Limulus polyphemus* is oxidised by K cyanomolybdate or $KMnO_4$ in absence of O_2 to methæmocyanin (I) and in presence of O_2 to oxymethæmocyanin (II). Reduction of the partial pressure of O_2 above aq. (II) produces deoxygenation; hence (I), unlike methæmoglobin, combines reversibly with O_2. (I) and (II), which are $Cu^{\cdot\cdot}$ compounds, are readily reduced, especially by $K_4Fe(CN)_6$ and 1 : 4-naphthoquinol when the reduction can be followed electrometrically or, with the latter reagent, titrimetrically using phenol-indophenol as indicator. F. O. H.

Mol. wt. of erythrocruorin. T. Svedberg and I. B. Eriksson (J. Amer. Chem. Soc., 1933, **55**, 2834—2840).—The term "erythrocruorin" for the red blood-pigment of invertebrates is revived. The erythrocruorins of *Arenicola marina* and *Lumbricus terrestris* are stable at p_H 2·6—8 and 2·6—10, have sedimentation const. 57·4 and $60{\cdot}9\times10^{-13}$, mol. wt. 2,850,000 and 2,730,000, and isoelectric point 4·56 and 5·3, respectively, thus differing from hæmocyanins. The pigments from *Spirographis spallanzanii* and *Pomatoceros triqueter* also have mol. wt. of the order of millions. R. S. C.

Position of the bands in the spectrum of oxyhæmoglobin. A. Krupski and F. Almasy (Nature, 1933, **132**, 242).—A marked shift of the band maxima towards the ultra-violet occurs with a decrease in concn. of oxyhæmoglobin. L. S. T.

Specific gravity, dry substance, and nitrogen content of leucocytes. H. Schlossmann and M. Grüter (Arch. exp. Path. Pharm., 1933, **171**, 317—318).—The following data were obtained with rabbit polymorphonuclear leucocytes and lymphocytes, respectively: sp. gr. 1·061±0·007, 1·065±0·0045; residue on drying in vac. over H_2SO_4, 20·40±0·87, 21·04±0·64% of the vol., 19·24±0·81, 19·75±0·56% of the wet wt.; N content on dry substance, 15·76±0·53, 15·99±0·27%. F. O. H.

Separation and zinc content of the nucleus [of blood-corpuscles]. N. Miyake (Keijo J. Med., 1933, **4**, 247—260).—The nuclei of hen's blood-corpuscles, separated by freezing in presence of 0·9% NaCl or NH_4Cl, have a Zn content > that of the cytoplasm or plasma; the Fe content is very low. F. O. H.

Distribution of calcium between blood-plasma and erythrocytes. R. G. Thomas (Austral. J. Exp. Biol., 1933, **11**, 109—118).—Blood-corpuscles (I) of the pig and man are devoid of Ca, whilst those of the ox contain 6·1 mg. Ca per 100 c.c. of (I). (I) of sheep, ox, and man are impermeable to $Ca^{\cdot\cdot}$. H. G. R.

Bromine of blood. F. L. Hahn (Klin. Woch., 1933, **12**, 390).—Crit. of the method of Roman and Pincussen for the determination of blood-Br. Nutr. Abs. (*b*)

Determination of "normal" bromine content of blood. I. A. Bier and W. Roman (Klin. Woch., 1933, **12**, 391). **II.** H. Fleischhacker and G. Scheiderer (Klin. Woch., 1933, **12**, 392).—I. The Pincussen method for the determination of blood-Br gives accurate results.

II. Crit. of the Pincussen method. Nutr. Abs. (*b*)

Determination of the iron content of the blood in children. I. P. Sobel and I. J. Drekter (Amer. J. Dis. Children, 1933, **45**, 486—497).—The venous blood of normal children contained 40—52 mg. Fe per 100 c.c. (average of 43·9 mg.). In various pathological conditions, the Fe content ranged from 18·2 to 74 mg. per 100 c.c. Nutr. Abs. (*b*)

Sulphur content of arterial and venous blood of the pancreas. S. Kumani (J. Biochem. Japan, 1933, **17**, 423—432).—In fasting and normal dogs the total S content of the venous blood of the pancreas is > that of the arterial blood. The difference is enhanced by feeding or by stimulation of the vagus, but not of the splanchnic, and is at least partly due to insulin secreted into the blood. F. O. H.

Mineral composition of the haemolymph of the crayfish. A. Bernard (Compt. rend. Soc. Biol., 1933, **112**, 880—882).—The ash content of crayfish hæmolymph is remarkably const., but the org. matter shows wide variations. The Na and Mg contents are similar to those previously reported, but the K and Ca contents differ. Nutr. Abs. (*b*).

Amino-acid-nitrogen in blood and its determination. I. S. Danielson (J. Biol. Chem., 1933, **101**, 505—522).—The Folin method for the determination of α-NH_2-acid-N (I) (A., 1922, ii, 540) is modified. NH_3 should be removed before analysis of the filtrates. Determinations of (I) in filtrates from laked and unlaked samples of blood show considerably higher vals. in the case of laked samples. In opposition to the findings of Simon (A., 1931,

1082) repeated washing of the corpuscles failed to give higher vals. The calc. distribution ratios of NH_2-acids between corpuscles and plasma was decreased by addition of (II) when the determination was made on laked blood filtrates, whilst when unlaked filtrates were used the ratio remained approx. the same. The same results were obtained by intravenous injection of (II) into dogs. It is concluded that the red blood-cells contain indiffusible substances capable of reacting with the reagents used. H. D.

Physico-chemical study of the flocculation of serum-albumin by resorcinol. A. Boutaric, M. Piettre, and M. Roy (Compt. rend., 1933, **197**, 357—358).—Flocculation is due to adsorption, solubility decreasing with the amount adsorbed and becoming zero at the saturation point. R. S. C.

Total pigment and bilirubin in normal human blood-serum. J. R. Peter (Biochem. Z., 1933, **262**, 432—460).—A method for spectrophotometric determination of normal human serum-pigments is described. Serum-pigment vals. of whole blood or serum, on keeping in the dark at a low temp., remain const. or only very slowly decrease. A method of prep. of azo-solutions is described. The absorption curves of the extracts from the serum of healthy fasting subjects resemble those of Na bilirubin, but show deviations due to the lipochrome content. The absorption curves of the corresponding azo-solutions resemble, above 560 mμ, the curves for azobilirubin, but below this the absorption shows differences due to the absorption of a yellow pigment formed on treatment with diazo-reagent. The normal bilirubin val. for the serum of fasting subjects is 0·3—0·6 mg. per 100 c.c., the serum-pigment val. being always higher. A correction of the results of the Van den Bergh method is given. P. W. C.

Keto-acids in blood-serum. H. Westerkamp (Biochem. Z., 1933, **263**, 239—244).—Using Warburg's carboxylase method, $AcCO_2H$ (I) was detected in fifteen human serum samples in amounts of 0·59—2·09 mg. per 100 c.c. Pig's serum contained 5—10 mg. per 100 c.c. The method detected not only (I), but also α-keto-butyric, -*iso*valeric, -hexoic, and -glutaric and oxalacetic acids. The keto-acid fraction of the serum is not solely (I), since treatment with 2 : 4-dinitrophenylhydrazine, although yielding the hydrazone of (I), gave this in small amounts and not in every case. P. W. C.

Lactic acid determination in blood. W. Müller-Parcham (Z. physiol. Chem., 1933, **218**, 209—217).—Minor modifications of the Lehnartz technique (A., 1929, 48) are advocated, chiefly in respect of the titration of the $NaHSO_3$. The compound with MeCHO is decomposed by Na_2HPO_4 in presence of excess of I and the unused I is titrated with Na_2HAsO_3. J. H. B.

Fluctuations of blood-sugar *in vitro*. I. S. Kleiner and R. Halpern (J. Biol. Chem., 1933, **101**, 535—545).—Hyperglycæmic blood, whether diabetic or artificially produced, when dialysed for a short time against Ringer's solution exhibits marked variations in its sugar content on removal from the dialysis chamber. Similar variations, however, are noticed in undialysed blood. H. D.

Comparative determinations of the blood-sugar of the ox. M. Demmel (Biochem. Z., 1933, **262**, 294—299).—Fujita and Iwatake's method (I) with ox serum gives blood-sugar vals. 8—36% < those given by the Hagedorn–Jensen method (II), and their modification of (II) has an error of ±2%. With glucose, the error of Herzfeld's methylene-blue method (III) is ±10% and of the osazone test (IV) −25%. With serum, (III) gives the same vals. as (I), whereas (IV) gives even lower vals. than with glucose. P. W. C.

$[H^{\cdot}]$ of the blood. W. Bladergroen (Chem. Weekblad, 1933, **30**, 526—532).—A crit. review of methods indicates that only the electrometric method of Michaelis is trustworthy; the quinhydrone electrode method is not recommended. For a given individual the p_H varies between very close limits, except under markedly abnormal conditions (diabetic coma etc.). Determinations of blood-p_H are not usually as important as determination of alkali reserve and free CO_2. H. F. G.

Relationship between the structure of antigens and the specificity of antibodies. H. Erlenmeyer, E. Berger, and N. Leo.—See this vol., 834.

Modification of antibodies by formaldehyde. S. Mudd and E. W. Joffe (J. Gen. Physiol., 1933, **16**, 947—960).—The isoelectric point of certain bacteria maximally sensitised with sp. antisera is shifted to the acid side to the extent of 0·6—0·8 of a p_H unit by the action of CH_2O. The properties of the sensitising films are the same whether CH_2O has been allowed to act on the antibody (I) before or after the combination of (I) and antigen (II). These results, together with the observations of other authors, suggest that the union of (II) and (I) does not involve, to any appreciable extent, the CH_2O-combining basic groups of the (I). A. W.

Embryo-chemistry of Amphibia. I. M. Tomita and H. Fujiwara. **II. Perivitelline fluid of salamander eggs.** H. Fujiwara and S. Tsunoo. **III. Inorganic constituents during incubation of salamander eggs.** T. Iseki and T. Kumon. **IV. Nitrogenous substances during incubation of salamander eggs.** T. Iseki, T. Kumon, I. Takahashi, and F. Yamasaki. **V. Carbohydrate metabolism during incubation of salamander eggs.** E. Kataoka and S. Tsunoo. **VI. Fatty substances during incubation of salamander eggs.** E. Kataoka and I. Takahashi (J. Biochem. Japan, 1933, **17**, 401—405, 407—408, 409—411, 413—415, 417—418, 419—422).—I. Following incubation for 1—4 weeks, the eggs of the salamander (*Chryptobranchus japonicus*) consist approx. of 75% perivitelline fluid (I), 21% gelatinous layer, and 4% yolk. The eggs or young embryos contain only traces of creatine, creatinine, and glucose, whilst the content of fat is inversely proportional to that of H_2O.

II. During 4 weeks' development, (I) changed in p_H from 7·1 to 6·9, whilst d remained practically = that of H_2O.

III. The ash and inorg. PO_4 increase.

IV. Whilst the total N tends to decrease, the residual N increases, especially during the fourth week.

V. The glycogen content decreases slowly.

VI. During the fourth week the free fatty acids and cholesteryl esters increase, whilst the saponification val. and the free and total cholesterol decrease.

F. O. H.

Lipins of human placenta. K. Klaus (Zentr. Gynäkol., 1933, **57**, 558—561).—The unsaponifiable fraction of placenta, its free, combined, and total cholesterol, and the fatty acid content and its I val. are tabulated. Nutr. Abs. (*b*)

Sulphur-containing lipin of brain cerebronsulphuric acid. G. Blix (Z. physiol. Chem., 1933, **219**, 82—98).—A lipin isolated from human brain is probably the K salt of *cerebronsulphuric acid*, m.p. 209—210°, since it yields on hydrolysis, in addition to H_2SO_4, the constituents of cerebron, viz., cerebronic acid, sphingosine, and galactose. Probably 20—25% of the cerebrosides of brain are esterified with H_2SO_4. J. H. B.

Lipins of mammalian liver. V. Nature of the "unsaponifiable fraction" of mammalian liver. E. Fränkel and G. Löhr (Z. physiol. Chem., 1933, **218**, 218—222; cf. this vol., 846).—From the unsaponifiable fraction of liver, after removal of cholesterol, an oil was obtained, which, when esterified with butanetetracarboxylic anhydride, yielded an *oil*, b.p. 152—158°/0·03 mm., C 80·5, H 12·3%, I val. 104, distilling without decomp. and not pptd. by digitonin. Fractionation of the unsaponifiable fraction with aq. EtOH gave a neutral saturated *substance*, m.p. 96—97°, of similar composition to, but differing in properties from, sphingosine.

J. H. B.

Determination of uric acid. Uric acid content of normal and diseased liver. O. Fürth and E. Edel (Biochem. Z., 1933, **263**, 9—23).—The material (*e.g.*, minced liver ground with sand) is extracted with hot 0·01% aq. Li_2CO_3, the extract is deproteinised with uranyl acetate, excess U is removed with Na_2HPO_4, and the uric acid in the filtrate is determined colorimetrically by Folin's method or by the method of Ludwig and Salkowski. Decomp. products of nucleic acid do not interfere, nor are the results affected if brief autolysis precedes the working up of the material, but hot dil. H_2SO_4 destroys much of the uric acid in a few hr. The normal uric acid content (I) (8—12 mg. per 100 g.) of rat's liver is reduced by fasting or by diet of pure protein, but increased by diet rich in purines. Administration of phenylquinolinecarboxylic acid (atophan) reduces (I) to $\not<$ 3—5 mg. per 100 g. The (I) of normal or only slightly parenchymatous human liver is 7—10 mg., that of the liver of cirrhosis patients 2—5 mg. per 100 g. W. McC.

Spectrographic investigation of the metallic content of the liver in childhood. H. Ramage, J. H. Sheldon, and W. Sheldon (Proc. Roy. Soc., 1933, **B**, **113**, 308—327).—Data are given for 111 children's and 14 fœtal livers, analysed spectrographically (A., 1929, 527). Fe and Cu are stored in the fœtal liver. The concns. of Fe, Cu, and Mn fall during nursing, and increase during childhood on a mixed diet. Mn and Rb are not stored in the fœtal liver. There is a parallelism between the amounts of Fe, Cu, and Ca, and between those of Rb and K in children's livers. The results are discussed in relation to the diseases causing death. A. C.

Iron and copper in liver extracts. H. G. Rees (Analyst, 1933, **58**, 384—388).—Fresh ox-liver contains 80 mg. of Fe and 24 mg. of Cu per kg. H_2O at 50° extracts 31·5 mg. of Fe and 1·75 mg. of Cu per kg. Part of the Fe is associated with coagulable protein, so that extraction at higher temp. is less effective than at 50°. E. C. S.

Affinity between lung-proteins and lung-tissue. P. Mascherpa (Arch. exp. Path. Pharm., 1933, **171**, 119—124).—Subcutaneous injection into rabbits of Co admixed with press-juice from rabbit's lung is followed by deposition of Co in the lung tissue; this deposition does not occur when Co is administered with serum. Hence confirmation is afforded for the affinity between various tissues and their constituent proteins (this vol., 423). F. O. H.

Preparation and properties of thyroglobulin. M. Heidelberger and W. W. Palmer (J. Biol. Chem., 1933, **101**, 433—439).—Minced washed thyroid glands (pig) are pressed out, re-extracted with 1% NaOAc, the combined juices freed from fat, adjusted to p_H 4·8—5·0, and the pptd. nucleoprotein is separated. The residual fluid is half-saturated with Na_2SO_4 at 35°, the ppt. dissolved in H_2O, and the pptn. with Na_2SO_4 repeated, yielding thyroglobulin (I), $[\alpha]_D$ −56° to −59°, 0·58% I, 15·8% N, which could not be further fractionated by varying concns. of aq. Na_2SO_4. Exposure of (I) to dil. AcOH at $p_H < 4·8$ even at low temp. results in partial denaturation. F. O. H.

Chemical analysis of muscles of marine invertebrates. O. Riesser and A. Hansen (Z. physiol. Chem., 1933, **219**, 62—71).—Creatine- (I), arginine- (II), pyro- (III), hexose- (IV) -phosphoric acids and glycogen were determined in the muscles of marine invertebrates. (I) was present in all cases, but in smaller amount than (II). (III), (IV), and (V) were also found, (IV) and (V) sometimes in considerable quantity. The total acid-sol. PO_4''' varied from 0·45% P_2O_5 in the cephalopods to 0·1% in representatives of the Echinoderms. J. H. B.

Phosphorus nucleus of ichthulin of the pike. S. Posternak and T. Posternak (Compt. rend., 1933, **197**, 429—430).—Ichthulin, a vitellin of pike spawn, affords "ichthiotyrin" (I), a glucosidic polypeptide containing 12·6% P, similar in properties to the ovotyrins (A., 1927, 1100). Hydrolysis (35% H_2SO_4) of (I) yields H_3PO_4 (II) 39·2, NH_3 2·3, $AcCO_2H$ (III) 6·4, arginine 4·6, and *l*-serine (IV) 26·1%, respectively, NH_3 and (III) arising from deamination of (IV). Hydrolysis of (I) with 15% H_2SO_4 yields a polypeptide (N : P = 1·05—1·3) which is further hydrolysed to mainly (II) and (IV) and deamination products of (IV). (I) is composed of serine-phosphoric acid chains in which H_3PO_4 is linked with the OH of (IV). A. C.

Succinic acid in shellfish. K. Aoki (J. Agric. Chem. Soc. Japan, 1932, **8**, 867—868).—Vals. are: *Corbicula atrata*, Prime, 6·4117; ligament of *Pecten yessoensis*, Jay, 0·3700; *Tapes philippinarum* 0·3300;

Cytherea meretrix, L., 0·1420; *Arca pectunculus*, 0·1010; *Turbo cornutus* 0·0720; *Ostrea talienwahnensis*, Cross, 0·0520; *Mactra sulcatoria* 0·0270; *Habliotis tuberculata* 0·0250%. Ch. Abs.

Chemistry of bioluminescence. I. Determination of luciferin. R. S. Anderson (J. Cell. Comp. Physiol., 1933, **3**, 45—59).—A photo-electric cell with appropriate recording instruments is utilised to follow the course of the luminescent reaction. The ratio of total light emitted to luciferin originally present was const. at p_H 6·8 over the experimental range of concns. of luciferin and luciferase. The ratio is influenced by temp., p_H, buffer and salt concns. A. G. P.

Discordant behaviour of accelerators, *e.g.*, of the darkening [of pigment precursors]. Hans Schmalfuss, Helene Schmalfuss, I. Heise, R. Käsler, and H. Haeussler (Biochem. Z., 1933, **263**, 278—294).—The ability of various accelerators (I) prepared from the bloods of seven species of Orthoptera, Coleoptera, Hymenoptera, and Lepidoptera in various dilutions to cause and accelerate the darkening of sixteen pigment precursors (II) containing 1 or 2 OH groups attached to Ph nucleus is investigated. The activity of a particular (I) is different for different (II), and the series of (II) darkened by a particular (I) is different for the various (I). Dilution of (I) decreases and concn. increases the no. of (II) darkened. P. W. C.

Darkening of the skin. III. P. Mulzer and H. Schmalfuss. **Free *l*-tyrosine from human skin, a pigment precursor.** H. Schmalfuss, A. Heider, and K. Winkelmann (Biochem. Z., 1933, **263**, 371—374).—A H_2O extraction method is described for the separation of *l*-tyrosine from the skin of corpses (2 kg. of skin gave 18 mg. of tyrosine). P. W. C.

Distribution of inorganic salts in birds. I, II. Inorganic salts in *Vanellus vanellus*, L. A. Bernardi and M. A. Schwarz (Biochem. Z., 1933, **262**, 380—386, 387—389).—I. Tables summarise the total inorg. salt content in fourteen types of tissue, both fresh and after drying at 40°, and their H_2O content in thirteen birds of different orders. The % salt contents of the fresh and dried organs and breast muscle were very const., but those of leg muscle showed large variations.

II. Tables show the H_2O, salt, total H_2O-sol. and acid-sol. PO_4, Cl, Ca, and Mg contents of eleven tissues, both fresh and after drying at 40°, of *V. vanellus*. P. W. C.

