BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

DECEMBER, 1934.

General, Physical, and Inorganic Chemistry.

Photographic intensity measurements of lines of the Paschen series of hydrogen in the infra-red solar spectrum. A. H. Rosenthal (Nature, 1934, **134**, 533—534). L. S. T.

General expression for the intensity of hydrogen lines. L. McLean (Phil. Mag., 1934, [vii], 18, 845—874).—Mathematical. A formula has been obtained for the total intensity of H lines in the general case of the transition $n \longrightarrow n'$. M. S. B.

Resonance bands of the HD molecule in the region 1650—1000 Å. K. Mie (Z. Physik, 1934, **91**, 475—492).—Analysis of rotation lines and bands in this region gives results in agreement with H_2 analysis; the zero point energy is 5·359 kg.-cal. A. B. D. C.

Dispersion of helium in the ground level according to wave mechanics. H. Körwien (Z. Physik, 1934, **91**, 1—36).—Theoretical. A. B. D. C.

Interference measurements in the spectra of noble gases. W. F. Meggers and C. J. Humphreys (J. Res. Nat. Bur. Stand., 1934, **13**, 293—309).—The wave-lengths of lines in the first spectra of He, Ne, A, Kr, and Xe have been measured between 3948 and 10,830 Å. E. S. H.

***C* state of Li_2.** W. H. Furry (Physical Rev., 1933, [ii], **43**, 361—362; cf. A., 1933, 1095). L. S. T.

New band system in nitrogen. J. Kaplan (Nature, 1934, **134**, 538; cf. this vol., 823).—Of new N bands, 2536, 2635, and 2740 Å. increase in intensity as pressure is reduced, and are (0,1), (0,2), and (0,3) bands of a new system. L. S. T.

Situation of the $A(^3\Sigma)$ level in the nitrogen molecule. L. Vegard (Nature, 1934, **134**, 697; cf. this vol., 1051). L. S. T.

Effect of inert gases on the afterglow spectrum of nitrogen. J. Ôkubo and H. Hamada (Sci. Rep. Tôhoku, 1934, **23**, 281—288).—The intensity max. of the bands in the afterglow spectrum with $v'=-11$ and -6 are displaced towards longer wave-lengths with increasing partial pressure of inert gas at const. N_2 pressure, the effect being He>Ne>A. For the first positive bands of N_2 excited by a very weak current, the max. at $v'=-11$ is displaced towards longer wave-lengths, but not that at $v'=-6$, in presence of He or Ne. J. W. S.

Light excitation in neon by lithium ions. A. J. Dempster and R. E. Holzer (Physical Rev., 1933, [ii], **43**, 365—366).—Light excitation of Ne by Li^+ has been observed at 160 volts, approx. 150 volts $<$ the ionisation potential observed by Beeck and Mouzon (A., 1932, 105). L. S. T.

Nuclear magnetic moments from the polarisation of resonance radiation. I. Sodium, $3^2S_{1/2}-3^2P_{3/2,1/2}$. L. Larrick. **II. Sodium, $3^2S_{1/2}-4^2P_{3/2,1/2}$.** A. Ellett and N. P. Heydenburg (Physical Rev., 1934, [ii], **46**, 581—583, 583—589).—I. An increase of 16·5—50% for 0—300 gauss range of field strength in the polarisation of Na *D* line resonance radiation, due to the Paschen–Back effect of the hyperfine structure, is observed, and is calc. and plotted on the assumption of a nuclear moment of 3/2.

II. Detailed calculations on the change in polarisation, due to the Paschen–Back effect of the hyperfine multiplet, of Na resonance radiation excited by unpolarised light are given. Measurements as a function of intensity of applied field were made. The hyperfine structure separation const. for $4^2P_{3/2}$ is $(1{\cdot}87\pm0{\cdot}05)\times 10^{-4}$ cm.$^{-1}$ N. M. B.

Spin interaction with exchange for alkali atoms. E. David (Z. Physik, 1934, **91**, 289—317).—Inverted alkali doublets cannot be explained without spin interchange. A. B. D. C.

Isotope effect in the band spectrum of sodium hydride. E. Olsson (Nature, 1934, **134**, 697—698). L. S. T.