Mineral composition of the skeletons of some recent *Echinodermata*. K. F. Terenteva (Trav. lab. biogéochim. acad. sci. U.R.S.S., 1932, **2**, 45—62).—Different parts of the same skeleton of *Echinoidea*, *Ophiuroidea*, and *Asteroidea* differ in composition. The distribution of $MgCO_3$ is regular. Ch. Abs.

Composition of insects during metamorphosis. G. G. Bergman (Trav. lab. biogéochem. acad. sci. U.R.S.S., 1932, **2**, 31—42).—*Rhagium indogator* contained H_2O 29·70—40·60, C 15·60—21·06, H 8·90—10·10, N 1·88—3·52, ash 3·18—4·17%. *Pieris brassicæ* and *Polistis gallica* gave analogous vals. The most marked change in composition takes place when the insect changes from pupa to adult. Ch. Abs.

Chemical changes during the life cycle of the tent caterpillar (*Malacosoma americana*). V. W. Rudolfs (J. N.Y. Entomol. Soc., 1932, **40**, 481—488).—Analyses are recorded. Ch. Abs.

Carbon content of the bodies of certain species of *Acridiidæ*. K. G. Kunasheva (Trav. lab. biogéochem. acad. sci. U.R.S.S., 1932, **2**, 27—30).—Comparative vals. for male and female insects are recorded. Ch. Abs.

Distribution of fixed mineral matter in mammalian spermatozoa. A. Policard (Compt. rend., 1933, **197**, 427—429).—Microscopical examination of incinerated rat and human spermatozoa shows that the neck and posterior part of the head are rich, whilst the tail and anterior part of the head are poor, in ash. The latter parts are more readily incinerated. In the rat the total spermatozoal ash is > in man. A. C.

Digestive enzymes of *Bombyx mori*. K. Yamafugi (J. Agric. Chem. Soc. Japan, 1933, **9**, 152—159).—A sucrose-hydrolysing enzyme with optimum p_H 9·5 and max. at 45° occurs in a glycerol extract of the fresh digestive ducts of *B. mori*. The diastatic activity of the extract varies with the species. Ch. Abs.

Reaction of Rivalta. S. Kozawa, R. Iwatsuru, and T. Adachi (J. Biochem. Japan, 1933, **17**, 375—383).—The % of constituent NH_2-acids and the isoelectric points (I) of the proteins of transudates, exudates, and other œdematous fluids are almost equal [p_H 4·4 for (I)], whilst the albumin/globulin ratio is approx. 1 for each protein mixture. The Rivalta reaction fails with a protein content of < 1%; the salt concn., however, also influences the reaction (cf. A., 1924, i, 243). F. O. H.

Secretion of phosphorus in the saliva of sheep. R. H. Watson (Austral. J. Exp. Biol., 1933, **11**, 67—74).—P of the saliva (I) is mainly inorg. and is of the order 20—60 mg. per 100 c.c. The ratio of P in (I) to that of the blood is between 5 : 1 and 8 : 1. 2·4—7·7 g. of P are secreted daily in (I). H. G. R.

Bile acids from fistulary bile of rabbits. S. Shibuya and T. Tanaka (J. Biochem. Japan, 1933, **17**, 391—393).—When fed with Na dehydrocholate, the bile of rabbits with biliary fistulæ contains glycocholeic acid, m.p. 186°, $[\alpha]_D^{20}$ +48·56° in EtOH (cf. A., 1931, 1179), deoxycholic acid, m.p. 172°, $[\alpha]_D^{20}$ +57·14° in EtOH, and $NH_2\cdot CH_2\cdot CO_2Et$. F. O. H.

Tests of gastric function. I. Studies of gastric juice by means of a protein-peptone solution. Heckmann (Z. ges. exp. Med., 1933, **87**, 506—528).—A test meal containing 20% of ovalbumin and 2% of Witte's peptone is to be preferred to one containing coffee or EtOH, particularly in the investigation of cases of hypoacidity. Nutr. Abs. (*b*)

Thiocyanate content of gastric juice in children. E. Riecke (Z. Kinderheilk., 1933, **54**, 408—412).—The CNS' content of gastric juice was lower in prematures than in full-term infants. It rose rapidly as age increased to 5 months, then more slowly to 5—10 years, after which there was a slight decline. In dyspepsia the content was greatly reduced, in dystrophy only slightly. Nutr. Abs. (*b*)

Clinical micropyknometry. I. E. Oliva and F. González Núñez. **II. Mikropyknometry of milk and determination of dietetic value.** F. González Núñez and E. Oliva (Anal. Fís. Quím., 1933, **31**, 68—70, 71—73).—I. 0·5 c.c. of liquid in a graduated pyknometer is used and *d* is obtained with an accuracy of 0·05%.

II. Total N, lactose, fat, and *d* are determined in an 8-c.c. sample of human milk. R. K. C.

Effect of diet on calcium and phosphorus content of human milk. B. Herz (Z. Kinderheilk., 1933, **54**, 413—420).—With change in diet of nursing women any changes in the Ca and P content of the milk (I) were in the same direction. The difference in the Ca content of (I) when the diet was changed from Ca-poor to Ca-rich was of the order of 8—15%, but the addition of salts such as Ca citrate or malonate caused no definite increase in the (I)-Ca. With the Ca-poor diets the total Ca secreted in (I) was > the Ca intake in the food. Nutr. Abs. (*b*)

Chemical changes produced in caseinogen by boiling. K. Ballowitz (Biochem. Z., 1933, **263**, 119—127; cf. this vol., 177).—When milk, or a solution containing caseinogen, is boiled, the chemical change which the protein undergoes is accompanied by appreciable binding of Ca by caseinogen, a two-phase process, similar to coagulation with rennin, taking place. The extent of pptn. increases as [Ca$^{\cdot\cdot}$] increases. An explanation is provided for the decreased nutrient val. of boiled as compared with unboiled milk. W. McC.

Effect of boiling on the coagulation by rennin of caseinogen. K. Ballowitz (Biochem. Z., 1933, **263**, 128—134).—Coagulation with rennin sets in later in boiled than in unboiled solutions of caseinogen prepared by Marui's method (A., 1926, 866) and the type of coagulation is altered by the boiling. The difference is due to the action of the $CaCl_2$. W. McC.

Antirachitic potency of the milk of human mothers fed previously on "vitamin-*D* milk" of the cow. J. W. M. Bunker, R. S. Harris, and R. S. Eustis (New Engl. J. Med., 933, **208**, 313—315).—The antirachitic potency is increased. Ch. Abs.

Lability of the reducing factor (vitamin-*C* ?) in milk. S. K. Kon (Nature, 1933, **132**, 64).—The amount of the substance in milk which reduces chlorophenol-indophenol reagent varies to a marked and irregular extent. L. S. T.

Methylene-blue reductase test [in milk]. C. S. Miles (J. Min. Agric., 1933, **40**, 414—419).—The reductase test is unsuitable for the examination of milk of low bacterial count. There is better correlation between the plate count and the keeping quality (I) of milk than between the reduction time and (I). E. C. S.

Bromothymol-blue reaction in freshly drawn milk. C. S. Bryan (Amer. J. Pub. Health, 1933, **23**, 721—724).—The determination of p_H of fresh milk cannot be used alone to detect mastitis (I), since positive reactions are obtained with animals free from (I) and *vice versa*. The test is of val. only in determining the relative disease or freedom from (I) in a herd. A. L.

Glycerol as a preservative for milk to be examined for hæmolytic streptococci. R. Gilbert and M. E. Clark (Amer. J. Pub. Health, 1933, **23**, 720).—Addition to milk of $\frac{1}{3}$ vol. of glycerol preserves it for hæmolytic streptococci examination for several days. A. L.

Yeast extract medium for determining the bacterial content of milk by the plate method. E. D. Devereux and J. L. Etchells (Amer. J. Pub. Health, 1933, **23**, 149—151; cf. *ibid.*, 1932, **22**, 1291, 1293).—Milk samples plated out on yeast extract agar give counts after 24 hr. incubation 18% >, after 48 hr. 45% >, on plain agar. E. C. S.

Accuracy of clinical methods of determining urinary protein. M. Hori (J. Biochem. Japan, 1933, **17**, 367—373).—Of the methods of Esbach, Tsuchiya, and Sueyoshi, the last is the most accurate. The accuracy of all three methods is increased by application of the centrifuge technique of Inoue (A., 1930, 1610). F. O. H.

Influence of foodstuffs on rate of urinary acid excretion. C. E. Brunton (J. Physiol., 1933, **78**, 65—97).—A standard breakfast was taken at 8 a.m. and the test foodstuff was taken at noon. If no meal was taken at noon, the acid excretion per min. increased 2½ hr. afterwards. Ingestion of raisins and prunes caused increase of the acid output. Ingestion of potato caused a decrease of 0·2 c.c. of 0·1*N*-acid. per min. with max. fall at 2½ hr. Ingestion of beet and banana also caused decrease. Meals of beans, rice, bread, grape fruit, and meat caused little change. Nutr. Abs. (*b*)

Excretion of cholesterol during the action of therapeutic substances on the intestine. F. Pendl and G. Berger (Arch. exp. Path. Pharm., 1933, **171**, 319—328).—The fæcal excretion of cholesterol (I) was investigated in two dogs fed approx. 0·2 g. (I) per day and a standard diet supplemented with mineral salts, cellulose (II), or an anthraquinone derivative. The excretion of (I) with the standard diet alone was fairly const. (II), however, produced marked increases in the wts. of fæces and (I) excreted. The other two diets gave results varying with the dog used. F. O. H.

Physical characteristics of residues from the small intestine. H. Landt and K. Daum (Arch. Int. Med., 1933, **52**, 96—104).—Residues (I) obtained from an ileal fistula varied in colour and consistency with the food (II). H_2O varied from 92 to 97%, N was approx. const. and independent of (II). The wt. of (I) varied with (II) and only slightly with the amount fed. No fæcal odour was noted. H. G. R.

Mode of occurrence of acidosis. S. M. Neuschlosz (Z. ges. exp. Med., 1933, **87**, 161—177).—During development of both renal and extra-renal acidosis the formation of NH_3 was delayed, indicating that there was a loss of fixed base from the body for neutralising purposes in the urine. Hence acidosis is in large part due to the abs. or relative inefficiency of the kidneys to form NH_3. In liver disease there was an increased amount of urinary NH_3 due to imperfect synthesis of urea. In cases of liver deficiency acidosis was present with high val. of Q (acid–base quotient), indicating that the NH_3 which formed as a result of defective urea formation had less neutralising power than the NH_3 formed by the kidneys. NUTR. ABS. (*b*)

Nutritional anæmia of the rat. VII. Parentally administered iron. M. W. EVELETH, F. C. BING, and V. C. MYERS. **VIII. Determination of hæmoglobin and erythrocytes on a single sample of blood.** R. W. HEINLE and F. C. BING (J. Biol. Chem., 1933, **101**, 359—368, 369—372).—VII. Intraperitoneal injection of Fe into young rats made anæmic by restriction to a diet of raw milk containing an average of 0·34 mg. Cu per litre, produced a rapid increase in growth, hæmoglobin (I) concn., and blood count. Doses of $>$ 0·025 mg. Fe produced a polycythæmia with low (I) concn. Injection of both Cu and Fe gives the same effects as Fe alone.

VIII. Blood is diluted in a hæmocytometer with 0·9% NaCl. A drop is used for the count and the residue expelled on to a watch-glass, from which 0·1 c.c. is taken for the benzidine–H_2O_2 determination of (I). H. D.

Hæmoglobin production factors in the human liver. I. Normal, infection, and intoxication. III. Anæmias. G. H. WHIPPLE and F. S. ROBSCHEIT-ROBBINS. **II. Liver degeneration, cancer, cirrhosis, and hepatic insufficiency.** F. S. ROBSCHEIT-ROBBINS and G. H. WHIPPLE (J. Exp. Med., 1933, **57**, 637—651, 671—677, 653, 670). CH. ABS.

Hæmopoietic factor in marmite. L. WILLS (Lancet, 1933, **224**, 1283—1286).—Clinical trials of preps. containing vitamins-B_1, -B_2, and -B_4 failed to show that these vitamins have hæmopoietic properties in tropical macrocytic anæmias. Marmite was active curatively in these cases. Its hæmopoietic factor is sol. in H_2O and 80% EtOH, and is heat-stable. L. S. T.

Metabolism of phenol and indole. I, II. Latent phenol–indole poisoning and arteriosclerosis. M. BIEBL (Z. ges. exp. Med., 1933, **87**, 416—435, 436—472).—I. A technique for the study of the relationship of PhOH–indole intestinal intoxication and various pathological conditions in rabbits is described.

II. Arteriosclerosis (I) produced by PhOH or indole administration was partly or completely prevented by doses of olive oil or Ca. The lesion is different from cholesterol-(I). NUTR. ABS. (*b*)

Calcinosis universalis. B. J. HEIN (Arch. Surg., 1933, **26**, 389—396).—Heliotherapy produced gradual disappearance of diffuse Ca deposition in fascias. CH. ABS.

Experimental production of malignant tumours. J. A. MURRAY (Proc. Roy. Soc., 1933, B, **113**, 268—292).—A discussion (see also Nature, 1933, **132**, 156—158). A. C.

Relation of carcinogenicity of mineral oils to certain physical and chemical characteristics of these oils. R. LYTH (J. Ind. Hygiene, 1933, **15**, 226—237).—In a large series of oil samples the carcinogenic activity (I) runs parallel to the refractivity $[(n-1)/d]$, but certain exceptions occur. Similarly, amongst samples of crude oil the I vals. and (I) show a direct correlation, but with refined oils this was less marked. The $KMnO_4$ val. did not indicate (I). W. O. K.

Composition of the lipins of normal and diseased organs. V. Lipins of carcinomatous, sarcomatous, and tuberculous human lymph glands. VI. Lipins of human melanotic carcinoma and sarcoma. B. LUSTIG and E. MANDLER (Biochem. Z., 1933, **263**, 50—57, 58—62; cf. this vol., 736).—V. The carcinomatous (I) glands contain more lipins than do sarcomatous (II) or tuberculous (III). (II) contain normal, (I) and (III) reduced, amounts of phosphatides (IV), and in (I) the P content of (IV) is greatly reduced, whilst the N content is increased. In all cases the amount of unsaponifiable matter (V) is high, the cholesterol (VI) content of (V) being 45—70% for (I) and 90% for (II) and (III). In (III) also one third of (VI) is esterified. The liquid fatty acids of the lipins of (I) contain one double linking; those of the lipins of (II) and (III) are to a great extent highly unsaturated.

VI. The composition of the lipins (I) of melanotic carcinoma (II) (from human liver) is the same as that of the (I) of melanotic sarcoma (III), but differs from that of the (I) of normal or carcinomatous liver. (II) and (III) have high contents of free fatty acid and low contents of phosphatide precipitable by $COMe_2$. W. McC.

Proteolysis in organ- and cancer-cells. E. MASCHMANN and E. HELMERT (Z. physiol. Chem., 1933, **218**, 142—152; cf. this vol., 628, 636).—The liver, spleen, and kidneys of carcinomatous and sarcomatous mice and hens contain much more cathepsin than the tumours; further, the organ-cathepsin shows a greater degree of activation. Thus proteolysis is or may be greater in the organ-cells than in cancer-cells. J. H. B.

Action of radium on cancer cells. I. Effects of hydrocyanic acid, iodoacetic acid, and sodium fluoride on metabolism and transplantability of cancer cells. II. Factors determining susceptibility of cancer cells to radium. H. G. CRABTREE and W. CRAMER (Proc. Roy. Soc., 1933, B, **113**, 226—238, 238—250).—(I) HCN ($M/1000$—$M/500$) causes 85—95% inhibition of tumour tissue respiration (I) and an increase of aërobic glycolysis (II) to approx. the anaërobic val. The effects, after treatment for 1 hr., are reversible up to a HCN concn. of $M/20$, the tumour being transplantable. $CH_2I\cdot CO_2H$ (III) (3×10^{-5} to $10^{-3}M$) causes gradually increasing inhibition of (I) and a greater inhibition of (II). At the lower concn. recovery is complete after treatment for 1 hr., but at $10^{-3}M$ the cells are killed and the tumour is not transplantable. NaF is similar in action to (III), but at higher concns. Recovery occurs at $M/100$, but not at $M/20$.

(II) The sensitivity to Ra of tumour cells, the respiration of which has been reversibly checked *in vitro*, has been determined in terms of transplantability after irradiation. Anaërobiosis diminishes, and HCN ($M/1000$) and low temp. (0°) increase, the sensitivity, which is not affected by $CH_2I \cdot CO_2H$ or NaF. A. C.

Effect of inhibiting factor from normal tissues on spontaneous tumours of mice. J. B. Murphy and E. Sturm (Science, 1933, **77**, 631—632).—Extracts from mouse placenta and embryo skin known to reduce the growth of transplanted cancer have an inhibiting effect on natural or spontaneous cancer. L. S. T.

Serum-proteins in diabetic acidosis. J. P. Peters, D. M. Kydd, and A. J. Eisenman (J. Clin. Invest., 1933, **12**, 355—376).—During severe acidosis the proteins were generally within or above normal limits owing to hæmo-concn. (I), falling during recovery to below the normal min. The initial loss of serum-H_2O was due in part to passage of fluid into the tissues, and restoration of serum vol. seemed to be largely independent of restoration of tissue fluids. Shock due to (I) is at least an aggravating factor of diabetic coma. Nutr. Abs. (*b*)

Nature of diabetic acidosis. J. P. Peters, D. M. Kydd, A. J. Eisenman, and P. M. Hald (J. Clin. Invest., 1933, **12**, 377—392).—Although great variation was found in the concns. of the various blood constituents, the results suggest the following processes: (*a*) displacement of CO_2 by keto-acids (I); (*b*) urinary elimination of a proportion of (I), free or neutralised by NH_3; (*c*) neutralisation of some of (I) by fixed base followed by excretion in the urine; (*d*) reduction of electrolyte concn. of body-fluids and consequent loss of H_2O. The base lost in combination with ketones is generally much < that excreted as Cl′. The actual deficiency of body-Cl′ is far > would appear from analyses of the serum if there is associated loss of body-fluid; there is a much greater decrease of base united with Cl′ than of base united with CO_2+ org. acids. Nutr. Abs. (*b*)

Diabetic acidosis. Electrolyte balances following the withdrawal and re-establishment of insulin therapy. D. W. Atchley, R. F. Loeb, D. W. Richards, jun., E. M. Benedict, and M. E. Driscoll (J. Clin. Invest., 1933, **12**, 297—326). Nutr. Abs. (*b*)

Utilisation of galactose in physiological and pathological conditions. II. Utilisation of galactose in diabetes mellitus. Galactose as substituent carbohydrate. III. Behaviour of galactose in the depancreatised dog during complete and partial insulin deprivation. IV. Galactose assimilation in the liver. H. Kosterlitz and H. W. Wedler (Z. ges. exp. Med., 1933, **87**, 397—404, 405—410, 411—415).—II. After oral administration of galactose (I) to diabetics the blood-sugar was lower than after an equal amount of glucose (II); less sugar was found in the urine. When frequent small doses (10—20 g.) of (I) were given, practically no galactosuria occurred. Addition of (I) to a measured diet over a long period caused less glycosuria than a corresponding amount of (II). (I) had a definite antiketogenic and protein-sparing effect.

III. (I) given *per os* to depancreatised dogs was not utilised, being completely recovered in the urine as (II). When insulin was given, (I) was not more utilised than (II).

IV. Oral administration of (I) to rats led to a rise in blood-(I), little change in -(II), and no evidence of (I) storage in the liver. (I) must, therefore, be changed into glycogen or some unknown substance. Nutr. Abs. (*b*)

Ketonic substance production and destruction in certain tissues of diabetic dogs. W. Goldfarb and H. E. Himwich (J. Biol. Chem., 1933, **101**, 441—448; cf. A., 1932, 80).—The concn. of ketones in arterial blood varies with time. Analysis of the efferent and afferent blood from and to the heart, striated muscle, brain, and testis shows a correlation between the striated muscle, the gastro-intestinal tract, and the heart in the production of these substances. H. D.

Hyperinsulinism. E. Ziskind (Arch. Int. Med., 1933, **52**, 76—85).—In a case of spontaneous hypoglycæmia, no improvement resulted from thyroid therapy. No abnormality was noted in the pancreas or in the endocrine glands. H. G. R.

Hypoglycæmia. C. Sippe and J. Bostock (Med. J. Austral., 1933, **1**, 207—218).—Hypoglycæmia in non-diabetic patients occurs as a symptom complex often associated with other disorders. Nutr. Abs. (*b*)

Glycine synthesis in pseudohypertrophic muscular dystrophy. I. K. Freiberg and E. S. West (J. Biol. Chem., 1933, **101**, 449—451).—In this disease the capacity to produce glycine in response to administration of BzOH is not different from that of the normal. H. D.

Etiology of gallstones. IV. Is cholesterol excreted by the gall-bladder mucosa? E. Andrews, L. E. Dostal, and L. Hrdina (Arch. Surg., 1933, **26**, 382—388).—Cholesterol, although excreted by the infected gall bladder, is not secreted in appreciable quantities by the mucosa of the normal gall bladder (I). Ca is excreted by (I) in large amounts. Ch. Abs.

Hypoproteinæmia. E. Moschcowitz (J. Amer. Med. Assoc., 1933, **100**, 1086—1092).—Review and description of illustrative cases. Nutr. Abs. (*b*)

Function of the liver. Modified glucose tolerance test. H. T. Ricketts (Arch. Int. Med., 1933, **52**, 147—157).—The test (A., 1930, 1470) is not a satisfactory measure of the metabolic function of the liver. H. G. R.

Non-protein-nitrogen of blood in health and in hepatic disease. M. T. Tindal (Arch. Dis. Children, 1933, **8**, 17—24).—After a dose of 15 g. of urea in 150 c.c. of H_2O, convalescent children showed a rise of blood-non-protein-N for the first hr. and a fall during the second hr. Children with diseased livers showed a higher fasting level, a slower rise, and a continued rise over the whole 2 hr. Nutr. Abs. (*b*)

Experimental hepatic insufficiency. Coefficient of Maillard and blood-nitrogen in the normal guinea-pig. F. Meersseman and J. Dorche (Compt. rend. Soc. Biol., 1933, **112**, 903—905).—In the normal guinea-pig, the NH_3 coeff. of the urine was < 1. The ratio of the urea-N of the blood to the total non-protein-N averaged 0·63.

Nutr. Abs. (*b*)

Experimental hepatic insufficiency. Coefficient of Maillard and blood-nitrogen in the guinea-pig during acute and subacute phosphorus poisoning. F. Meersseman, J. Dorche, and F. Morelon (Compt. rend. Soc. Biol., 1933, **112**, 905—907).—Guinea-pigs poisoned with 4 drops *per diem* of 1% P in oil died in about 6 days. On the fifth day in three animals of six, the NH_3 coeff. of the urine was > 13. In one animal the blood-urea-N increased and in three animals the ratio of urea-N to total non-protein-N was 0·32—0·54. Nutr. Abs. (*b*)

[Absence of] pressor substance in the blood in essential hypertension. G. E. Wakerlin and H. D. Bruner (Arch. Int. Med., 1933, **52**, 57—65).

H. G. R.

Hysteria in dogs. H. D. Walston (Nature, 1933, **132**, 243).—Canine hysteria appears to be connected with vitamin-*A* deficiency coupled with a substance (" *E*-substance ") occurring in dog biscuits and other cereal foods. L. S. T.

Methods of increasing the defensive power of the peritoneum: behaviour of the serous membrane with increased defences in the course of acute bacterial infections. M. Tabanelli (Arch. Ist. Biochim. Ital., 1933, **5**, 155—174).—Guinea-pigs were injected intraperitoneally with different quantities of colloidal Ag, arsenobenzene (I), and $MgCl_2$, at varying periods both before and after intraperitoneal inoculation with the min. lethal dose of *B. coli*. In general, animals treated with Ag survived, with (I) to a smaller degree, whilst $MgCl_2$ retarded death.

R. N. C.

Calcium content of blood-serum in leprosy. A. G. Badenoch and F. E. Byron (Trans. Roy. Soc. Trop. Med. Hyg., 1932, **26**, 253—258).—When the lepra reaction was positive the serum-Ca was definitely subnormal (average 8·9 mg. per 100 c.c.); in most other cases the Ca was, or approached, normal. Clinical improvement was usually associated with a rise in Ca in both " reaction " and " non-reaction " cases. A few patients showed an abnormally high serum-Ca which appeared to be correlated with rapid advance of the leprotic process. Nutr. Abs. (*b*)

Plasma-protein and plasma-colloid osmotic pressure in pathological conditions with special reference to the occurrence of œdema. E. Muntwyler, C. T. Way, D. Binns, and V. C. Myers (J. Clin. Invest., 1933, **12**, 495—504).—Nephritic œdema is usually accompanied by lowering of plasma-protein and -colloid osmotic pressure (normally 29—36 cm. of plasma). Ch. Abs.

Calcium. VII. Calcium effects on thoracic lymph flow of dogs. A. L. Lieberman. **VIII. Therapeutic effects of calcium gluconate on thrombophlebitic œdema.** A. L. Lieberman and L. M. Zimmerman (J. Pharm. Exp. Ther., 1933, **48**, 293—299, 301—304).—VII. Ca, when rapidly injected, tends to retard the lymph flow in dogs, possibly by lowering cell permeability.

VIII. Subcutaneous and, to a smaller extent, oral administration of Ca gluconate and parathyroid extract hastens the disappearance of experimental thrombophlebitic œdema in dogs. J. H. B.

Galactose (?) in the blood of pregnant women. S. Battistini, L. Herlitzka, and B. Cossu (Biochem. Z., 1933, **263**, 24—32).—In women, towards the end of pregnancy, the glucose content and total reducing power of the blood decrease, although the content of reducing non-sugars remains normal. Methods are described by which it is shown that there is also present another reducing substance (I) which does not occur in normal blood. (I), which is not adsorbed by yeast and is found in the filtrate after deproteinisation by Somogyi's method, is probably galactose.

W. McC.

Relationship of iodine to the basal metabolic rate and to the changes in the thyroid gland in pregnant rabbits. J. D. Stewart and F. R. Menne (Endocrinol., 1933, **17**, 93—102).—Pregnant rabbits fed with I (0·001—0·003 mg. per kg. per day) showed a smaller increase in metabolic rate and thyroid activity, presumably through protection of the thyroid against over-function. Nutr. Abs. (*b*)

Gas exchange in new-born and premature infants. A. Schlossmann and H. Murschhauser (Z. Kinderheilk., 1933, **54**, 301—316).—In the normal infant the O_2 consumption averaged 27·9 c.c. per min. and the R.Q. was 0·828; in the premature the O_2 consumption was 6·2—12·7 c.c. and the R.Q. 0·852—0·891. The low val. for premature infants is attributed to very low body-temp. Nutr. Abs. (*b*)

Diastase content of saliva of premature infants. G. Hensel (Z. Kinderheilk., 1933, **54**, 367—376).—The amylase (I) content (determined by the Wohlgemuth–Michaelis–Pechstein method) of the saliva of premature infants was considerable, falling within the same limits as in full-term infants; in children it was 2·5 times and in adults 5 times as great. The (I) content varied irregularly in any one infant and could not be raised by the use of food rich in starch.

Nutr. Abs. (*b*)

Mineral and water metabolism of premature infants. H. Paffrath and J. Massart (Z. Kinderheilk., 1933, **54**, 343—366).—In premature infants receiving breast- (I) or butter-milk (II) or mixtures of these, the mineral retention increased with increase in intake. Ca may be retained without any H_2O, but alkali retention was always associated with corresponding increase in H_2O storage. With a subcaloric diet there appeared to be a dry retention of alkali, but this was due to endogenous formation of H_2O resulting especially from fat catabolism. When the diet was changed from the mineral-rich (II) to the mineral-poor (I) both H_2O and alkali were excreted in excess. The H_2O and alkali metabolism appear to be the same as in œdematous adults.

Nutr. Abs. (*b*).

Creatinuria in premature infants. H. Paffrath and W. Ohm (Z. Kinderheilk., 1933, **54**, 377—

379).—The creatinine (I) coeff. [(I)-N in 24 hr./body-wt. in kg.] was 4·4—6·5 in premature and 4·2—7·8 in full-term infants. In the first 3 weeks of life the prematures excreted very little or no creatine (II); from 4 to 7 months they excreted 10% of the total (I) as (II), so that prematures excrete less (II) than full-term infants of the same age. The reduced (II) excretion is attributed to the lower muscular activity in the prematures. NUTR. ABS. (*b*)

Bromine of blood in manic depressive psychoses. J. M. SACRISTÁN and M. PERAITA (Klin. Woch., 1933, **12**, 469—470).—Cases of manic depressive psychosis show diminished vals. of blood-Br. Cases of post-encephalitis show normal or high vals. NUTR. ABS. (*b*)

Blood-urea clearance test. G. S. ORTIZ (Semana Méd., 1933, i, 865—874).—In renal insufficiency the val. is $\not> 50\%$; addition of NaCl to the diet causes a decrease. Vals. $> 75\%$ are normal. CH. ABS.

Blood-phosphate fractions in experimental rickets. E. JACOBSEN (Biochem. Z., 1933, **263**, 313—315).—The decrease of total acid-sol. PO_4 in red blood-cells in experimental rickets is due chiefly to a decrease in the pyrophosphate fraction. Since the inorg. PO_4 fraction is equally decreased, there appears to be an equilibrium between ortho- and pyrophosphate in blood, such that decrease of ortho- results in corresponding decrease of pyro-phosphate. P. W. C.

Behaviour of cholesterol in saturnism. U. BASSI and G. CASTROVILLI (Arch. Ist. Biochim. Ital., 1933, **5**, 119—154).—Cholesterol (I) tests were carried out on 56 cases of saturnism (II). Blood-(I) increased in chronic (II), but was normal in pre-(II), whilst during saturnine colic it was decreased. The intradermic reaction with colloidal (I) was positive in (II), strongly positive during colic. Serum flocculation by colloidal (I) was positive in chronic cases in general, but was negative during colic, tending, however, to become positive after it. In cases where (II) was accompanied by other diseases, results were discordant. R. N. C.

Incidental hyperguanidæmia in dogs in parathyroid tetany. W. R. BRYAN and A. S. MINOT (Proc. Soc. Exp. Biol. Med., 1933, **30**, 595—597).—Only 50% of animals had an increased blood-guanidine after parathyroidectomy and the concn. was not proportional to the symptoms of tetany. A disturbance of Ca metabolism is probably the main cause of tetany. NUTR. ABS. (*b*)

Substances in thymus and urine producing tetany. II. Occurrence of tetanising substances in urine of children and adults. H. SELZER (Z. Kinderheilk., 1933, **54**, 421—434).—Convulsions and 30% lowering of serum-Ca were found in two children with tetany and three children and five adults with conditions associated with tissue destruction. In five patients the findings were only partly positive, whilst in sixteen, including three infants with tetany, they were negative. NUTR. ABS. (*b*)

Thyroxine content of blood during hyperthyroidism. U. S. VON EULER and A. G. HOLMQUIST (Arch. exp. Path. Pharm., 1933, **171**, 201—205).—Hyperthyroidism in man is accompanied by an increase in the thyroxine content of the peripheral venous blood, the increase with non-febrile patients being logarithmically related to that in the basal metabolism. F. O. H.

Blood-cholesterol in thyroid disease. II. Effect of treatment. L. M. HURXTHAL (Arch. Int. Med., 1933, **52**, 86—95).—Blood-cholesterol (I) is low in toxic thyroid states. Determination of (I) is of distinct but limited val. in diagnosis of hyperthyroidism. H. G. R.

Lipase content of the urine and blood-serum in kidney tuberculosis. R. YASUDA (Tôhoku J. Exp. Med., 1933, **20**, 265—274).—Normal urine contains 0·0007 and blood-serum 0·0039 [unit ?] of lipase; in tuberculosis without kidney involvement the vals. are 0·0009 and 0·0040, respectively. When one kidney is involved the lipase in the urine secreted by that kidney may be much > or < that in urine secreted by the other kidney. CH. ABS.

Tuberculosis and the deficiency of vitamin-*A* in the diets of young children in India. N. K. BASU (Z. Vitaminforsch., 1933, **2**, 190—193).—A protective action of vitamin-*A* against tuberculosis is indicated. E. B. H.

Enzyme content of human pancreas [in disease]. J. BALÓ and L. LOVAS (Virchow's Arch., 1933, **288**, 326—332).—There is generally a parallelism between the contents of lipase, trypsin, and diastase in the pancreas of persons who have died of various diseases; an exception, however, occurs with septic diseases, when the tryptic action is very much decreased. All three enzymes are diminished in quantity in cases where the diseases have led to cachexia, especially in tuberculosis. In two cases of fat necrosis there was an increase in lipase. NUTR. ABS. (*b*)

Liver-glycogen content. IV. Glycogen and fat content of liver in toxic states in infancy. H. C. GLOTZ. **V. Glycogen content of liver in meningitis and brain injuries.** L. BECK (Z. Kinderheilk., 1933, **54**, 394—403, 404—407).—IV. The vals. found for the glycogen (I) content of the livers of infants who died with toxæmic symptoms by Dische and Popper's method varied between 1·4 and 4·0%, *i.e.*, were relatively high in comparison with those found in infants dying of other diseases. The slightly lower vals. than those reported in infants without disease are attributed to partial inanition. The fat content of the livers of the toxæmic infants was relatively low. The toxæmia of infants is not a primary disturbance of carbohydrate metabolism.

V. In cases of meningitis with and without convulsions the % of liver-(I) was high, whilst in convulsions due to epilepsy, cerebral hæmorrhage, and icterus gravis it was lower. NUTR. ABS. (*b*)

Oxidation-reduction potential of retina. M. NAKASHIMA and K. HAYASHI (J. Biochem. Japan, 1933, **17**, 315—341).—The oxidation-reduction potential (I) of suspensions or extracts of frog's retina in physiological saline or Ringer's solution rises when the prep. is exposed to light and falls again when the light is removed. The effect is influenced by the duration of exposure to darkness and by the p_H and concn. of the medium. $Fe^{\cdot\cdot\cdot}$ but not $Cu^{\cdot\cdot}$ augments the action of light, whilst KCN decreases (I) to $\frac{1}{5}$ the initial val. Addition of PhMe is followed after 24 hr. by a diminution in (I). The bearing of the results on vision is discussed. F. O. H.

Sensitivity of tissue respiration to action of cyanide. B. Kisch (Biochem. Z., 1933, **263**, 75—97; cf. this vol., 305).—Tissues (kidney, liver, diaphragm, heart, retina, Jensen rat sarcoma) differ greatly in regard to the extent to which their respiration (I) in Ringer solution containing no org. matter is checked by 0·01*N*-NaCN. The extent to which (I) resists the action of NaCN increases with the age of the tissue and is usually greater in "phosphate Ringer" than in "carbonate Ringer." When KCN replaces NaCN an additional effect due to $K^{\cdot}$ is observed. The increased (I) caused by adding org. matter (glucose, NH_2-acids, lactate, pyruvate, sarcosine) is checked by NaCN to extents which differ according to the substance added and to the tissue concerned. Although 0·02*N*-pyruvate checks the (I) of ox-kidney, it increases the extent to which (I) resists the action of NaCN. These results are best explained by supposing the existence of various respiratory catalysts. W. McC.

Chlorophyll. XX. Transformation of chlorophyll in the animal organism. L. Marchlewski and W. Urbańczyk (Biochem. Z., 1933, **263**, 166—172).—Spectroscopic and other examination shows that anhydro-β-phyllotaonin from the fæces of the silk-worm is probably identical with Conant's phæopurpurin-18 (A., 1930, 1299) and closely related to Fischer and Hendschel's phyllobombycin (A., 1932, 659). All these substances are closely related to phyllocyanin, which itself is very similar to chlorophyll. Structural formulæ are suggested. There is no evidence that chlorophyll serves as a source of blood-pigments in the animal body. W. McC.

Fate of dehydrocholic acid in the toad. S. Shibuya (J. Biochem. Japan, 1933, **17**, 385—390).—Following subcutaneous injection of Na dehydrocholate and glycine into toads, the urine contains a diketohydroxycholanic acid, iso*reductodehydrocholic acid*, m.p. 258°, $[\alpha]_D^{20}$ +28·7° in $COMe_2$ [*Me* ester, m.p. 126° ($1H_2O$), 136° (anhyd.), $[\alpha]_D^{20}$ +28·44° in MeOH (*dioxime*, m.p. 248°, $[\alpha]_D^{20}$ +24·59° in MeOH)]. It appears to be an isomeride of reductodehydrocholic acid (A., 1922, i, 1158). F. O. H.

Pigment deposits in intestinal muscle coats and their relation to diet factors. E. Nachtnebel (Amer. J. Pathol., 1933, 9, 261—269).—The muscle coats of the intestinal tracts of dogs previously fed on liver diets showed brown or buff-coloured pigmentation. The pigment was found to bear some similarity to that observed in human hæmochromatosis (hæmofuscin) and in old age, and may be due to the absorption of some constituent of liver. Nutr. Abs. (*b*)

Effect of dietary and environmental factors on the p_H of intestinal tract. F. E. Mussehl, M. U. Blish, and C. W. Ackerson (Poultry Sci., 1933, **12**, 120—123).—There was no marked difference in the p_H vals. of the contents of different parts of the alimentary canal of young cockerels receiving diets high in various substances, such as $NaHCO_3$, NH_4Cl, and different carbohydrates, or of birds with rickets and healing rickets. Nutr. Abs. (*b*)

Fat absorption. G. Farkas and L. von Thanhoffer (Z. Biol., 1933, **93**, 560—565).—Feeding of olive oil (I) to frogs is followed by an intensive absorption, (I) penetrating to the centre of the alimentary canal cells and leaving the cell-membrane free from (I). No absorption occurs when milk or (I), emulsified with bile, is directly injected into the intestine under conditions whereby hydrolysis is inhibited. Bile is not essential to fat absorption, whilst no difference could be detected between the rates of absorption at p_H 9—10 and 4—5. The intracellular re-synthesis of fat and the mechanism of absorption are discussed. F. O. H.

Decomposition of fat infused directly into the animal body. III. Formation of sugar and ketonic substances from infused fat. T. Babaa (Tôhoku J. Exp. Med., 1933, **20**, 452—470).—Intravenous infusion into depancreatised dogs of highly dispersed fat emulsions, in amounts which could produce considerable lowering of the R.Q., did not bring about either increase of blood-sugar or increased excretion of sugar in the urine, but caused an increase of both blood- and urinary ketones. Injection of ketonic substances caused hyperglycæmia as determined by the Hagedorn–Jensen method, but this is not necessarily the result of their conversion into sugar. Nutr. Abs. (*b*)

Relationship of muscle metabolism to formation of ketones. C. Brentano (Deut. med. Woch., 1933, **59**, 448—451).—Creatinuria (I) always accompanies the breakdown of muscle- (but not of liver-)glycogen, and also diabetic and other severe ketoses. In all cases of (I) an increased formation of ketonic substances takes place from both exogenous and endogenous sources. This may be an indication of increased conversion of fat into carbohydrate associated with the destruction of muscle-glycogen. Nutr. Abs. (*b*)

Relation between mitochondria and glucose–glycogen equilibrium in the liver. E. M. Hall and E. M. MacKay (Amer. J. Pathol., 1933, **9**, 205—220).—Histological examination of the liver mitochondria in rabbits, dieted so as to give varying liver-glycogen (I) contents, revealed marked changes in these structures relative to the (I) content. Nutr. Abs. (*b*)

Rate of absorption of glucose from the intestinal tract. E. M. MacKay and H. C. Bergman (J. Biol. Chem., 1933, **101**, 453—462).—The coeff. of intestinal absorption (I) of glucose (II) was determined in rats by feeding variable amounts of (II) and subsequent determination of that remaining in the intestine after killing. (I) is raised by increasing the concn. or amount of (II) fed; it decreases with time after feeding. H. D.

Action of the parenteral administration of sugars on the hydrogen-ion concentration of

normal and malignant tissues in living animals. C. Voegtlin, H. Kahler, and R. H. Fitch (Science, 1933, 77, 568).—Injection of pure natural sugars into the voluntary muscle of rats, and into various standard sarcomata, forces the production of lactic acid to such an extent that [H˙] is increased. Acid–base equilibrium is therefore a function of carbohydrate metabolism. L. S. T.