Absorption spectra of mixed vapours of sodium and potassium with mercury, cadmium, and zinc. E. Matuyama (Sci. Rep. Tôhoku, 1934, **23**, 334—342).—The absorption spectra of mixtures of vapours of Hg, Cd, or Zn with Na or K show two types of band, one having intensity fluctuations and appearing in very narrow regions with K alloys, the other, with discrete heads, appearing with Na alloys. It is considered that the two types of bands occur for both series of mixtures, but that they are masked by the Na_2 and K_2 band systems. J. W. S.

Hyperfine structure in the Al III line, 5722·6 Å. R. C. Williams and G. B. Sabine (Physical Rev., 1933, [ii], **43**, 362).—No hyperfine structure has been detected with certainty. L. S. T.

Nuclear mechanical moment of cobalt. K. R. More (Physical Rev., 1934, [ii], **46**, 470—473).—Components and interval ratios in the hyperfine structure of the lines λλ 4191, 4234, 6082, 6231, 6450, and 6592 of the arc spectrum give a val. of $I=7/2$. The estimated nuclear magnetic moment is of the order 2—3 small magnetons. N. M. B.

Selenium arc spectrum Se I. K. W. Meissner, O. Bartelt, and L. Eckstein (Z. Physik, 1934, **91**, 427—443). A. B. D. C.

Selenium arc spectrum Se II. O. Bartelt (Z. Physik, 1934, **91**, 444—470). A. B. D. C.

Magnetic extinction of the fluorescence of diatomic selenium molecules. J. Genard (Compt. rend., 1934, **199**, 784).—The fluorescence of Se_2 excited by the Hg lines λλ 4047, 4359 Å. is decreased 40—50% by a field of 43,000 gauss, different terms of the same series being differently affected. H. J. E.

Absorption spectra due to excitation of inner electrons. VII. The rubidium spectrum between 900 and 600 Å. due to excitation of the $(4p)^6$ shell (Rb I^b). H. Beutler (Z. Physik, 1934, **91**, 131—142). A. B. D. C.

Band spectra of rubidium in absorption and in emission. E. Matuyama (Sci. Rep. Tôhoku, 1934, **23**, 308—321).—The spectrum due to Rb_2 mols. includes bands at 4300, 4800, 6800, and 8600 Å. of discrete vibrational structure, diffuse bands due to polarisation mols. and appearing only in emission, and a continuous spectrum at 6000 Å. The vibration quantum of the ground state is 58 cm.$^{-1}$ J. W. S.

Multiplets in the Ag III spectrum. B. V. R. Rao (Proc. Indian Acad. Sci., 1934, **1**, 28—33).—From the Moseley diagram for the terms of the isoelectronic sequence Rh I, Pd II, and Ag III, the terms $4d^{8}\,{}^{3}F5s\,{}^{4}F$ and ${}^{2}F$, and $4d^{8}\,{}^{3}F5p\,{}^{4}F'$ and ${}^{2}F'$ of Ag III are identified. The approx. ionisation potential is 29·25 volts. N. M. B.

Band fluorescence of cadmium vapour. J. Świetosławska (Z. Physik, 1934, **91**, 354—360).—The long-wave limit and first fluctuation max. of these bands vary with the exciting wave-length. A. B. D. C.

Wave-length shifts of the spectral lines of antimony due to change of pressure. T. Yuasa (Sci. Rep. Tokyo Bunrika Daigaku, 1934, **2**, 57—72).—Comparison of the emission spectra of Sb at pressures of a few cm. Hg and atm. pressure indicates that the higher are the principal and inner quantum nos. defining the spectral terms the greater is the wave-length change due to pressure and the greater the change in mode of appearance. J. W. S.

Continuous emission spectra of iodine. K. Asagoe and Y. Inuzuka (Sci. Rep. Tokyo Bunrika Daigaku, 1934, **2**, 73—87).—Data are given for the intensity max. of the bands excited in a Geissler tube containing I vapour, over the range 2560—4735 Å. The effects of intensity of excitation and of pressure are discussed. J. W. S.

Intensity distribution of hyperfine structure components of the cæsium line at 4555 Å. and the nuclear moment of the cæsium atom. H. Barth (Z. Physik, 1934, **91**, 272—283).—This moment is 5/2. A. B. D. C.