Behaviour of the alkaline reserve of rats after feeding with glucose and fructose. R. Stöhr (Z. physiol. Chem., 1933, **218**, 263—268).—0·2 g. of glucose per 100 g. of body-wt. fed to fasting rats lowered the alkaline reserve after 15—30 min., but it became normal after 1 hr.; fructose had no effect. J. H. B.

Influence of various organic acids on the ability of the rat's liver to store carbohydrate. E. H. Majer and H. Reisner (Biochem. Z., 1933, **263**, 340—352).—The total carbohydrate (I) of rat's liver can be determined by combining the methods of Dische and Popper (A., 1926, 1282) with the reduction method of Bertrand. By feeding rats with a carbohydrate-poor diet only transient changes of (I) occur, and by adding the Na salts of succinic, malic, and citric acids, only in exceptional cases were any considerable increases in (I) obtained. After 24 hr. fasting, the mean (I) val. of rat's liver was 0·4%. After administration to these starved animals of the Na salts of AcOH, $EtCO_2H$, butyric, valeric, hexoic, *dl*-lactic, succinic, malic, and citric acids, (I) vals. were increased only by $EtCO_2H$, lactic, and succinic acids, and then became 2 or 3 times the normal fasting val. P. W. C.

Duration of recovery period following strenuous muscular exercise. O. M. Solandt and J. H. Ridout (Proc. Roy. Soc., 1933, **B**, **113**, 327—344).—Recovery from 30—45 sec. of strenuous exercise, *i.e.*, a permanent return of CO_2 production and O_2 intake to within the normal range of basal control vals., was complete in $<$ 1·5 hr. in three subjects. A prolonged slight increase in O_2 intake in two of the subjects is regarded as not due to the recovery process. A. C.

Effect of long-continued muscular exercise on the chemical composition of the muscles and other tissues of beef cattle. H. H. Mitchell and T. S. Hamilton (J. Agric. Res., 1933, **46**, 917—941).—Exercise had no effect on the H_2O, Fe, hæmoglobin, or red cell content of the blood or on the Fe or hæmoglobin of the tissues except in the case of the Fe content of the bone-marrow, which was considerably reduced. The Et_2O-sol. matter of all tissues tended to decrease with muscular work, but decisive effects were evident only in the liver. The H_2O content of the liver, heart, and skeletal muscle was also reduced, but no evidence of changes in the proportion of free and bound H_2O was obtained. Light work reduced the N content of the liver, the result being intensified and extended to muscular tissue with heavier work. This N change results from a decrease in N extractives and an increase in glycogen and lipins not extractable by Et_2O. The creatine content and the % of collagen-N in total N of the muscle are reduced. Ash contents of tissues are not appreciably altered by work. A. G. P.

Soya-bean (vegetable) milk in infant feeding. F. R. Rittinger and L. H. Dembo (Amer. J. Dis. Children, 1932, **44**, 1221—1238).—The fat, protein, and vitamin contents are approx. equal to those of cow's milk. Ch. Abs.

Infant nutrition. VII. Lactic acid milk. J. R. Gerstley (Amer. J. Dis. Children, 1933, **45**, 538—554).—Lactic acid milk is less effective in reducing the alkalinity of infants' intestinal contents than cow's milk+lactose. Ch. Abs.

Feeding experiments with decomposition products of proteins. III. S. Mayeda (Proc. Imp. Acad. Tokyo, 1933, 9, 277—279; cf. A., 1932, 643, 1060).—A cryst. substance, m.p. 220° (decomp.), necessary for the growth of rats fed on a basal diet of pure NH_2-acids, starch, butter, yeast extract, and salts, has been isolated from the mono-NH_2-mono-CO_2H fraction of the acid hydrolysate of fish-meat protein. The C, N, and H contents agree with the formula for aminohydroxyvaleric acid. E. C. S.

Loss of nitrogen during protein inanition. A. Roche (Compt. rend., 1933, **197**, 279—280).—Rats which died of protein inanition had a ratio of loss of tissue-N/loss in body-wt. 0·5—1·5, whilst when death was due to total inanition the ratio was 0·5, which indicates partial disintegration of muscular protein in the former case. R. S. C.

Comparative chemical composition of normal animal muscle and after death due to total or protein inanition. A. Roche (Compt. rend., 1933, **197**, 431—432).—Total fasting (I) diminishes, and protein fasting (II) increases, nucleic P in fat- and ash-free rat muscle. The ratio NH_2-N : $(NH_2)_2$-N is the same in normal rats and (I), but is considerably higher in (II). (I) causes only slight variations from the normal in the content of individual NH_2-acids. The effect of (II) is irregular; histidine is unchanged, tryptophan, tyrosine, lysine, and, to a smaller extent, arginine diminish, whilst cystine increases slightly, as in (I). The results are explained by partial degradation of muscle-protein to provide necessary NH_2-acids for maintenance. A. C.

Influence of nutrition on the mechanical properties of [sheep's] hairs. W. Spöttel (Bied. Zentr. [Tierernähr.], 1933, **B**, **5**, 13—64).—Protein-rich feeding-stuffs tend to increase the breaking strength and extensibility of hairs, but the effect is not uniform among hairs of different fineness. Deficiency of protein affects the quality especially of the finest and coarsest hairs. In general, dietary changes influence the extensibility more than the breaking strain. A. G. P.

Some aspects of intermediary protein metabolism. E. Brand and M. M. Harris (Science, 1933, 77, 589—590). L. S. T.

Metabolism of *d*- and *l*-methionine. R. W. Jackson and R. J. Block (Proc. Soc. Exp. Biol. Med., 1933, **30**, 587—588).—Growth in rats was stimulated equally effectively by *d*-, *l*-, and *l*-formyl-methionine, but the *d*-formyl derivative was without action. Nutr. Abs. (*b*)

Degradation of amino-acids in the animal body. H. A. Krebs (Z. physiol. Chem., 1933, **218**, 157—159; cf. this vol., 856).—In the oxidative deamination of aspartic (I) or glutamic (II) acid by the kidney of the rabbit, guinea-pig, or dog, the primary keto-acid products undergo further reaction unless the cells are poisoned with $0{\cdot}001M$-H_3AsO_3, when the keto-acids may be isolated. (I) affords oxalacetic acid (yielding $AcCO_2H$ and CO_2), (II) gives α-ketoglutaric acid (2 : 4-*dinitrophenylhydrazone*, m.p. 222°). J. H. B.

Embryochemical investigations with the injection method. VI. Behaviour of creatine or creatinine in the hen's egg on amino-acid injection. I. Takahashi (Z. physiol. Chem., 1933, **219**, 31—33; cf. A., 1932, 298).—Eggs were incubated for 17 days after injection with various NH_2-acids. Only arginine and creatine produced a definite increase in the creatinine content. J. H. B.

Formation of urea in vertebrates. H. Manderscheid (Biochem. Z., 1933, **263**, 245—249).—In the liver of amphibians (*Rana esculenta*) and of reptiles (*Testudo graeca*) synthesis of urea is strongly accelerated by addition of ornithine as in mammalian liver. Formation of urea in the whole of the vertebrates occurs always by way of citrulline and arginine. P. W. C.

Energy of urea synthesis. H. Borsook and G. Keighley (Proc. Nat. Acad. Sci., 1933, **19**, 626—631).—The respiration of rat-liver slices has been studied. An increased O_2 consumption accompanies the synthesis of urea from NH_4HCO_3 in Ringer's solution, and it is considered that this process is probably responsible for part ($\not>$ 20%) of the sp. dynamic action of proteins. A. W.

Chemical structure and physiological response. IV. Conjugation of salicylic acid with glycine and its action on uric acid excretion. A. J. Quick (J. Biol. Chem., 1933, **101**, 475—485; cf. A., 1932, 1277).—The formol titration method (A., 1926, 539) for hippuric acid was applied to the determination of salicyluric acid (I) and an adaptation of the Day and Taggard bromination method (cf. A., 1932, 1061) for total salicylic acid (II) was used. (I) is obtained from the urine after a diet of fruit and vegetables and administration of Na salicylate (III) by acidifying and extraction with Et_2O and leaching the residue, after the removal of Et_2O, with toluene and $CHCl_3$. Acetylsalicylic acid is determined in the Et_2O extract of urine by Br titration before and after hydrolysis with 5% aq. NaOH. The excretion of (I) after doses of (III) is uninfluenced by exogenous glycine (IV). The excretion of (II) is not rapid, only 50% excretion occurring after feeding 2 g. in 24 hr. Whilst 5 g. of (IV) has practically no effect on the excretion of uric acid, 1·5 g. when given with 2 g. of (II) produces a large augmentation; (IV) also shortens the period of stimulation of excretion due to (II). A crit. concn. of (II) in the body exists below which no stimulation occurs. H. D.

Phosphorus metabolism in embryonic life. III. Phosphagen in avian development. E. Baldwin and D. M. Needham (J. Exp. Biol., 1933, **10**, 105—112).—The inorg. P of the chick embryo as % of the body-wt. rose gradually from the 70th to the 240th hr. of incubation, when there was a sudden and enormous increase due to ossification of bone. Creatine phosphate was present at the earliest stage investigated. As a % of the body-wt. it rose up to the 4th day and then slowly fell. At the 4th day there was also a max. in the phosphagen considered as a % of the inorg.+labile P. Nutr. Abs. (*b*)

Effect of pasteurisation of milk on the utilisation of its calcium for growth in the rat. M. Ellis and H. H. Mitchell (Amer. J. Physiol., 1933, **104**, 1—9).—Rats were fed for 30 days by the paired feeding method on a low-Ca ration supplemented by raw or pasteurised milk. The milk supplement provided 57% of the total Ca intake, which was restricted to about half that normally retained during the period of rapid growth. All rats gained in wt. (4·4—5·4 g. daily), with a slight difference in favour of raw milk. Analysis of the carcases showed no consistent differences between pair mates as regards % of H_2O, fat, and ash, but the % of Ca in the ash was higher for the rats on raw milk. The pasteurisation of milk thus lowered by 12·3% the availability of its Ca for the growing rat. Under conditions of severely restricted Ca intake, the Ca retention was as high as 98% for the rats on raw milk and 92% for those on pasteurised milk. Nutr. Abs. (*b*)

Behaviour of the lungs in intermediate chlorine metabolism. T. Maki (Biochem. Z., 1933, **263**, 410—420).—The lungs normally retain blood-Cl and give it back again to the blood in fasting and hypochloræmic conditions and in periods of high and low temp. P. W. C.

Mineral metabolism—copper and iron. S. W. Kletzien, K. W. Buchwald, and L. Hudson (Proc. Soc. Exp. Biol. Med., 1933, **30**, 645—647).—Rats given 5·43 mg. Cu daily, as $CuSO_4$, with a diet containing 2 mg. Fe and 0·033 mg. Cu daily, for 12 weeks, showed small increases over controls in the Fe content of all the tissues analysed. There was a definite decrease in the Cu content of the spleen. Nutr. Abs. (*b*)

Development and functional activities of the albino rat as affected by diets deficient in iron. T. B. Keith and R. C. Miller (J. Agric. Res., 1933, **46**, 943—961).—Normal growth was obtained with a daily intake of 0·06 mg. of Fe supplied in skim-milk powder, but reproduction was less successful, especially in the second generation, than when adequate Fe was given. A. G. P.

Resorption of iron of food as ferrous iron. W. Lintzel (Biochem. Z., 1933, **263**, 173—186).—In growing rats prolonged oral administration of 2 : 2′-dipyridyl (I) causes reduction of Fe assimilation and of hæmoglobin production and checks growth, but (I) given parenterally has no such effect. Part of (I) given orally or parenterally is excreted unchanged in the urine. The Fe compound of (I) is not resorbed, but is excreted quantitatively in the fæces when given orally and is partly retained, partly excreted in the urine, when given parenterally. Since (I) forms a complex with $Fe^{\cdot\cdot}$ but not with $Fe^{\cdot\cdot\cdot}$, it follows that the symptoms mentioned are due to the fixing of $\text{Fe}^{\cdot\cdot}$ by (I) in the stomach and intestine and that the Fe of food is resorbed as $\text{Fe}^{\cdot\cdot}$. Since (I) given orally and parenterally does not cause excretion of the complex in the urine it follows that $\text{Fe}^{\cdot\cdot}$ probably plays no part in the intermediate Fe metabolism. W. McC.

Oxidation within the tissues and hot carbon dioxide baths. A. Mougeot and V. Aubertot (Compt. rend., 1933, **197**, 282—283).—Emanation (I) enters the body through the skin; this is accompanied by increased respiratory activity, absorption of O_2, and reabsorption of CO_2. No (I) is absorbed from a radioactive bath in absence of excess of CO_2, nor is there increased absorption of O_2 in presence of excess of CO_2, but in absence of (I). C. A. S.

Stimulation of tissue respiration by small amounts of cyanide. B. Kisch (Biochem. Z., 1933, **263**, 187—194).—The respiration of fresh and old tissues from the organs of mammals in "carbonate" and "phosphate" Ringer solution in the presence or absence of org. nutrient matter is increased (up to 60%) by addition of low concn. (0·0005—0·000002*N*) of NaCN, the extent of the increase and the optimum concn. being different for different tissues. W. McC.

Effect of administration of cyanides on the thyroid gland of chickens. A. W. Spence (J. Pharm. Exp. Ther., 1933, **48**, 327—331).—Chickens are extremely resistant to injections of MeCN both as regards thyroid reaction and toxic effect. This is due to their lack of power to liberate the CN group of MeCN; the fæces contain only 0·1% of the CN injected as CNS′, although with allyl, K, and benzyl cyanides the vals. are 4·5%, 20—30%, and 24·4%, respectively. J. H. B.

Administration of bilirubin to herbivorous animals under normal and pathological conditions. F. Heimann (Biochem. Z., 1933, **263**, 316—322).—The serum of rabbits on a normal diet (alkaline) does not contain a determinable amount of bilirubin (I) until the amount injected is 20 mg. and on an acid diet is 7·5 mg. After P poisoning the serum on injection of 10 mg. of (I) contains considerable amounts of (I). After keeping the animals under reduced pressure and injecting large amounts of (I), none was detectable in the serum. After establishing a condition of hæmolytic jaundice (prsodin poisoning) and injecting (I), the serum on an alkaline diet did not, but on an acid diet did, contain a determinable amount of (I). Results with guinea-pigs are also recorded. P. W. C.

Fate of "cardiazol" in man. A. Esser and A. Kühn (Arch. exp. Path. Pharm., 1933, **171**, 284—288).—Ingestion of 100 c.c. of 10% "cardiazol" (I) produced convulsions and death in 1 hr. Analysis of the intestinal contents indicated that 7·4 g. were absorbed from the stomach, but the greater part of this could not be found. The (I) actually detected occurred mainly in the liver and blood. F. O. H.

Pharmacological activity of ethyl nitrite, U.S.P. M. R. Thompson, M. J. Andrews, and C. T. Ichniowski (J. Amer. Pharm. Assoc., 1933, **22**, 487—495).—The action of fresh and deteriorated preps. of $EtNO_2$ was investigated. The main action is on the circulation, whilst diuresis is not produced. Deterioration, which is accompanied by a change in p_H, produces no toxic substance. A high EtOH content enhances the stability of the prep. F. O. H.

Alteration of the blood-[$H^{\cdot}$] and mineral metabolism during narcosis. II. Blood-[$H^{\cdot}$]. J. Bečka (Arch. exp. Path. Pharm., 1933, **171**, 244—249; cf. this vol., 744).—Rabbits narcotised for short periods (with one of fifteen narcotics tested) experienced a decrease in blood-p_H. A max. decrease occurred with $CHCl_3$ (0·14—0·24) and with veronal (0·20). The decrease persisted for some time after recovery excepting with amylene and chloral hydrates. Morphia, however, produced hyperpnœa and alkalosis, the p_H increasing 0·40—0·49. F. O. H.

Post-operative hyperglycæmia. F. Lefèvre (Rev. belge Sci. méd., 1933, **5**, 5—20).—The post-operative hyperglycæmia, produced when a mixture of scurocaine and adrenaline is used as local anæsthetic, is absent when either is used alone. Nutr. Abs. (*b*)

Local anæsthetic action of *p*-aminobenzoates of diethylaminoethoxy-alcohols. W. H. Horne and R. L. Shriner (J. Pharm. Exp. Ther., 1933, **48**, 371—374).—The compounds $NEt_2\cdot[CH_2\cdot CH_2\cdot O]_n\cdot CH_2\cdot CH_2\cdot OH$, where $n=1$—4, were prepared (A., 1932, 935), converted into the *p*-nitrobenzoate hydrochlorides (oils), and reduced to *p*-aminobenzoates (oils). When $n=1$, the compound has low toxicity and high anæsthetising power, the ether linking producing surface as well as injection anæsthesia. The higher homologues are too irritating for use. J. H. B.

Hæmaturia from handling 5-chloro-*o*-toluidine. A. N. Currie (J. Ind. Hygiene, 1933, **15**, 205—213). W. O. K.

Hæmolysis by Australian snake venoms. I, II. C. H. Kellaway and F. E. Williams (Austral. J. Exp. Biol., 1933, **11**, 75—80, 81—94).

Comparison of the action of sapotoxin, strophanthin, and certain snake-venoms on the heart. J. W. C. Gunn and D. Epstein (Quart. J. Pharm., 1933, **6**, 182—186).—The high tolerance of the toad to digitalis (I) and the absence of tolerance to sapotoxin are suggested as a biological test for distinguishing these. Two cobra venoms (*Naia flava* and *N. nigricollis*) have (I)-like action. H. G. R.

Standardised preparation of digitalin for injection. J. C. Gage (Quart. J. Pharm., 1933, **6**, 161—168).—Assay of digitalin (I) by the frog and the guinea-pig methods gives results which do not differ significantly. The Knudson–Dresbach colorimetric method does not agree with the biological methods, but the results are of the same order. H. G. R.

Paraldehyde in digitalis standardisation by the cat method. D. Epstein (Quart. J. Pharm., 1933, **6**, 169—173).—Paraldehyde is recommended for anæthesia in the assay of digitalis by the cat method. H. G. R.

Solanine poisoning. S. G. Willimott (Analyst, 1933, **58**, 431—438).—An extract in AcOH is evaporated at alkaline reaction and extracted with 95% EtOH, and the solanine pptd. with aq. NH_3 and purified by dissolution in AcOH and repptn. Amounts found per 100 g. were 2·7—9·1 mg. in Irish and Cyprus potato tubers, and 27—49 mg. in the shoots, the lowest vals. being obtained for plants from high altitudes. Cases of poisoning are cited. Solanine sets to a firm jelly in hot EtOH or C_5H_{11}·OH and (like solanidine) produces a red colour with Na_2SeO_4 in H_2SO_4; reddish-yellow changing to reddish-brown with Fröhde's reagent; orange-yellow changing to violet with NH_4VO_3 in H_2SO_4; pink to red with warm H_2SO_4 in EtOH (2 : 3); reddish-brown with conc. HNO_3; and deep red with the $SbCl_3$ vitamin reagent.

J. G.

Action and rate of elimination of atropine and genatropine. M. Haferkorn and L. Lendle (Arch. exp. Path. Pharm., 1933, **171**, 276—283).—That genatropine (I) has a lower toxity than atropine (II) is confirmed (cf. A., 1926, 82). The action of (II) on the cat's vagus, however, is 4—5 times as strong as that of (I); the therapeutic indices of (I) and (II) are therefore approx. equal. The min. rates of continuous effective injection indicate that, when allowance is made for the difference in the single effective dose, the rates of elimination of (I) and (II) are practically equal. F. O. H.

Morphine and enzymes. II. E. Keeser (Arch. exp. Path. Pharm., 1933, **171**, 311—316; cf. A., 1932, 1167).—The action of lecithinase (I), phosphatase, urease, or tyrosinase is modified by the presence of small amounts of morphine (II), heroin, and codeine. Thus subcutaneous injection of low concns. of (II) into man activates the blood-(I) and produces decomp. of lecithin with liberation of choline and methylguanidine. These substances are probably concerned with the symptoms of abstinence in (I) addicts.

F. O. H.

Comparison of the toxicity of nicotine and anabasine. W. A. Gersdorff (J. Amer. Chem. Soc., 1933, **55**, 2941—2945).—The theoretical thresholds of toxicity for rotenone, nicotine, and anabasine towards goldfish are 0·012, 8·0, and 9·5 mg. per litre, and the rate of increase of the theoretical velocity of fatality with increase in concn. 90, 5·6, and 5·2 c.c. per mg. per min., respectively. R. S. C.

Physico-chemical properties of some new choline derivatives in relation to their chemical constitution and pharmacological action. W. F. von Oettingen and R. O. Bowman (J. Pharm. Exp. Ther., 1933, **48**, 333—340).—Choline hydrochloride, $NMe_3Cl·CH_2·CH_2Cl$, $[·CH_2·NMe_3Cl]_2$, $NMe_3Cl·CH_2·CH_2·NH_2$, and $NMe_3Cl·CH_2·CH_2·NHMe$ in 0·01*M* concn. do not affect surface tension, are not sol. in oil, do not ppt. serum and lecithin emulsions, and do not affect rate of sedimentation of erythrocytes. The velocity of diffusion through living frog-skin is in inverse ratio to their pharmacological action.

J. H. B.

Aminohydroxy-compounds which show the biuret reaction. IX. Fate of some ω-amino-hydroxy-acids in phloridzin glycosuria and phosphorus poisoning. T. Kawada (Z. physiol. Chem., 1933, **219**, 34—37; cf. A., 1932, 1118).—In passage through phloridzinised dogs *iso*serine, but not γ-amino-β-hydroxybutyric acid (I), is converted into glucose. In dogs poisoned with P, a substance (*chloroaurate*, m.p. 182°; *chloroplatinate*, m.p. 225°), probably γ-butyrobetaine, was isolated from the urine. About ¼ of the (I) was recovered unchanged.

J. H. B.

Permeability and variation of permeability. Influence of surface-active and hydrotropic substances on the permeability of acids and of sucrose. A. N. Rao (Biochem. Z., 1933, **262**, 332—350).—The permeability is investigated of aq. solutions of $H_2C_2O_4$, tartaric and lactic acids, and sugar solutions through membranes of collodion, parchment, rubber, collagen, pig's bladder, and intestine with and without addition of saponin (I), $PhSO_3Na$ (II), a series of alcohols, etc. (I) generally (except with a rubber membrane) causes increased permeability to sugar solutions, the effect being greatest with medium to small concns. of (I). Surface-active substances also cause increased permeability. Na salicylate and (II) increase the permeability to acids, especially of biological membranes. P. W. C.

Electrical potential difference across living frog skin. H. B. Steinbach (J. Cell. Comp. Physiol., 1933, **3**, 1—26).—The skin is mounted as a diaphragm between two neutral salt solutions and the p.d. across the skin is equal to the sum of the "partial" p.d. from skin to solution on either side. Addition of KCl to either solution lowers the p.d. between skin and solution irrespective of the nature of the dissolved salt. $CaCl_2$ lowers the p.d. between skin and both solutions when applied to the outside but not when applied to the inside of the skin. The skin has a low sensitivity to changes in electrolyte concn. of the inside solution, but responds quickly to small changes in the outside medium. The curve relating p.d. and log [NaCl] shows a max. corresponding with 0·006*M*-NaCl. A. G. P.

Actual reaction of the skin, in normal, morbid, and different experimental conditions. E. Rastelli (Arch. Ist. Biochim. Ital., 1933, **5**, 175—208).—The skin-p_H has been measured by intradermic injection of vital indicators. In the normal condition it is neutral. Gangrene is accompanied by a fall in p_H in direct relation with the extent of the gangrenous lesion, and probably also with its duration. In ordinary cutaneous inflammation p_H is normal, but tends to fall if suppurative exudations occur. Experimental arterio-venous stasis induces a fall of p_H for the duration of the stasis; venous stasis has no effect. Injection of adrenaline and histamine produces short periods of acidosis, that for adrenaline being double the length of that for histamine. The time for re-establishment of neutral conditions after intradermic injection of solutions of known p_H varies for each subject with the difference between the p_H of the solution used and neutral p_H, on either side of neutrality.

R. N. C.

Measurement of polarisation in skin. H. Schaefer (Z. Biol., 1933, **93**, 570—577).—The nature of the polarisation produced by application of a const. current to human skin indicates a marked sensitivity to electrical currents. The phenomena associated with the resistance and polarisation capacity of the skin are discussed. F. O. H.

Neuromuscular excitability in relation to the biochemistry of minerals. II. Influence of change of Ca/P and Na/K ratio in the diet. L. Seekles and B. Sjollema (Biochem. Z., 1933, **262**, 367—379).—Using the same technique (this vol., 532), the authors further investigate the changes of *AS/AO* (I) ratio with changes of diet. Increase of P relative to Ca in the rabbit's diet led to a condition of latent tetany characterised by increased (I). Using the normal salt ratio, excitability was low, (I) being usually < 1, whereas abnormal ratios of Na/K=1/542 and Ca/P=1/8·4, and still more diets combining both of these ratios, led to considerable increase in (I). P. W. C.

Effect of sensory stimulation on the blood-sugar content of rabbits, splanchnicotomised or suprarenalectomised. F. Ohmi (Tôhoku J. Exp. Med., 1933, **20**, 498—505).—Whilst double splanchnicotomy considerably diminishes the hyperglycæmia due to sensory stimulation in rabbits, double adrenalectomy has little effect. Nutr. Abs. (*b*)

Stimulation by mineral and fatty acids in the barnacle, *Balanus balanoides*. W. H. Cole and J. B. Allison (J. Gen. Physiol., 1933, **16**, 895—903).—Stimulation of *B. balanoides* by HCl, H_2SO_4, HNO_3, and the first seven members of the normal fatty acids has been measured by recording the % closure over a range of $[H^{\cdot}]$ from $3{\cdot}2\times10^{-8}$ to $5{\cdot}889\times10^{-6}$. The intensity of stimulation is proportional to the effects of two forces, one related to the change in $[H^{\cdot}]$ and the other to the field of force around the anion of the acid added. The order of stimulating activity is $HCl > H_2SO_4 > HNO_3$ and for the fatty acid series heptoic > hexoic > valeric acid > $PrCO_2H = AcOH > EtCO_2H = HCO_2H$. A. W.

Storage of halogens in hens' eggs and therapeutic application of halogenised eggs. I. L. Berkesy and K. Gönczi (Arch. exp. Path. Pharm., 1933, **171**, 260—268).—The greater part of the I of hens' eggs is organically combined, the yolk being richer in I than the white. Intravenous injection of 1·25% aq. $NaIO_3$ into hens produces a marked increase in the I content of the eggs. The feeding of such eggs to persons with thyroid diseases results in an increase in the blood-I. F. O. H.

Daily administration of inorganic iodine in Dutch tap-water. J. F. Reith (Biochem. Z., 1933, **263**, 395—399).—A method is described for the determination of various I fractions (EtOH-insol, EtOH-sol., etc.) in drinking H_2O. In spite of the high I content, those who drink this H_2O show no ill effects. P. W. C.

Case of chronic lead poisoning. H. E. Monk (Analyst, 1933, **58**, 397).—The liver, brain, kidney, and right tibia of a stereotyper dying 4 years after the last exposure to Pb contained 35, 8, 8, and 27 p.p.m. of Pb. E. C. S.

Experimental variation of the distribution and excretion of medicinal preparations. F. Serio and R. Indovina (Biochem. Z., 1933, **262**, 308—320).—A series of complex Au and As compounds is injected into rabbits and the distribution of Au and As investigated by analysis of the organs and tissues. The effect on this distribution of a preliminary injection of substances which accelerate (I) or inhibit (II) blood coagulation is then determined. (I) facilitate the storage of these compounds, especially in the liver, and (II) accelerate their elimination. P. W. C.

Variations in blood-cholesterol immediately after a single irradiation with rays intermediate between ultra-violet and *X*-rays. S. Malczynski (Compt. rend. Soc. Biol., 1933, **112**, 925—927).—Irradiation of the shaved skins of two dogs at 10 cm. distance for 15 min. produced transient falls of 4% and 7% in blood-cholesterol. After 10 min. at 8 cm. there were temporary increases of 18% and 22%. Such rays are less potent than *X*-rays. Nutr. Abs. (*b*)

Variations in mineral elements of blood as affected by irradiation with rays intermediate between ultra-violet and *X*-rays. S. Malczynski (Compt. rend. Soc. Biol., 1933, **112**, 928—931).—Irradiation for 15 min. at 10 cm. distance produced temporary increases of about 25% in K and 28—29% in Ca content, the effect being most permanent in the latter case. The Na content also increased immediately after irradiation, this being followed by a fall. The effect on P content was indefinite. Nutr. Abs. (*b*)

Quinones as enzyme models. X. Activation by salts of bivalent cations of the catalysis of oxidative deamination of amino-acids. B. Kisch. **XI. Rôle of the anions in this process.** B. Kisch and K. Schuwirth (Biochem. Z., 1933, **263**, 98—104, 195—197; cf. this vol., 634).—X. The oxidative deamination of glycine in presence of hydroxyquinol or resorcinol [as measured by yield (I) of NH_3] is not affected by NaCl, KCl, LiCl, or TlCl and only very slightly affected by $BaCl_2$. The other alkaline-earth metals (II) greatly (up to 200%) increase (I); in this connexion they form the series $Ba < Sr < Mg < Ca$. The optimum concns. for $MgCl_2$ and $CaCl_2$ are 0·001*M* and 0·002*M*, respectively, and the optimum p_H for $SrCl_2$, $MgCl_2$, and $CaCl_2$ is 9—11. Colloidal factors are not involved in the process, but the ability of the halides of (II) to combine with NH_3 may play a part.

XI. The activity of $Mg^{\cdot\cdot}$ and $Ca^{\cdot\cdot}$ is not affected by the anions (Cl′, Br′, I′, NO_3', SO_4'', formate, acetate, lactate) with which they are combined. W. McC.

Yellow oxidation enzyme. O. Warburg and W. Christian (Biochem. Z., 1933, **263**, 228—229; cf. this vol., 753).—The dye $C_{13}H_{12}O_2N_4$ (I), when heated at 100° with $0{\cdot}2N$-$Ba(OH)_2$ in an indifferent atm., gave a pale yellow cryst. *substance* (II), $C_9H_{10}O_2N_2$, m.p. 210—211°. The absorption spectrum of (II) resembles that of (I), having three bands, but these are shifted in (II) towards the ultra-violet. (II) is not decolorised by $Na_2S_2O_4$. W. McC.

Rôle of phosphate in oxidations. I. Activity of catalase in phosphate solutions. II. Peroxidase activity in phosphate solutions. A.

Malkov (Biochem. Z., 1933, 263, 268—273, 274—277).—I. The activity of yeast-catalase (I) is inhibited by PO_4'''. Added Fe inhibits (I), but PO_4''' removes this effect.

II. The activity of yeast-peroxidase (II) is decreased by PO_4''' most strongly at first. Added Fe increases the activity of (II). P. W. C.

Oxidation–reduction potential of peroxidase preparations. M. Padoa and N. Nerozzi (Biochem. Z., 1933, 263, 375—386).—The r_H vals. of peroxidase preps. do not support the view that active O is present, the latter in presence of peroxides never being detected. On the contrary, the greater is the activity of the enzyme prep., the more strongly reducing is the medium. P. W. C.

Potentiometric study of the Schardinger reaction. J. Toyama (J. Biochem. Japan, 1933, 17, 433—439).—Using a Au or Pt electrode, the oxidation–reduction potential of a system containing the Schardinger enzyme (I) is not influenced by the addition of MeCHO, salicylaldehyde, or PhCHO, whilst methylene-blue produces an abrupt change to a reduction potential (cf. A., 1926, 1175). With a Pt but not with a Au electrode, CH_2O produces a small reducing effect which is increased by presence of (I). F. O. H.

Coupled reactions in biological systems. H. F. Schott and H. Borsook (Science, 1933, 77, 589).—In (i) the reduction of pyruvate to lactate by means of the energy of the anaërobic oxidation of formate to H carbonate and (ii) the reduction of fumarate to succinate through the anaërobic oxidation of lactate to pyruvate intermediary substances, methylene-violet for (i) and methylene-blue for (ii) were necessary for reaction to occur. PhMe-treated *B. coli*, the enzyme system for (i) and (ii), contain no mediators or energy carriers capable of serving these two systems. L. S. T.

Coupled redox potential of the lactate–enzyme–pyruvate system. J. P. Baumberger, J. J. Jürgensen, and K. Bardwell (J. Gen. Physiol., 1933, 16, 961—976).—The term "coupled redox potential" (I) is defined as the potential at which an irreversible system comes into equilibrium with a reversible system when a suitable catalyst is present. The system lactate–pyruvate is reversible in the presence of lactic acid dehydrogenase. Thermodynamic calculations have been made to determine the free energy of the reaction lactic ion $\longrightarrow$ pyruvic ion and an approximation for the standard free energy of formation of $AcCO_2H$. The importance of (I) as a factor in the regulation of the equilibrium of metabolites is indicated. A. W.

Eleutoamylase, an anti-sistoamylase. T. Chrzaszcz and J. Janicki (Biochem. Z., 1933, 263, 250—261).—Amylase (I) is normally accompanied by sistoamylase (II), which combines with and inactivates (I). Witte's peptone and other protein degradation products act as an eleutoamylase antagonistic to (II). These peptones inhibit the union of (I) and (II), they can liberate active (I) from the inactive compound of (I) and (II), and they show a protective action against the inactivation of (I) by shaking. P. W. C.

Glycolytic co-enzymes. H. Matsuzaki (J. Biochem. Japan, 1933, 17, 457—481).—Whilst the degradation of glucose by various tissues [rabbit sarcoma (I), mouse tumour, mouse diaphragm (II), and guinea-pig cerebral cortex] is marked, that of hexose diphosphate (III) is very slight: the reverse is true, however, for rabbit red-muscle (IV) and mouse liver (V). The glycolytic co-enzyme from (I) (A., 1928, 1274) accelerates the decomp. of glucose by (I), (II), and kidney, but not that by (IV) and (V); acceleration by the co-enzyme from baker's yeast (A., 1927, 590) or by extract of adrenal cortex occurs with (IV), but not with the tumour tissues. (IV) has a high content of both phosphatase and phosphatese, whilst the tumour tissues are poor in the latter. Oxidation of (III) by (IV), but not that of glucose by tumour tissue, is attended by a marked H-activation. The tissues decompose AcCHO and, to a smaller extent, dihydroxyacetone and glyceraldehyde. F. O. H.

Action of iodine on glycolytic metabolic processes, especially fermentation by yeast. Effect of iodoacetic acid. A. Sturm and J. Schulz (Biochem. Z., 1933, 263, 198—218; cf. A., 1931, 761).—The fermentation (I) of surviving liver and (I) by yeast or yeast extract is increased by low (0·0001—0·01*M*) concn. of I′. With yeast the extent of the effect depends on the concn. of I′, the species of yeast, the p_H, and (in particular) on the stage of (I) at which the I′ is added. The optimum conditions are: baker's yeast at p_H 7·2, I′ in 0·001*M* concn. added as (I) sets in. The I′ affects the phosphorylation of the sugar and its action is inhibited if $CH_2I·CO_2H$ (II) is present. The inhibiting action of (II) on the (I) of yeast decreases and vanishes (*e.g.*, with baker's yeast buffered with phosphate at p_H 6·9) as the p_H increases; under certain conditions (II) even accelerates (I). (II) also inhibits co-enzyme action, (I) of hexose diphosphate, and (I) of $AcCO_2H$ only at $p_H < 6·5$. Possibly (II) acts by combining with NH_2-compounds which accelerate (I). There is parallelism between changes in the I content of the animal organism and changes in its metabolism. W. McC.

Thiocyanate formation in the animal body. II. K. Lang (Biochem. Z., 1933, 263, 262—267).—The author's previous work (this vol., 637) on the synthesis of thiocyanate under the action of an enzyme rhodanese widely spread through the animal body is confirmed in the perfusion of cat's liver and kidney preps. with mixtures of cyanide and thiosulphate. The formation of CNS′ from mustard oil and thiocyanate esters is also demonstrated. Investigation of the CNS′ balance in man shows that CN′ is a regular product of intermediate metabolism. P. W. C.

Stability and separation of phosphatases. E. Jacobsen (Biochem. Z., 1933, 263, 302—312).—The destruction of the non-sp. phosphatases (I) of kidney, bone, and liver at different p_H are investigated. Whereas (I) are destroyed by heating for a short time in feebly acid reaction in presence of NH_4Cl, the sp. adenylpyrophosphatase (II) is much more stable, and a separation by differential heat inactivation is described. (II) so purified attacks only that

PO_4 which is readily hydrolysed by acid. The optimum p_H is 7·2. Sp. (II) is detected in most tissues. P. W. C.

Influence of electrolytes on mono- and pyrophosphatase. S. Munemura (J. Biochem. Japan, 1933, **17**, 343—366).—Monophosphatases with p_H optima at 3, 5·6, and 9 and pyrophosphatases with p_H optima at 4, 5—6, and 9 were prepared from pig's kidney and rice bran (A., 1932, 305) and freed from proteins and electrolytes by autolysis and dialysis. The acceleration of some of the enzymes by $Mg^{\cdot\cdot}$ is noteworthy. $Ca^{\cdot\cdot}$ has no action, whilst in some cases F' has an inhibiting effect. AsO_4''' inhibits all types, whilst PO_4''' has a similar but less marked effect. The bearing of the results on glycolysis is discussed. F. O. H.

Lipases in the animal organism. I. A. I. Virtanen and P. Suomalainen (Z. physiol. Chem., 1933, **219**, 1—21).—The lipase (I) contents of various organs of guinea-pigs and rabbits show wide individual and seasonal variations. The liver contains most (I), next come pancreas, lungs, and kidneys in that order. Intravenous injection of (I) from pig's pancreas into rabbits almost doubled the (I) content of the liver; moreover, the extract showed the characteristics of liver (I) (inhibition by atoxyl, no action on olive oil), not of pancreatic (I). Pancreas (I) and liver (I) are probably identical, the differences being due to concomitants. J. H. B.

Determination of lipase. H. Steudel (Biochem. Z., 1933, **263**, 231—238).—The hydrolysis of olive oil by pancreatic lipase, using preps. from three different pigs and from the mixed sample from twenty pigs, as determined by Willstätter's method, gives very different curves for the various preps., and the curve for the mixed sample is not the mean of those for the individual samples. P. W. C.

Esterase action. IV. E. A. Sym (Biochem. Z., 1933, **262**, 406—424).—The influence on the reaction velocity of increasing the concn. of the substrates in enzymic and acid–base catalysis is investigated. Increasing the concn. of alcohol, acid, and ester had almost the same effects on the reaction velocities in the synthetic and hydrolytic reactions with esterase of pig's pancreas as in the corresponding acid–base-catalysed reactions. H_2O, on the other hand, accelerated both the hydrolytic and synthetic enzyme reactions, but inhibited both reactions when catalysed by HCl. The reaction products also inhibited the reaction when catalysed by esterase, by HCl, and by picric acid, the inhibition with acid–base being $<$ with enzymic catalysis. The sp. character of the pancreatic, liver, and gastric esterases is also investigated in comparison with the acid–base catalysis. P. W. C.

Biochemical synthesis of fatty esters of *cyclo*hexanols. L. Velluz and P. Sauleau (Compt. rend., 1933, **197**, 277—279).—The enzyme from *Ricinus* seeds (modified prep.) forms the following % of esters from oleic acid and the alcohol in 2 days at 16—18°: *cyclo*hexanol (I) 33 (63 in 12 days), *cyclo*hexane-1 : 2- and -1 : 4-diol, 26 and 35, respectively. It forms 30% of the hexoate of (I) and 12% of that of glycerol in 2 days. Esterification is hindered sterically ($o > p > m$), as shown by the methyl- and dimethyl-*cyclo*hexanols. R. S. C.

A product of the action of pepsin on glycine. A. Blanchetière (Compt. rend., 1933, **196**, 1926—1927).—From the residues after isolation of diketopiperazines (I) in the product of the hydrolysis of glycine (II) with pepsin (A., 1931, 1090) is isolated unchanged (II) (total recovery 50%) and a *substance* which does not give Abderhalden and Komm's reaction (A., 1924, i, 1361) and is pptd. from aq. solution by careful addition of dil. alkali or alkali carbonate, but its solution in excess of *N*-NaOH cannot be pptd. by neutralisation after 24 hr., the solution then dissolving $Cu(OH)_2$ like an NH_2-acid. Hence the substance is probably the enolic form of (I). J. W. B.