Absorption band spectra of cæsium. E. Matuyama (Sci. Rep. Tôhoku, 1934, **23**, 322—333).—Bands at 7200, 7600, 8200, and 8700 Å. have been observed near the resonance lines in the spectrum of Cs vapour. The bands at 7200 and 7600 Å., together with the previously known band at 6300 Å., have been analysed. The vibration quantum for the normal state of the Cs_2 mol. is 40 cm.$^{-1}$ Relationships are developed between the vibration quanta of diat. mols. and the at. wts. of the constituent atoms. J. W. S.

Fifty-three electron spectra of cæsium and barium: Cs III and Ba IV. (Miss) M. A. Fitzgerald and R. A. Sawyer (Physical Rev., 1934, [ii], **46**, 576—580).—The separations of the lowest levels $5s^25p^5\,{}^2P$ have been predicted and observed. The separations found were 13,870 and 17,830 cm.$^{-1}$ in the case of Cs III and Ba IV, respectively. New terms and classifications are tabulated. N. M. B.

Nuclear magnetic moment of lanthanum. O. E. Anderson (Physical Rev., 1934, [ii], **46**, 473—476; cf. this vol., 824).—From an investigation of the hyperfine structure of 25 lines, in order to determine the overall widths of each member of the $5d^26s\,{}^4F$ levels, a nuclear g-factor of 0·719 and a magnetic moment of 2·5 small magnetons are calc. The interaction energy between the d as well as the s electrons and the nucleus must be considered in accounting for the observed intervals. N. M. B.

Nuclear moment of terbium. H. Schüler and H. Gollnow (Naturwiss., 1934, **22**, 730).—Investigation of the hyperfine structure of the Tb spectrum in the range 6500—4000 Å. shows that no line is split into > four components. The nuclear moment is 3/2. A. J. M.

Nuclear moment of lutecium. H. Schüler and T. Schmidt (Naturwiss., 1934, **22**, 714).—Hyperfine structure of the Lu spectrum gives 5/2 for the nuclear moment. A. J. M.

Rare gas–mercury vapour lamps. W. Gerlach and K. Siebertz (Z. Physik, 1934, **91**, 37—42).—Hg discharge tubes with Ne transform suddenly from Hg to Ne discharge near 12°, and with A near 0°. A. B. D. C.

Concentration of excited atoms in the mercury discharge at high pressures. V. Fabrikant and V. Pulver (Compt. rend. Acad. Sci. U.R.S.S., 1934, **3**, 435—442).—Concn. of Hg atoms in the 2^3P_0, 2^3P_1, and 2^3P_2 states and its dependence on conditions have been determined from absorption measurements. H. J. E.

Hyperfine structure of some Hg II lines. B. Venkatesachar and L. Sibaiya (Proc. Indian Acad. Sci., 1934, **1**, 8—13).—Data for the λλ 3983·96, 2847·67, and 2262·33 ultra-violet spark lines are tabulated and discussed. N. M. B.

Spectrum of trebly-ionised mercury. T. S. Subbaraya (Proc. Indian Acad. Sci., 1934, **1**, 39—43).—From the fundamental multiplets and term vals. a classification of about 200 lines of Hg^{IV} is tabulated. N. M. B.

Effect of temperature and pressure on the mercury afterglow. D. W. Carpenter and W. M. Nielsen (Physical Rev., 1934, [ii], **46**, 607—612).—Measurements were made of the rate of escape of resonance radiation from a length of Hg vapour 4 cm. thick, for the pressure range 0·133—0·720 mm. Hg and temp. range 390—585° abs. Results are discussed in relation with the predictions of Kenty's theory of radiation diffusion (cf. *ibid.*, 1932, [ii], **42**, 823). N. M. B.

Dark interval in mercury fluorescence. (LORD) RAYLEIGH (Proc. Roy. Soc., 1934, **A**, **146**, 272—280).—Using direct photography through suitable filters, the various features of the Hg fluorescence spectrum have been separated. The phenomenon of the dark interval occurs only in the visual Hg fluorescence, which has continuous spectrum, photographic max. 4850 Å., and visual max. in the green. The appearance of the dark interval is dependent on the source of excitation. L. L. B.