Influence of reducing and oxidising treatment on the function of organ cathepsins. P. Rondoni and L. Pozzi (Z. physiol. Chem., 1933, **219**, 22—30).—Cysteine promotes autoproteolysis of extracts of rabbit liver and mouse carcinoma, as measured by pptn. of residual protein with $CCl_3{\cdot}CO_2H$. Fe^{II} salts increase and glycogen inhibits the action. Oxidising agents (H_2O_2 or a stream of O_2) and increase of p_H inhibit proteolysis and in some cases produce an increase in the amount of protein pptd. J. H. B.

Autolysis of muscle. I. Influence of temperature on the distribution of nitrogen in ox flesh. I. A. Smorodincev, N. V. Schirokov, and P. V. Zyganova (Biochem. Z., 1933, **262**, 425—431).—During autolysis of flesh, the changes in the protein fraction both at room temp. (17—18°) and at 4° and 25—37° are followed by means of determinations of total, NH_2- and residual N of the flesh extract, and the results tabulated. Only small differences of total N were obtained at the different temp. The highest NH_2-N vals. were obtained at all temp. after 6 hr. autolysis and the curve for residual N at 17—25° followed, but lay $>$ that at 4—8°. P. W. C.

Nuclein metabolism. XXXI. Enzymic depolymerisation of animal nucleic acid. W. Klein. **XXXII. Ribodeoseguanylic acid.** W. Klein and S. J. Thannhauser (Z. physiol. Chem., 1933, **218**, 164—172, 173—180; cf. A., 1932, 776, 1167).—XXXI. Nucleophosphatase from intestinal mucosa contains two enzymes: thymonucleinase (I), which depolymerises thymus-nucleic acid to the mononucleotide (II), and a sp. phosphatase (III), which eliminates H_3PO_4 from (II). The action of (III) is suppressed by the addition of Na_2HAsO_4, thus permitting the isolation of (II). Yeast-nucleic acid is not attacked by (I). Hydrolysis of glycerophosphate and hexose diphosphate by (III) is only slightly suppressed by AsO_4'''.

XXXII. (II) was obtained in the manner indicated from thymus-nucleic acid and isolated as the cryst. *dibrucine* salt. This was converted into the unstable cryst. *ribodeoseguanylic acid* by way of the sec. *Ba* salt (IV), browns at 200°. (III) eliminates H_3PO_4 from (IV) yielding guaninedeoxyriboside. J. H. B.

Conversion of the intermediate term of the permanganate oxidation of uric acid into allan-

toic acid in the presence of soya enzymes and potassium cyanide. R. Fosse, P. de Graeve, and P. E. Thomas (Compt. rend., 1933, **197**, 370—374).—Allantoic acid (I) is produced by the action of soya-bean extract on hydroxyacetylenediureincarboxylic acid (II) (A., 1932, 864), confirming the view (Schuler and Reindel, this vol., 427) that (II) is the intermediate compound between uric acid and (I) in enzymic uricolysis. A. C.

Tannase. H. Dyckerhoff and R. Armbruster (Z. physiol. Chem., 1933, **219**, 38—56).—Extracts of the mycelium of *Aspergillus niger* contain at least two enzymes catalysing the hydrolysis of esters, tannase (I) hydrolysing Me gallate (III) and mould-esterase (II) hydrolysing PhOAc. (II) is destroyed by warming at p_H 8·9 at 40°, (I) being mostly unchanged. In order to undergo fission by (I) the acid component of the ester must contain two phenolic OH groups. The esterified CO_2H must be attached directly to the oxidised Ph ring and must not be in the *o*-position to an OH. The specificity of (II) is probably coincident with that of liver-esterase. The hydrolysis of (III) by (I) is unimol., optimum p_H 5—6. J. H. B.

Mechanism of enzyme action. XII. Cryolysis and the absorption of gases by lyophile colloids. II. F. F. Nord and G. Weiss (Biochem. Z., 1933, **263**, 353—365).—In continuation of previous work (A., 1932, 337, 909, 1203) curves show the changes of surface tension of various lyophile colloids (gum-arabic, saponin, and metacholesterol sols) in the unfrozen condition and after freezing for 2 hr. at −18° and −79° and also after treatment with C_2H_4, C_2H_2, and N_2O. Using the results of such methods, the enhanced activity of a cell-free lyophile-colloidal zymase solution after freezing and thawing is explained in terms of increased surface of the enzyme carriers. P. W. C.

Separation from yeast of an alcohol-dehydrogenase. D. Müller (Biochem. Z., 1933, **262**, 239—247).—Lebedev's maceration extract of bottom yeast contains an alcohol-dehydrogenase, obtained as a dry prep. by pptn. with $EtOH–Et_2O$. The enzyme, which is destroyed by heating at 90° for 30 min., oxidises $Pr^{\beta}OH$ to $COMe_2$. In this reaction, O_2 and methylene-blue do, but benzoquinone does not, act as a H_2 acceptor, the latter strongly inhibiting the reaction. Addition of cytochrome-*C* and of indophenoloxidase has no effect on the formation of $COMe_2$. P. W. C.

Action of yeast on glycerophosphoric acid. C. Neuberg and M. Kobel (Biochem. Z., 1933, **263**, 219—227; cf. this vol., 637).—*l*-Glycerophosphoric acid (I), prepared from the Ba H salt by a modification of Nilsson's method (A., 1930, 641), is converted by yeast into $AcCO_2H$. Concurrently a decarboxylation reaction (II) occurs. At appropriate p_H, if sufficient yeast is present, (II) becomes the main reaction. If dry yeast or yeast extract is used, the fermentation of (I) yields CO_2, MeCHO, and acetoin. W. McC.

Influence of organic dyes on cell and organ function. IV. Absorption by living cells (yeast). F. Axmacher (Arch. exp. Path. Pharm., 1933, **171**, 289—310; cf. this vol., 751).—$NHPh_2$ and, to a smaller extent, $CHPh_3$ dyes are absorbed by living and, to a greater extent, by dead top-yeast cells. Certain azo-dyes are absorbed only by dead cells. Cells rendered lipin-free by $COMe_2$, Et_2O, or $CHCl_3$ absorb to practically the same extent as normal cells. The mol. dimensions and surface activity of the dyes used indicate that a process of adsorption occurs. F. O. H.

Pantothenic acid, a growth determinant of universal biological occurrence. R. J. Williams, C. M. Lyman, G. H. Goodyear, J. H. Truesdail, and D. Holiday (J. Amer. Chem. Soc., 1933, **55**, 2912—2927).—Extracts (usually prepared by 80% MeOH) of rice bran, beef liver, eggs of *Cancer productus* and of *Strongylocentrotus purpuratus*, oysters, earthworms, planarian worms, *Physarum polycephalum*, *B. subtilis*, *Aspergillus niger*, *Spyrogyra*, *Oscillatoria*, milk, and egg-white stimulate the growth of yeast. Fractional electrolysis, diffusion, and other tests lead to the belief that all the extracts contain the same *pantothenic acid*, a polyhydroxylic acid, mol. wt. about 150, stable at 119° at p_H 5 or 7, but not at p_H 9. It is destroyed by N_2O_3, but can be esterified to an inactive ester and recovered in partly active form by acid or very dil. alkaline hydrolysis. It has no amphoteric properties, does not contain a reducible (hydrogenation) or carbohydrate (Ag_2O) group, and is closely related to vitamin-B_2. It is probably accompanied in the extracts by toxic substances. R. S. C.

Inhibition of growth by heparin. A. Fischer and P. Nyström (Biochem. Z., 1933, **262**, 364—366).—Crude liver extracts and pure samples of heparin inhibit the growth of yeast. P. W. C.

Oxidisability and rate of growth [of fungi]. A. Artundo and E. Aubel (Compt. rend. Soc. Biol., 1932, **108**, 1111—1112; Chem. Zentr., 1932, ii, 3904).—The growth of *Aspergillus niger* in solutions of glucose, citric and succinic acids is affected by changes in p_H in the same sense as the oxidisability of the nutrient at the active C. L. S. T.

Utilisation of aliphatic acids by moulds. O. Fürth and E. H. Majer (Biochem. Z., 1933, **263**, 332—339).—The dry wts. of mycelium obtained under comparable conditions by growing *Aspergillus niger*, *Penicillium glaucum*, and *Mucor mucedo* on a medium containing a series of Na salts of aliphatic acids and on sugars as the source of C are given. Of the acids, lactic and acetic are most readily utilised, then butyric, succinic, malic, and citric acids, and lastly HCO_2H, $EtCO_2H$, valeric and hexoic acids. Sugars are still more readily available, pentoses (arabinose are xylose) and hexoses (glucose, fructose) being equally readily utilised. P. W. C.

Biochemical transformation of formic acid by moulds. Chemistry of the process. T. Chrzaszcz and M. Zakomorny (Biochem. Z., 1933, **263**, 105—118; cf. this vol., 536, 749).—Moulds attack formates much more easily and rapidly than oxalates. The biochemical transformation of sugar by moulds normally proceeds thus: sugar ⟶ AcOH ⟶ fumaric acid ⟶ glyoxylic acid ⟶ $HCO_2H \longrightarrow CO_2 + H_2$, but there are also other stages.

$H_2C_2O_4$ is a secondary product. The variations which the process undergoes may be due to the presence of "sisto" and "eleuto" substances. W. McC.

Acid formation by moulds. R. Falck, W. Schoeller, and S. Michael (Biochem. Z., 1933, 262, 280—293).—Whereas *Aspergillus niger* converts mono- and di-saccharides into a mixture of gluconic, citric, and oxalic acids, with starch only citric and oxalic acids are detected. The quotient CO_2/O_2 is 1 in neutral and feebly acid medium so long as the process is aërobic, but becomes > 1 when anaërobic processes occur. P. W. C.

Action of iron on formation of kojic acid by means of *Aspergillus flavus*. A. Di Capua (Gazzetta, 1933, 63, 296—302).—Fe promotes the growth of *A. flavus*, and within certain limits accelerates and increases the formation of kojic acid (I) from sucrose or from glucose. It also promotes growth of the mould on Ca salts of fatty acids, but no (I) is formed from these. E. W. W.

Biochemistry of micro-organisms. XXIX. 2 : 5-Dihydroxybenzoic acid (gentisic acid), a new product of the metabolism of glucose by *Penicillium griseo-fulvum*, Dierckx. H. Raistrick and P. Simonart. **XXX, XXXI. Molecular constitution of the metabolic products of *P. brevi-compactum*, Dierckx, and related species. (I.) Acids $C_{10}H_{10}O_5$, $C_{10}H_{10}O_6$, and $C_{10}H_{10}O_7$.** A. E. Oxford and H. Raistrick. **(II.) Mycophenolic acid.** P. W. Clutterbuck and H. Raistrick.—See this vol., 949.

Nutrition of trypanosomes. M. Lwoff (Ann. Inst. Pasteur, 1933, 51, 55—116).—Trypanosomes (I) require for growth and reproduction proteoses and polypeptides. *Strigomonas oncopelti* is the only (I) requiring only peptones; the others need blood in small amounts [1 : 20,000 for *S. fasciculata*, 1 : 5000 for *Leptomonas pyrrhocoris* (Zotta), 1 : 500 for *L. ctenocephali*]. The active portion of blood is hæmatin; it can be replaced by animal catalase or vegetable peroxidases. The nutrition of (I), like that of the hæmophilic bacteria, is characterised by the need for active Fe, with which is linked a deficiency in respiratory enzyme. J. H. B.

***Pseudomonas Lindneri–Kluyver* (*Termobacterium mobile*, Lindner). Aërobic and anaërobic fermentation. Acid formation.** K. Schreder, R. Brunner, and R. Hampe (Woch. Brau., 1933, 50, 233—237, 243—245; cf. this vol., 428).—Under aërobic (I) and anaërobic (II) conditions the bacterium produces CO_2, lactic acid (III), AcOH (IV), and a small amount of succinic acid from glucose in presence of inorg. nutrients. MeCHO and fusel oil are also produced with (I) and glycerol and esters with (I) and (II). The total acid formation remains approx. const. with increase of initial sugar concn. The production of (IV) is much stronger than that of (III) with (I) and (II), but the difference is not so great with (II). Similar products are obtained by using wort as nutrient, when malic acid is also produced. R. H. H.

Preparation of diacetyl by fermentation. R. Heublyum, M. Barlas, M. Klyachko, and A. Zevalina-Blokh (Masloboino-Zhir. Delo, 1932, No. 4—5, 54—60).—The best yields (400—500 mg. per litre) of Ac_2 were obtained by fermenting a 2% sugar solution, to which 0·1% of MeCHO was added, with a mixture of yeast and *B. bulgaricus* at 32° for 18 hr. CHMeAc·OH was oxidised to Ac_2 by $FeCl_3$. Ch. Abs.

Action of *Staphylococcus* on oxalated plasma and on fibrinogen. O. Gengou (Ann. Inst. Pasteur, 1933, 51, 14—31).—The coagulation of oxalated plasma by *Staphylococcus* and the lysis of the clot are due to a single substance secreted by the organism even in media not containing fibrinogen (I), *e.g.*, bouillon. Pure (I) shows a short and incomplete coagulation followed by rapid digestion; the active substance is a fibrinolytic agent, coagulation being merely a stage in the process. Antilytic substances in plasma and inactivated serum have a retarding effect; serum-globulins and to a much greater extent -albumins show this inhibitory action. The lytic agent is resistant to ageing, drying, and heat and cannot be dialysed or filtered. J. H. B.

Nitrogen metabolism of *Bacillus mycoides*. VI. Utilisation of various sources of nitrogen. E. Glinka-Tschernorutzky (Biochem. Z., 1933, 263, 144—148; cf. A., 1929, 608).—Provided that K_2HPO_4 (0·2%) is present, *B. mycoides* grows satisfactorily in a mineral nutrient medium containing NH_4 salts as N source (I) and glucose as C source. Sol. NH_2-acids also serve as (I), but growth is then not so satisfactory as when NH_4 salts are used, whilst, in both cases, it is less satisfactory than when peptone is the medium. Mixtures of NH_2-acids (15), however, provide a medium not less satisfactory than peptone. Except with glycine and *d*-lysine hydrochloride K_2HPO_4 has no effect on the efficiency of NH_2-acids as (I). W. McC.

Chemistry of bacteria. V. Fat and phosphatide of diphtheria bacteria. E. Chargaff (Z. physiol. Chem., 1933, 218, 223—240; cf. this vol., 867).—The fat consists mainly of free fatty acids; from the esterified portion no glycerol or insol. carbohydrates were isolated on hydrolysis, but a $COMe_2$-sol. amorphous substance. The unsaponifiable portion contained highly unsaturated substances (I val. 140). Sterols were not detected. The solid saturated fatty acid (about ⅓ of total) was palmitic exclusively. The chief constituent of the liquid unsaturated acids was Δ^{θ}-*hexadecenoic acid* (*Me* ester, b.p. 110°/0·01 mm.), since it was catalytically hydrogenated to palmitic acid and gave on oxidation with $KMnO_4$ in alkaline solution θι-*dihydroxypalmitic acid*, m.p. 130° (corr.), and with $KMnO_4$ in $COMe_2$, azelaic and *n*-heptoic acids. 1% of the fatty acids consisted of an *acid*, $C_{14}H_{26}O_2$. The higher unsaturated acids form a complex mixture from which *diphtheric acid*, probably $C_{35}H_{68}O_2$, m.p. 35—36°, $[\alpha]_D^{23}$ +2·6° in $CHCl_3$, was isolated.

Acid hydrolysis of the phosphatide gave aldohexoses, fatty acids, and a high-mol. compound and traces of a base. The solid fatty acid was exclusively palmitic acid; the liquid acids contained a substance *corynin*, probably $C_{50}H_{100}O_4$, m.p. 70—71° (corr.), b.p. 220°/0·005 mm. [cryst. *Ac* (? Ac_2) derivative, m.p. 75—76° (corr.)], having 1 CO_2H and 2 OH groups. J. H. B.

Neutralisation of diphtheria toxin by heterocyclic compounds. L. Velluz (Compt. rend., 1933, **197**, 359—361).—10 mg. of ninhydrin neutralise 2000 lethal doses of diphtheria toxin in 24 hr. at 39°; an indigo-blue solution is formed, indicating the protein nature of the toxin. 5 mg. of rotenic acid or 10 mg. of *l*-dihydrorotenic acid neutralise 2000 doses in 4—5 days at 39°, as also does 0·5 mg. of *iodorotenic acid*, m.p. 239° (prepared by I and HgO), in 15 days. R. S. C.

Non-specific flocculation of diphtheria antitoxin, toxin, and toxoid and its bearing on the *Lf* titre. J. F. Anderson, G. F. Leonard, and A. Holm (Amer. J. Pub. Health, 1933, **23**, 681—686).—The Ramon flocculation test of diphtheria toxin and antitoxin is not always a measure of antigenic val., and may be influenced by bacillary proteins, phosphates, and pyrophosphates which increase the flocculation val. and decrease the time of flocculation. The reaction may therefore consist of a combination of the reactions occurring between inorg. constituents of toxin and serum, bacillary proteins and serum precipitins, and toxin and antitoxin. A. L.

Immunisation of human beings against diphtheria with purified diphtheria anatoxin and aluminium hydroxide. A. Schmidt (Dansk Tidsskr. Farm., 1933, 7, 123—133).—Tests on rabbits showed that Ramon's anatoxin is much more effective when mixed with 10% of $Al(OH)_3$. R. P. B.

Lipins of tubercle bacilli. XXXIII. Isolation of trehalose from acetone-soluble fat of human tubercle bacillus. R. J. Anderson and M. S. Newman (J. Biol. Chem., 1933, **101**, 499—504).—The fat (A., 1927, 1114) was saponified, unsaponifiable matter and fatty acids were separated, and the aq. residue was neutralised with KOH and conc. in vac. to dryness. The residue consisted of KCl and a syrup which on purification with neutral and basic Pb acetates yielded trehalose. The neutral $COMe_2$-sol. fat from human tubercle bacilli therefore appears to be not a glyceride but a complex ester of fatty acids with trehalose. F. O. H.

Absence of α-cellulose in tubercle bacilli. O. Binder (Compt. rend., 1933, **197**, 197—198). F. R. S.

Examination of immune-serum lipins for complement-fixing antibodies of tuberculosis. A. Hambleton (Canad. J. Res., 1933, 8, 553—562).—The antibodies are not removed from the protein fraction of immune serum by extraction with lipin solvents before or after digestion with trypsin or by desorption. They are therefore not lipoidal. R. S. C.

Mechanicism, vitalism, and the growth of bacteria. J. M. Sherman and G. M. Cameron (Science, 1933, 77, 537—538).—Abrupt environmental changes within the range of growth of *Bacterium coli* result in high mortality among the young cells. L. S. T.

Effect of carbon dioxide on bacterial growth. F. P. Coyne (Proc. Roy. Soc., 1933, **B**, **113**, 196—217; cf. B., 1932, 749).—The inhibition of the growth of several types of *Achromobacter*, and other bacteria isolated from fish, by CO_2 increases as the $[CO_2]$ is increased and the temp. is lowered from 37° to 0°. Growth of bacteria responsible for deterioration of fish is completely inhibited at 0° in an atm. containing 20% of CO_2. The inhibition is not due to a change of p_H in the agar culture medium, but is probably due to an intracellular p_H change and/or an effect of CO_2 on cellular enzyme systems. A. C.

Phenomenon of Charrin and Roger (serum agglutination of bacteria). P. Lasseur, A. Dupaix, and J. G. Marchal (Compt. rend., 1933, **196**, 1930—1932).—The limits of agglutination of the plastids (I) of *B. caryocyaneus* have been studied to explain the presence of free (I) in an agglutinating system containing an excess of antibodies (II). With high concn. of agglutinin all the (I) are coagulated, but a portion of the (II) remains free, whereas in medium or small concn. all the (II) are fixed, but some of the (I) remain free. J. W. B.

Significance of the colloidal carrier for the stability of the virus of foot-and-mouth disease. G. Pyl (Z. physiol. Chem., 1933, **218**, 249—262).—The virus (I) has two stability max. at p_H 3·0 and 7·6 with a min. at 6·0—6·5. Although active (I) solutions at the alkaline p_H can be acidified to 3·0 without entirely losing activity, when the p_H is increased from 3·0 to 7·6 the solution becomes inactive. The isoelectric point is at p_H 3·5—3·9, and at 3·9 there is a pptn. optimum, but these properties are probably due to the colloidal carrier, which markedly increases the stability of (I). (I) has two carriers, one for each stability max., acidification or alkalisation being accompanied by exchange of carrier. Each exchange damages (I). The stability min. corresponds with the isoelectric point of the free (I). The ampholyte nature of (I) indicates its protein character. J. H. B.