Space-charge distribution in the mercury arc. J. PAWLIKOWSKI (Acta phys. polon., 1933, **2**, 59—66; Chem. Zentr., 1934, i, 2097). H. J. E.

Continuous transition from the glow to the arc discharge in mercury vapour at higher pressures. E. MATULA (Acta phys. polon., 1932, **1**, 433—446; Chem. Zentr., 1934, i, 2097). H. J. E.

Absorption series of the thallium arc spectrum (Tl I) and their perturbation terms $6s(6p)^{2\,4}P_{1/2}$. H. BEUTLER and W. DEMETER (Z. Physik. 1934, **91**, 143—150). A. B. D. C.

Absorption spectra due to excitation of inner electrons. VIII. Thallium spectrum between 2500 and 1400 Å. due to excitation of the $(6s)^2$ shell (Tl I^b). IX. Thallium spectrum between 900 and 600 Å. due to excitation of the $(5d)^{10}$ shell (Tl I^c). Comparison of terms of the Tl I^c spectrum with ultra-soft *X*-rays. H. BEUTLER and W. DEMETER (Z. Physik, 1934, **91**, 202—217, 218—229). A. B. D. C.

Specific isotope effect in the hyperfine spectrum of the lead atom. (MISS) B. H. DICKINSON (Physical Rev., 1934, [ii], **46**, 598—604).—Mathematical. The method of Hughes (cf. A., 1930, 1328) is used to calculate the sp. isotope separation of Pb^{206} and Pb^{208} levels. N. M. B.

Production of spectrally pure carbon electrodes.—See this vol., 1194.

Investigations of gas discharges with an electrolyte as cathode. W. BRAUNBEK (Z. Physik, 1934, **91**, 184—201).—Glow discharges obtained with H_2SO_4, KOH, and NaOH as electrodes show that metals are not necessary for production of free electrons. A. B. D. C.

Production of light from discharges in gases. S. DUSHMAN (Gen. Elec. Rev., 1934, **37**, 260—268).—A review. Data on luminous efficiencies, ionisation, and resonance potentials are tabulated.

CH. ABS. (*e*)

Nuclear magnetic moments and their origin. A. LANDÉ (Physical Rev., 1934, [ii], **46**, 477—480).—The origin of the nuclear moments is, in most cases, one proton or one neutron only. Analysis of hyperfine structure gives magnetic moments: proton $\sim$ 2·0 magnetons, neutron $\sim$ —0·6 magneton.

N. M. B.

Spectral multiplets belonging to configurations of the type d^kms and d^kmsns. R. A. MERRILL (Physical Rev., 1934, [ii], **46**, 487—501; cf. this vol., 576).—Mathematical. N. M. B.

Calculation of optical terms and in particular of ionisation potentials of bivalent metals by means of the statistical potential of Fermi. U. FANO (Atti R. Accad. Lincei, 1934, [vi], **20**, 35—39).—Theoretical. O. J. W.

Limitation of the potential theory of the broadening of spectral lines. H. KUHN and F. LONDON (Phil. Mag., 1934, [vii], **18**, 983—987).—The spectral intensity of an atom, moving in a perturbing field, agrees with the "occurrence distribution" for infinitely slow motion only, of the atom. The amount of deviation in other cases, and its dependence on the velocity, are discussed. M. S. B.

Pressure shift and broadening of spectral lines. H. KUHN (Phil. Mag., 1934, [vii], **18**, 987—1003).—Inter-at. forces may be studied by determining the effect of pressure on spectral lines. Small vals. of $\Delta\nu$ are due to the simultaneous presence of many neighbouring atoms and the shift of the max. $\propto d^2$. Larger vals. of $\Delta\nu$ are due to the influence of single atoms only. M. S. B.

Corona discharge in various gases. H. F. BOULIND (Phil. Mag., 1934, [vii], **18**, 909—921).—The discharge between concentric cylinders through O_2, H_2, CO_2, and air has been studied for different vals. of *p*. The mobilities of the ions have been calc. for all the gases except CO_2 in which the discharge is disruptive. M. S. B.