Influence of monoiodoacetic acid on the bacterial and enzymic hydrolysis of glucosides. K. Meyer (Biochem. Z., 1933, **262**, 329—331).—$CH_2I{\cdot}CO_2H$ has the same sp. inhibitory action on the hydrolysis of β-glucosides (I) by lactic acid streptococci as on lactic acid formation from glucose. The inhibitory action of the acid on the hydrolysis of (I) by emulsin is 500 times feebler, the bacterial β-glucosidase being different from that of emulsin. P. W. C.

Antiseptic and trypanocidal properties of some anil and styryl derivatives of 4-aminoquinaldine. J. N. Ashley, C. H. Browning, J. B. Cohen, and R. Gulbransen (Proc. Roy. Soc., 1933, **B**, **113**, 293—299; cf. A., 1929, 1109).—4-Chloro-2-methylquinoline is converted by NH_3 or suitable amines into 4-amino- [*methosulphate*; *methiodide*, decomp. 270°; *Ac* derivative, m.p. 176—178° (*methosulphate*; *methiodide*, decomp. 274—275°)], 4-*dimethylamino*-, an oil (*methiodide*, decomp. 290—295°), 4-*diethylamino*-, an oil (*methiodide*, m.p. 157—159°), and 4-β-*diethylaminoethylamino-2-methylquinoline*, an oil (*dimethiodide*, decomp. 279°). Condensation of these with $p\text{-}NO{\cdot}C_6H_4{\cdot}NMe_2$, $p\text{-}CHO{\cdot}C_6H_4{\cdot}NMe_2$, or $p\text{-}CHO{\cdot}C_6H_4{\cdot}NEt_2$ affords *methiodides* of the correspond-

ing 2-(*p*-dimethylaminoanil), 2-(*p*-dimethylaminostyryl), and 2-(*p*-diethylaminostyryl) derivatives. The antiseptic action of the anils on *B. coli* is weak. Some of the styryl derivatives of the *tert.* aminoquinolines are active towards *S. aureus*. None of the above is curative to mice infected with *T. brucei*.
A. C.

Antiseptic and trypanocidal action of some benzamidoquinoline anil and styryl compounds. C. H. Browning, J. B. Cohen, K. E. Cooper, S. Ellingworth, and R. Gulbransen (Proc. Roy. Soc., 1933, B, **113**, 300—307; cf. A., 1932, 522, 623).—6-Amino-2-methylquinoline and p-$NO_2\cdot C_6H_4\cdot COCl$ afford 6-(p-*nitrobenzamido*)-, m.p. 266—267° (*methoacetate*), which is reduced to 6-(p-*aminobenzamido*)-2-*methylquinoline* (I) m.p. 197—199° [*methosulphate*; *methochloride*; *Ac* derivative, m.p. > 300° (*methochloride*)]. (I) and Me_2SO_4, followed by treatment with NaCl or KI, yield 6-(p-*dimethylaminobenzamido*)-2-*methylquinoline methochloride* and *methiodide*, respectively. The appropriate methochloride condenses with *p*-substituted benzaldehydes or p-$NO\cdot C_6H_4\cdot NMe_2$, yielding the following styryl and anil derivatives, respectively, methoacetates being prepared from methochlorides by treatment with AgOAc; 2-(p-*acetamidostyryl*)-6-(p-*aminobenzamido*)*quinoline methoacetate* and -6-(p-*dimethylaminobenzamido*)*quinoline methochloride*; 2-(p-*dimethylaminostyryl*)-6-(p-*aminobenzamido*)- and -6-(p-*acetamidobenzamido*)-*quinoline methochlorides*; 2-(p-*aminostyryl*)-6-(p-*acetamidobenzamido*)*quinoline methoacetate*; the *methochlorides* of 2-(p-*dimethylaminoanil*)-6-(p-*acetamidobenzamido*)- and -6-(p-*aminobenzamido*)-*quinoline*. The anils and, to a smaller extent, some of the styryl derivatives are antiseptic towards *B. coli* and *S. aureus*. Slight to marked trypanocidal action is shown by the anil and styryl derivatives, with the exception of the 2-(*p*-dimethylaminostyryl) compounds, which are inactive.
A. C.

Ketogenic diet. Nature of bactericidal agent. A. T. Fuller (Lancet, 1933, **224**, 855—856).—Specimens of urine from patients on ketogenic diets were inoculated with an emulsion of *B. coli* and subcultured on agar, immediately, after 5, and after 20 hr. Urine containing 100 mg. of $CH_2Ac\cdot CO_2H$ per 100 c.c. showed bacteriostatic power at 5 hr., with 200 mg. per 100 c.c. frequently inhibition of growth after 20 hr. *l*-β-Hydroxybutyric acid was identified as the bacteriostatic substance. Acid urines showed greater bacteriostasis than alkaline urines of the same concn.
Nutr. Abs. (*b*)

Influence of parenterally introduced liver-cell constituents on the amount of urobilin in the urine. I. Effect on normal excretion of urobilin. II. Effect on experimental urobilinuria due to injection of hæmolysed blood. III. Effect on experimental urobilinuria due to injection of urobilin. R. Watarai (Japan. J. Exp. Med., 1932, **10**, 325—345, 347—358, 359—371).—In normal rabbits intraperitoneal injection of an emulsion of rabbit's liver (0·05 g. per kg.) decreases or (0·5—1·0 g.) increases the urinary urobilin. The smaller dose decreased urobilinuria induced by intramuscular injection of hæmolysed blood or subcutaneous injection of urobilin. Emulsions of other tissues (except kidney; occasional decrease) had no effect. The effects are due to the action of a hepatic auto-hormone on the liver.
Ch. Abs.

Specific effect on the stomach of the secretions of the fundic glands. II. Influence of the parenteral injection of emulsions of gastric mucosa on the secretory activity of the Pavlov pouch. I. Sugishima (Japan. J. Exp. Med., 1932, **10**, 177—201, 303—323).—Stimulation observed with optimal small doses is due to the sp. action of an auto-hormone.
Ch. Abs.

Effect of insulin on amino-acid- and urea-nitrogen in laked and unlaked blood. H. H. Powers and F. Reis (J. Biol. Chem., 1933, **101**, 523—527).—Injection into rabbits of 1 unit of insulin (I) and analysis of the blood before and after injection shows a decrease in NH_2-acid-N (II) uninfluenced by the method of preparing the filtrate, indicating that the diffusible portion of the (II) alone is affected by (I). No significant change in the blood-urea-N was observed.
H. D.

Effect of hormones on enzyme action. I. Effect of insulin on blood- and liver-amylase. A. Utevski, S. Epstein, and V. Osinskaja (Klin. Woch., 1933, **12**, 388—389).—Insulin (I) has no activating action on blood-amylase (II) *in vitro*. Injected into rabbits, (I) produces an increase in the amount of (II), probably owing to transference of the enzyme from the tissues.
Nutr. Abs. (*b*)

Effect of subcutaneous injections of trypsin on the blood-sugar and on insulin action. O. B. Buckley (Brit. J. Exp. Path., 1933, **14**, 57—62).—Subcutaneous injection of trypsin resulted in a rise of blood-sugar in the rabbit and an inhibition of the action of insulin subsequently administered.
Nutr. Abs. (*b*)

Distribution of carbohydrate in tissues and organs during insulin- and synthalin-hypoglycæmia, hunger, and liver-storage. K. Matsuura (J. Biochem. Japan, 1933, **17**, 441—455).—Insulin (I) and synthalin (II), injected into rabbits, produce a decrease in the true sugar (III) and glycogen (IV) levels of the lung, muscle, and kidney, whilst the non-glucose sugar (V) remains fairly const. With (I) but not with (II), the (III) and total reducing substances of the liver are increased. When the liver is damaged by P or CCl_4, all the tissues excepting the brain show normal vals. for (V), whilst (III) and (IV) decrease, the fall in (IV) with (II) being > with (I). Starvation for 8—12 days is followed by a steady fall in the levels of (III), (IV), and (V), that of (IV) becoming practically zero. (I), (II), and starvation have entirely different effects on carbohydrate metabolism.
F. O. H.

Accuracy of insulin assay on white mice. II. A. M. Hemmingsen (Quart. J. Pharm., 1933, **6**, 187—218).—The convulsion rates plotted on a probability scale against the logarithm of the dose give a straight line. A method of injection has been devised to eliminate errors due to changes in sensitivity; in calculating the average of the results of single tests, the logarithms of the results should be averaged. For mice with low body-wt. the sensitivity is greater in the evening. H. G. R.

Anti-insulin principle occurring in the pancreas. I. Presence in external secretion of the pancreas of non-diabetic and diabetic persons. W. Wohlenberg and K. Müller (Arch. exp. Path. Pharm., 1933, **171**, 340—345).—The ultra-filtrate (free from diastase) of 2·5—8·0 c.c. of pancreatic secretion (from the duodenum) of non-diabetic and, to a greater extent, of diabetic persons has a marked hyperglycæmic action when intravenously injected into rabbits (cf. A., 1929, 103). F. O. H.

Determination of adrenaline and thyroxine in blood. U. S. von Euler (Arch. exp. Path. Pharm., 1933, **171**, 186—200).—Normal human serum in concns. ≮ 1 : 200—1 : 400 accelerates the oxidation by finely-divided muscle as measured by the methylene-blue technique (cf. A., 1929, 474). A similar action by rabbit's serum is inhibited by adrenalectomy of the animal, by alkalis, and by ergotamine, and hence is due to adrenaline, the normal level of which is $10^{-12·5}$ to 10^{-13} g. per c.c. in man and rabbit. A similar but transient action is produced by thyroxine, the level of which in the blood is approx. 10^{-15} g. per c.c. F. O. H.

Calorigenic action of thyroxine polypeptide. W. T. Salter, J. Lerman, and J. H. Means (J. Clin. Invest., 1933, **12**, 327—334).—The calorigenic effect of thyroxine polypeptide (40% I) administered orally is equal to that when administered intravenously. The polypeptide is as active as an equiv. amount of thyroxine. Ch. Abs.

Determination of functional activity of the thyroid by urine or serum. II. Influence of Ca, K, Na, and Mg. M. Koh (Keijo J. Med., 1933, **4**, 291—299).—The ability of the urine or serum to inhibit the mydriatic action of atropine when incubated together at 37° for 2 hr. affords a criterion of the thyroid activity (I) of the animal. Intravenous injection into rabbits of 2·5% aq. $CaCl_2$ or NaCl increases, whilst that of KCl or $MgCl_2$ inhibits, (I). F. O. H.

Pituitary and thyroid. VIII. Action of extract of the anterior pituitary lobe on the weight of the thyroid. B. A. Houssay, A. Biasotti, and P. Mazzocco. **XV. Thyroidectomy and the thyroid-exciting action of the anterior pituitary of diverse species.** B. A. Houssay, A. Novelli, and R. Sammartino. **XVI. Action of extract of the anterior pituitary on the blood-iodine of animals with thyroid or pituitary removed.** B. A. Houssay, A. Biasotti, and P. Mazzocco (Rev. soc. argentina biol., 1932, **8**, 122—129, 514—522, 554—555).—XVI. The extract elevates the blood-I in normal or hypophysectomised dogs and lowers it in thyroidectomised dogs. Ch. Abs.

Factors influencing the functional development of the male gonad. J. M. Robson and H. Taylor (Proc. Roy. Soc., 1933, **B**, **113**, 251—267).—An account is given of the effects of anterior pituitary substance (I), gonadotropic urine of pregnancy (II), suprarenal extracts (III), and rabbit's heart muscle (IV) on the growth of testes (V) and spermatogenesis (VI) in rats. Inhibition of (V) is caused by (I), (III), and (IV), and an increase by (II). (VI) is inhibited by (I) and not affected by (II) and (IV). A. C.

Mucification of the vaginal epithelium of immature mice following injections of follicular fluid. S. B. D. Aberle (Science, 1933, **78**, 17—18).—Follicular fluid from the ovary of the sow may cause mucification for approx. 60 hr. of the vaginal epithelium in the normal immature mouse. L. S. T.

Fat-soluble vitamins. XXXVI. Carotene and vitamin-*A* content of butter. XXXVII. Stability of carotene solutions. C. A. Baumann and H. Steenbock (J. Biol. Chem., 1933, **101**, 547—560, 561—572).—XXXVI. Carotene (I) was determined in butter-fat (II) by comparison of the absorption vals. of ultra-violet light of λ 460 and 480 mμ with a solution of pure (I) in refined cottonseed oil (III). Vitamin-*A* (IV) was determined by photographing the intensity of the 328 mμ band of the unsaponifiable matter purified by cooling at −72° in MeOH, filtering, and washing with cold MeOH. (I) accounts for only 15% of the total (IV)-activity of (II), amounting to $2·0\times10^{-3}$ and $8·6\times10^{-3}$ g. per g. of April and July (II), respectively. (IV) vals. ranged from 9×10^{-3} to 20×10^{-3} g. per g. of April and June (II), respectively. Neither storage for 6 months at 0° nor ultra-violet radiation influences the content of either component.

XXXVII. Solutions of (I) in (III), sesamé, olive, maize, wheat-germ, and coconut oils stored at 4° in the dark for 5 months lost 8, 15, 38, 45, 62, and 25% of their activity, respectively. The losses were uninfluenced by the presence of quinol (V). In (III) the stability of (I) is influenced unfavourably by exposure to air, daylight, and room temp.; (V) did not influence the effects of these factors. Addition of Et_2O to solutions of (I) in (III), or the use of rancid (III), was without effect on the stability of (I). In C_6H_6 and light petroleum losses up to 46% were sustained and in Et_2O, $CHCl_3$, *cyclo*hexane, $COMe_2$, PhMe, and C_5H_5N > 75% losses in activity occurred, which, however, were considerably reduced by addition of (V). (I) was very unstable in the Et esters of stearic, lauric, lævulic, and malonic acids, and in the di- and tri-acetates of glycerol. In EtOAc and Et succinate (I) was comparatively stable. H. D.

Vitamin-*A* in the livers of native mine labourers. F. W. Fox (Lancet, 1933, **224**, 953—955).—Abnormally low vitamin-*A* reserves (I) have been found in apparently healthy individuals. Persons dying from pneumonia tend to have low (I) in the liver. L. S. T.

Determination of vitamin-*A* expressed in international units. A. Scheunert and M. Schieblich (Biochem. Z., 1933, **263**, 444—453).—The difficulties of obtaining standardised animals in the biological assay of vitamin-*A* are discussed and a new procedure is described. The limiting dose is that amount which fed to a group of 10 rats over 35 days is sufficient to keep ≮ 8 alive and cure or prevent xerophthalmia. P. W. C.

Stability of international standard carotene in solution in oil. A. Scheunert and M. Schieblich

(Biochem. Z., 1933, **263**, 454—457).—International standard carotene (1% in sesamé oil) if kept cool and in the dark retains its activity without loss for 18 months. P. W. C.

Separation of forms of vitamin-*A* based on the antimony trichloride reaction. M. van Eekelen, A. Emmerie, H. W. Julius, and L. K. Wolff (Nature, 1933, **132**, 171).—Fuller's earth has been used previously to $Ca(OH)_2$ (this vol., 805) for the separation of vitamin-*A* into two fractions. L. S. T.

Sterols of rice embryo. K. Tanaka (J. Biochem. Japan, 1933, **17**, 483—494).—Fractionation of the sterols gave a *myricyl alcohol*, $C_{30}H_{62}O$, m.p. 86—87° (*acetate*, m.p. 71—72°; *benzoate*, m.p. 70°) (cf. B., 1926, 713), and dihydrositosterol (I) (A., 1924, i, 1153, 1217). Following the removal of (I), the residue was acetylated, the product fractionated by EtOH, and the fractions brominated to yield tetrabromostigmasteryl and dibromo-α-sitosteryl acetates. Debromination and repeated crystallisation from EtOH then gave β-*sitosteryl acetate*, m.p. 127—128°, $[\alpha]_D^{20}$ −39·0° in $CHCl_3$, and γ-*sitosteryl acetate*, m.p. 142—143°, $[\alpha]_D^{20}$ −46·09° in $CHCl_3$. β-*Sitosterol*, m.p. 139—140°, $[\alpha]_D^{20}$ −37·7° in $CHCl_3$, and *dihydro*-β-*sitosterol*, m.p. 139—140°, $[\alpha]_D^{20}$ +24·0° in $CHCl_3$ (*acetate*, m.p. 137—138°, $[\alpha]_D^{20}$ +13·57°), were also prepared. F. O. H.

Antimony trichloride reaction with compounds containing 5-membered monoheterocyclic rings. V. E. Levine and E. Richman (J. Biol. Chem., 1933, **101**, 373—390).—With $SbCl_3$ in $CHCl_3$, pyrrole, thiophen, furan, and their derivatives give characteristic colour reactions which are intensified and often modified by addition of Ac_2O (cf. A., 1931, 988). The intensity and rapidity of development of the colour are, to a certain extent, governed by the substituents in the mol. The non-specificity of the reaction for vitamin-*A* (I) is confirmed. Vegetable and animal oils contain a chromogenic substance [other than (I)] which gives a more intense reaction when oxidised. That oxidation readily destroys the colour response of (I) indicates an alcohol or aldehyde. F. O. H.

Effects of cod-liver oil concentrate injections. B. Gordon and R. J. Titherington (Amer. Rev. Tuberc., 1933, **27**, 368—374).—In animals signs of vitamin-*A* deficiency decreased. There was no evidence of a sp. effect on tuberculous lesions. Ch. Abs.

Alleged toxic action of cod-liver oil and concentrates of vitamin-*A*. M. E. Bell, E. Gregory, and J. C. Drummond (Z. Vitaminforsch., 1933, **2**, 161—182).—A disturbance of growth of rats occurs when their diet contains 15% of cod-liver oil (I) and sufficient "vitamin-*B* complex" (II) for a diet containing 2% of (I). This disturbance may be alleviated by increasing the amount of (II). The apparent toxic effect was not caused by vitamin-*A* itself, by nitrogenous bases in fish-liver oils, by an oxidation product of (I), or by an over-dosage of vitamin-*D*, and could not be produced by ingestion of large amounts of provitamin-*A* (carotene). No evidence that rats "overdosed" with (I) failed to assimilate it, or that it affected the normal reaction of the gastric and intestinal contents, was obtained. E. B. H.

Is there a vitamin-*A*-hypervitaminosis? G. Rossi (Z. Vitaminforsch., 1933, **2**, 194—207).—Rabbits and guinea-pigs showed no unfavourable effects with large doses of vitamin-*A*, but in white rats this treatment resulted in diarrhœa. Large doses of vitamin-*A* together with an over-dose of -*D* retarded growth of rabbits. E. B. H.

Ascorbic acid (vitamin-*C*). A. Szent-Györgyi (Bull. Soc. Chim. biol., 1933, **15**, 694—705).—A lecture.

Antiscorbutic property of suprarenal cortex. R. Deotto (Z. Vitaminforsch., 1933, **2**, 182—190).—Aq. extracts of suprarenal cortex (acidulated with citric acid 1 : 3) has an antiscorbutic power, whilst similar extracts from liver have no such property, and neither has adrenaline. E. B. H.

Experimental scurvy. XVI. Effect of irradiated narcotine. J. Shimada (J. Biochem. Japan, 1933, **17**, 395—400).—The cryst. product, m.p. 173°, from ultra-violet-irradiated narcotine has no antiscorbutic properties (cf. A., 1932, 310). F. O. H.

Absorption spectrum of the vitamin-*E* fraction of wheat-germ oil. F. P. Bowden and T. Moore (Nature, 1933, **132**, 204—205).—The pigment of wheat-germ oil (I) gives an absorption spectrum practically identical with that of xanthophyll. The absorption of the vitamin-*E* fraction of (I) is due to > one kind of mol. The visible absorption is due to xanthophyll (II), which can be removed by charcoal. (II) is probably not the vitamin, since treatment with HCl and by catalytic hydrogenation both destroy the visible bands but not biological activity. The ultra-violet absorption between 2850 and 2400 Å. cannot always be correlated with this activity, but that between 3200 and 2850 Å. closely follows it, since both are destroyed by Ac_2O and irradiation, and both resist the action of HCl, hydrogenation, and oxidation. At liquid air temp. this absorption shows a structure. It is probable that the vitamin-*E* mol. has a high resistance to hydrogenation. L. S. T.

Auxins. F. Kögl (Angew. Chem., 1933, **46**, 469—473).—A lecture. Previous work (this vol., 435, 612) is summarised, and hypotheses of the structure of auxin *a*, based on oxidation experiments, are discussed. *Auxin* b, $C_{18}H_{30}O_4$, m.p. 183°, a keto-acid, has been isolated from maize oil and malt. Experiments on the diurnal variation in the potency of auxin indicate the existence of an atmospheric-electrical influence. R. K. C.

Growth-promoting substance and illumination. A. E. Navez (Proc. Nat. Acad. Sci., 1933, **19**, 636—638).—The growth-promoting substance, auxin (I), is formed more abundantly in apical portions of seedlings of *Lupinus albus* when these are exposed to light. The relative amounts of (I) produced in illuminated and dark-grown seedlings are of the order of 2 to 1, as measured by the angle of curvature induced in decapitated coleoptiles of *Avena*. A. W.

Oxidising power of chondriome. P. JOYET-LAVERGNE (Compt. rend., 1933, **197**, 184—185).—The oxidising power of the chondriome of *Elodea canadensis* on leuco-derivatives has been examined. F. R. S.

Carbohydrate changes in shelled green peas. Z. I. KERTESZ (New York [Geneva] Agric. Exp. Sta. Bull., 1933, No. 622, 14 pp.).—Carbohydrates (I) in shelled peas are consumed during respiratory changes. Other products than (I) contribute to the increase in solid contents of stored peas. Starch formation from sugars was not apparent, but increased proportions of other acid-hydrolysable higher (I) and matter insol. in 80% EtOH are recorded. A. G. P.

Transport of carbohydrates in the cotton plant. III. Polar distribution of sugar in the foliage leaf. E. PHILLIS and T. G. MASON (Ann. Bot., 1933, **47**, 585—634; cf. A., 1928, 1061).—Sugars present in leaves include glucose, fructose, sucrose (I), and a polyglucoside (sol. in H_2O and 80% EtOH; reducing power approx. doubled on hydrolysis). (I) is the principal form in which carbohydrates travel from assimilating cells to the phloem of the bundle ends and longitudinally through the phloem to the stem etc. Concn. gradients of (I) in various tissues are determined and the influence of external conditions on its movement is examined. A. G. P.

Growth processes in oats during water shortage and in early-sown winter wheat. IV. H. WAGNER (Z. Pflanz. Düng, 1933, **30**, A, 208—232; cf. B., 1932, 696).—H_2O-deficiency results in a temporary heavy decrease in H_2O content of the leaves of oats and a relative increase in that of the straw. With the beginning of drought there is a transition of K from straw to leaves, but no movement of minerals from roots back to the soil. Changes in the N, P, K, and Ca of stems, leaves, and panicles with high and with low supplies of H_2O are recorded. Winter wheat sown in May produces much vegetative growth, but no ears, and the straw has a high N content. The plant-K was high, but the high Ca of the young plants declined rapidly. Relationships are indicated between Ca content and sugar formation and between K and polysaccharide production. The wilting of plants during drought is ascribed to high concn. of dissolved substances, among which K and N compounds are of prime importance. A. G. P.

Course of growth of potato plants. V. H. WAGNER (Z. Pflanz. Düng., 1933, **30**, A, 232—249).—The process of transition of mineral nutrients from aërial parts to the tubers is examined and the interrelationships between Ca and K contents on the one hand and sugar and starch accumulation on the other are discussed. A. G. P.

Chemistry of tobacco. I. P. KOENIG and W. DÖRR (Biochem. Z., 1933, **263**, 295—301).—The methods for the isolation from natural nicotine-free tobacco of chlorogenic acid, m.p. 206°, and quinic acid (Cu salt, m.p. 226°) are described. P. W. C.

Effects of chlorine, bromine, and fluorine on the tobacco plant. L. B. WILSON (J. Agric. Res., 1933, **46**, 889—899).—Thickening of leaves caused by cell enlargement results from applications of Cl′, Br′, or F′ to tobacco plants, Cl′ producing the greatest effect. This action is correlated with increased osmotic pressure in the cell sap. Plants receiving excessive amounts of Cl′ or Br′ have less bound H_2O in leaves than plants deficient in mineral nutrients. Treatment with NaF causes a transition of free to bound H_2O. Under field conditions, the sap of Cl′-injured plants has a lower osmotic pressure and % bound H_2O than those of plants receiving complete fertiliser. A. G. P.

Catabolism of the non-volatile organic acids of tobacco leaves during curing. G. W. PUCHER and H. B. VICKERY (Proc. Nat. Acad. Sci., 1933, **19**, 623—626).—Modified methods (to be described elsewhere) have been used to determine the changes which occur to the non-volatile org. acids of tobacco leaves (I) during curing. The polybasic org. acids were pptd. as Ba salts, these decomposed with H_2SO_4, and the liberated acids extracted with Et_2O. The acids were then esterified and the esters distilled. The bulk of the distillate was Et_2 malate, and this ester + Et_3 citrate account for 90% of the esters derived from the partly and fully cured (I). Another procedure is necessary for the determination of $H_2C_2O_4$. The curing of (I) is accompanied by very little change in the amounts of oxalic and malic acids, but there is a very marked increase in the amount of citric acid. Other analyses seem to suggest that the extra citric acid is derived from unknown polybasic acids and as a result of carbohydrate metabolism. A. W.

Reactions of *Valonia* and of *Halicystis*: (*a*) to colloids; (*b*) to injections of certain proteins. E. M. EAST and B. WHITE (J. Gen. Physiol., 1933, **16**, 925—935, 937—945).—(*a*) *Valonia* (I) and *Halicystis* (II) cells have a high tolerance for ovalbumin (III), animal peptone, and animal proteoses ("bacto-protone"). Yeast nucleic acid (dissolved in sea-H_2O containing NaOH) has an injurious effect, more pronounced on (I). (II) has a very high, and (I) a very low, tolerance towards diphtheria toxin, and the converse applies for edestin. (III) does not pass through the membrane to any significant extent, but it is possible, particularly in the case of the proteose of the scarlet-runner bean, that there is some passage of the proteins with smaller mols.

(*b*) Cryst. (III), animal peptone, animal proteose, and diphtheria toxin have been injected into (I) and (II) cells to determine the tolerance of these algæ to the presence of foreign proteins in the vacuole, and to determine whether antibodies are formed. (I) cells injected twice with (III) show no change in susceptibility to its effects, and neither species of algæ gives evidence of having formed antibodies against the antigens used. A. W.

Carbon dioxide narcosis. I. Specific effects of carbon dioxide on protoplasmic streaming and consistency in *Nitella* and on the life of the cell. II. Effect of carbon dioxide compared with that of the hydrogen ion. Threshold of tolerance in *Nitella* to carbon dioxide and to the hydrogen ion. D. L. FOX (J. Cell. Comp. Physiol., 1933, 3, 75—88, 89—100).—I. Typical narcotic effects were produced by CO_2 in unbuffered aq. solutions on *N. clavata.*

II. The action of CO_2 is not due to the [H˙] produced. A. G. P.

Permeability of living cells. XV. Penetration into *Valonia ventricosa* of oxidation–reduction indicators including *m*-bromophenol-indophenol and guaiacol-indophenol. M. M. Brooks (J. Cell. Comp. Physiol., 1933, 3, 61—73).—Guaiacol-indophenol penetrates in the reduced form into the sap of *Valonia,* and its redox potential probably approximates to that representing the limit of the ability of the plant to reduce. A. G. P.

Relation between cell volume and penetration of a solute from an isosmotic solution. M. H. Jacobs (J. Cell. Comp. Physiol., 1933, 3, 29—43).—Mathematical discussion. A. G. P.

Accumulation of ions by living cells. S. C. Brooks (Nature, 1933, 132, 97—98). G. E. Briggs (*ibid.*, 98).—Polemical. L. S. T.

Physiological factors influencing the production of flax fibre cells. B. B. Robinson (J. Amer. Soc. Agron., 1933, 25, 312—328).—In field trials, fertiliser combinations containing N produced the longest stems in seedlings, but at maturity these were equalled or exceeded by those receiving P and K. In H_2O cultures, media high in P and moderately high in K produced the best yields of fibre in cu.mm. per stem. A. G. P.

Influence of length of day on the response of plants to boron. K. Warington (Ann. Bot., 1933, 47, 429—457).—The delayed appearance of B deficiency in plants during spring and autumn results from the shortened day rather than lowered temp. B is an important factor in meristematic activity, but in no other respect was evidence obtained of relationship between B supply and flower production. A. G. P.

Evolution of ammonia by the nodules of the roots of *Leguminosæ*. S. Winogradsky (Compt. rend., 1933, 197, 209—212).—The nodules on or detached from the roots of peas liberate NH_3. Poisons, *e.g.*, $CHCl_3$, and drying at 40—50° do not stop this action. Roots freed from nodules and roots of maize etc. do not evolve NH_3. R. S. C.

Phytochemistry of *Gillenia stipulata*. L. L. Manchey (J. Amer. Pharm. Assoc., 1933, 22, 520—528).—Analysis of commercial preps. of the root indicates the presence of a terpene-rich volatile oil, glucose, tannin, protocatechuic and benzoic acids, a wax associated with a phytosterol, $C_{26}H_{44}O$, m.p. 135° (acetate, m.p. 121°), an *alcohol,* $C_{30}H_{62}O$, m.p. 78° (*acetate,* m.p. 63—63·5°), stearic and palmitic acids, a trihydric *alcohol,* $C_{28}H_{50}O_5$ (*triacetate,* m.p. 162°), myristic acid, and an EtOH-sol. substance, m.p. 237—241° (decomp.). No glucoside or alkaloid could be detected. F. O. H.

Unsaponifiable fraction from spinach fat. II. F. W. Heyl and D. Larsen (J. Amer. Pharm. Assoc., 1933, 22, 510—513).—Purification of the alcohol, m.p. 87—88°, previously described (A., 1929, 855) yields an alcohol, $C_{26}H_{54}O_2$, m.p. 103·5°. The predominant paraffin alcohol is *n*-tetracosanol (A., 1932, 204), whilst *n*-hexacosanol, *n*-tetracosoic acid, m.p. 82·5—83°, and *n*-hexacosoic acid were isolated. From the sterols pptd. by digitonin was separated β-*spinasterol,* $C_{27}H_{46}O$, m.p. 145—148°, $[\alpha]_{546}$ +7·65° (*acetate,* m.p. 150—154°, $[\alpha]_{546}$ +7·2°), which on reduction yields the same spinastanol as spinasterol. F. O. H.

Fat from the seeds of *Vateria indica,* Linn. S. V. Puntambekar and S. Krishna (J. Indian Chem. Soc., 1933, 10, 203—211).—The fat contains the glycerides of myristic, stearic, lignoceric, elaidic (? *iso*oleic), and oleic acids together with sitosterol, m.p. 133—134°. Contrary to Jones (cf. B., 1932, 354), no palmitic or arachidic acid can be isolated. J. L. D.

Fat from the seeds of *Picramnia Sow.* A. Steger and J. van Loon (Rec. trav. chim., 1933, 52, 593—600).—Light petroleum extracts 58·6% of the seeds, the extract consisting mainly (89·8%) of stearolic acid (I). (I) affords adipic acid and lauric acid with O_3, ζη-diketostearic acid with $KMnO_4$, and a ζη-dibromide with Br in Et_2O at —10°. J. L. D.

Chlorophyll content of leaves of barley mutants. H. von Euler, H. Hellström, and D. Burström (Z. physiol. Chem., 1933, 218, 241—248).—The deviations from the mean of a no. of determinations of chlorophyll (I) in barley mutants under const. conditions follow the normal mathematical curve. Normal (green) mutants form the same amount of (I) as an ordinary strain. The (I) ratio between deficient and normal mutants varies from 1 : 4 to 1 : 30. There is a linear relation between the (I) content at various points in the leaf from base to tip and the position of the sample. J. H. B.

Primitive cellulose and lignin in the wood-forming plant-saps as chemical builders of the wood substance. H. Wislicenus (Papier-Fabr., 1933, 31, Fest- u. Auslands-heft, 65—77).—An account is given of the mechanism of tree growth and the accompanying physical and chemical changes. Theories of the formation of cellulose (I) and lignin (II) together with recent developments of work in this field are discussed, and the collection and examination of the sap of the cambium, which is the source of primitive (I) and (II), in attempts to build up (II) from it, are described. D. A. C.

Hemicelluloses of mesquite wood. L. Sands and W. Y. Gary (J. Biol. Chem., 1933, 101, 573—581).—The hemicelluloses were prepared from the fat- and pectin-free wood by extraction with 5% NaOH, acidification, and addition of $COMe_2$. The two fractions thus obtained were purified by repeated pptn. from alkaline solution with EtOH. By further fractionation with EtOH the existence of two distinct hemicelluloses was shown, differing in the amount of xylose in the mols. The relation of these hemicelluloses to mesquite gum is slight. H. D.

Floridoside, trehalose, and glycogen in red, fresh-water algæ (*Lemanea, Sacheria*). H. Colin and J. Augier (Compt. rend., 1933, 197, 423—425; cf. this vol., 652).—Extraction of sugar- and gum-free *L. nodosa,* or spores thereof, with 5% aq. KOH leads to the isolation of a glycogenic substance, $[\alpha]_D$ +105°, giving a violet I reaction. This property is lost under the action of pancreatin, and further hydrolysis by dil. H_2SO_4 yields glucose. A. C.

Presence of maltose in fresh tubercles of *Lathyrus tuberosus*, L. A. MEUNIER (Compt. rend., 1933, **197**, 98—100).—Maltose is isolated from an aq. extract of the tubercles by pptn. with $Ba(OH)_2$ after treatment with invertase. H. A. P.

Non-fermentable reducing sugar in koji extract. II. F. HEMMI and N. TSUKITARI (J. Agric. Chem. Soc. Japan, 1933, **9**, 179—185).—Treatment with 90% $EtOH+Et_2O$ at the end of the fermentation afforded a sugar resembling *iso*maltose [phenylosazone, m.p. 160—161°, $[\alpha]_D^{20.5}$ +22·53° (in 95% EtOH), +23·26° (in MeOH); Ac derivative, m.p. 72—78°, $[\alpha]_D^{20}$ +135·97° in $CHCl_3$]. CH. ABS.

***i*-Inositol in citrus fruits.** E. K. NELSON and G. L. KEENAN (Science, 1933, **77**, 561).—The residue insol. in MeOH obtained in the isolation of ascorbic acid from citrus fruits is *i*-inositol. L. S. T.

Minor constituents of the sweet potato. I. I. OSE (J. Agric. Chem. Soc. Japan, 1933, **9**, 165—179).—Maltose, and two monoaminophosphatides, each containing glucose and probably of the lecithin and cephalin types, respectively, are present. CH. ABS.

Organic acids of grape-juice. L. SEMICHON and M. FLANZY (Compt. rend., 1933, **197**, 198—201).—The juice contains tartaric, malic, glyoxylic, and other aldehydic acids. F. R. S.

Alkaloids of fumaraceous plants. VII. *Dicentra eximia* (Ker), Torr. R. H. F. MANSKE (Canad. J. Res., 1933, **8**, 592—599; cf. this vol., 841).—The base, previously (A., 1930, 122) called eximine is *d*-dicentrine (I). The roots of *D. eximia* contain (I) (0·41), glaucine (II) (0·03), protopine (0·45), *eximine* (III) (0·30), *eximidine* (IV) (0·04), and an *alkaloid* δ (V) (0·01%). (III), +MeOH, m.p. 116—117° (decomp.), and anhyd. m.p. 142° [*hydrobromide*, m.p. 270° (decomp. from 248°); *methiodide*, $+2H_2O$, m.p. 212° (decomp.)], and (IV), m.p. 133° (*methiodide*, decomp. 218° after darkening at 190—195°), both phenolic, $C_{17}H_{14}ON(OMe)_3$, are probably aporphine bases. (V) has m.p. 239° (decomp. from 235°) (*hydrochloride*, decomp. 237—238°, commencing at 234°). (I) gives a *methine*, m.p. 158—159° [*hydrochloride*, m.p. 302° (decomp.)], the *methiodide*, cryst., of which with aq. KOH gives NMe_3 and a cryst. substance. (II) affords N-*carbethoxy*-2 : 3 : 5 : 6-*tetramethoxy*-8-β-*methylaminoethylphenanthrene*, m.p. 115°. R. S. C.

Organic bases in germinated soya beans. K. SASAKI (J. Agric. Chem. Soc. Japan, 1933, **9**, 115—119).—The mother-liquor after removal of asparagine from an aq. extract of soya beans germinated in the dark afforded (per kg. from two species): adenine 0·52, 0·42; guanine 0·12, 0·08; histidine 1·60, 2·01; arginine 3·33, 3·09; choline 1·44, 1·71; cadaverine 1·22, 1·16 (g. ?). CH. ABS.

Presence of allantoic acid in fungi. R. FOSSE and A. BRUNEL (Compt. rend., 1933, **197**, 288—290).—Twenty-two varieties of fungi (dried) contain 0·014—0·672% of allantoic acid, the amount increasing greatly with development of the plant. R. S. C.

Chemical composition and grades of barley and oat varieties. D. D. HILL (J. Amer. Soc. Agron., 1933, **25**, 301—311).—Analytical data of numerous samples are recorded. Relationships between nutrient contents and the official system of grading are discussed. A. G. P.

Toxic substance in mulberry leaves damaged by tobacco. Toxic action of nicotine and trimethylamine on silkworms. T. YABUTA and T. KOZU (J. Agric. Chem. Soc. Japan, 1932, **8**, 770—775).—The toxic substance in damaged mulberry leaves appears to be nicotine. CH. ABS.

Enzymic activity of the plant organism and some phenomena of physiological immunity. K. SUCHORUKOV (Z. Opytn. Agron. Jugo-Vostoka, 1930, **8**, 237).—Peroxidase activity is related to resistance to rust in *Helianthus*, *Artemisia*, and *Xanthium*, being lowest in immune parts and individuals; catalase and the albumin enzymes play no part in the establishment of immunity. Alteration of the soil acidity affects peroxidase activity in the roots of sunflowers, the greatest depression of activity being obtained with neutral soils. The presence of antioxidases could not be detected. CH. ABS.

Effect of decay caused by white rot fungi on the chemical composition of wood. J. WIERTELAK (Bull. Acad. Polonaise, 1932, **B**, 19—36).—Decomp. of pine and fir wood by *Trametes pini* (I) and *Polystictus hirsutus* (II) results in the more rapid destruction of lignin than of cellulose. (II) attacks cellulose more rapidly than does (I). Neither organism could be grown on pure lignin. A. G. P.

Biological applications of semi-conducting photo-electric cells. T. KOFMAN (Bull. Soc. Chim. biol., 1933, **15**, 623—636).—The application of the Cu_2O–Cu and Se photo-electric cells to nephelometry and blood colorimetry is described. F. O. H.

Colorimetric calibration of micro-pipettes. F. C. BING (J. Lab. Clin. Med., 1933, **18**, 531—534).—Pipettes delivering 0·0005—1·0 c.c. are calibrated by colorimetric determination of the hæmoglobin content of dilutions of the blood delivered. CH. ABS.

Pipette electrode for determining the p_H of biological fluids. H. E. GORESLINE (J. Bact., 1933, **25**, 435—438).—A Au-plated Pt electrode is sealed into a bulb blown into the stem of a small pipette. The electrode vessel has a total capacity of 1·5—2·0 c.c. A. G. P.

Determination of thiocyanate in biological material. K. LANG (Biochem. Z., 1933, **262**, 14—19; cf. this vol., 637).—After removal of protein the CNS′ is pptd. as AgCNS, the ppt. is decomposed with H_2S, and the liberated CNS′ converted into the $Cu–C_5H_5N–CNS$ complex, which is then determined, after extraction with PhBr, by means of a step photometer. Blood (30 c.c. used) contains 0·1—0·2 mg. of HCNS per 100 c.c. Methods previously used are untrustworthy. W. McC.