Electron energies in the negative glow. K. G. EMELÉUS and D. KENNEDY (Phil. Mag., 1934, [vii], **18**, 874—878).—A recalculation of the fraction (about 1/6) of the energy of the cathode dark space which becomes available as the energy of fast electrons entering the negative glow, has been made from Linder's data (A., 1931, 1210). M. S. B.

Scattering of light by liquid surfaces. S. JAGENNATHAN (Proc. Indian Acad. Sci., 1934, **1**, 115—119).—The Mandelstamm–Gans theory of light scattering is criticised. A Hg surface can be cleansed for light-scattering experiments by scraping with a clean steel edge. Such a surface shows a polarisation of light scattered nearly parallel to the Hg surface with the electric vector normal to the surface.

J. W. S.

Production of *X*-rays by swiftly-moving mercury ions. W. M. COATES (Physical Rev., 1934, [ii], **46**, 542—548).—Using an improved tube (cf. this vol., 1283) the production of soft *X*-rays (4—9 Å.) by Hg ions of energies up to $2{\cdot}38\times10^6$ e.v. was investigated. By absorption measurements in Al and in air the wave-length of the radiation was determined for Al, S, Br, Mo, Ag, Sn, and Pb targets. No radiation was detected from Li, Be, C, O_2, Na, Ni, or Cu. The *X*-ray intensity increased rapidly with the energy of the ions above crit. min. energies of 700 kv. for Br, Mo, and Al, and 400 kv. for Pb and Ag. Ag gave one *X*-ray quantum per 1 in 2000 Hg ions. A theory of excitation of *X*-rays by positive ions is proposed. N. M. B.

Natural width of *X*-ray lines. L. PINCHERLE (Atti R. Accad. Lincei, 1934, [vi], **20**, 29—35).—The natural widths of *X*-ray lines are calc. on the basis of quantum mechanics and compared with recent experimental data. O. J. W.

Absorption coefficients for *X*-rays. H. Lay (Z. Physik, 1934, **91**, 551—555).—Absorption coeffs. of various elements are given for wave-lengths between 0·5 and 5·3 Å. A. B. D. C.

***K* satellites of potassium and calcium.** H. Tazaki (J. Sci. Hiroshima Univ., 1934, *A*, **4**, 185—190; cf. this vol., 3).—Using K and KCl as emitting substances $K\alpha_5$ and $K\alpha_6$, and from Ca and CaO $K\alpha_{5\ 6}$, were observed and measured; respective wave-lengths are 3688·2, 3683·6, and 3310·3 X. From KCl $K\alpha_5$ was not found. N. M. B.

Two-crystal study of the structure and width of *K* *X*-ray absorption limits. W. H. Zinn (Physical Rev., 1934, [ii], **46**, 659—664; cf. Barnes, A., 1933, 993).—Structure on the short wave-length side of the main absorption limit or in the limit itself was found in the case of Se, SeO_2, Na_2SeO_4, Rb, RbCl, Zr, ZrO_2, $Zr(SO_4)_2$, Mo, Mo_2O_3, and MoO_3. Intensity and location are discussed with reference to Kronig's theory of sec. structure. Widths of absorption limits were approx. const. for elements of at. no. < 32, and, above this, increase as (at. no.)^4. N. M. B.

Anomaly in the niobium *K* absorption limit. C. J. Burbank (Physical Rev., 1933, [ii], **43**, 83). L. S. T.

Fluorescence efficiency in the *L* region. H. Lay (Z. Physik, 1934, **91**, 533—550).—*L* fluorescence is determined for elements from at. no. 40 to 92, and *K* fluorescence from 8 to 54. A. B. D. C.

Structure and width of the L_{III} absorption limits of tantalum, tungsten, and gold. H. Semat (Physical Rev., 1934, [ii], **46**, 688—691).—Using the free metals and Ta_2O_5, K_2TaF_7, H_2WO_4, Au_2O_3, and $KAu(CN)_2$, data and curves are given. The widths, in volts, increase with at. no. N. M. B.

Intensities of satellites of $L\beta_2$. (Miss) A. W. Pearsall (Physical Rev., 1934, [ii], **46**, 694—697).—The integrated intensity, investigated in the at. no. range 40—53, is about 4% of that of $L\beta_2$ for Nb (41), rises to a max. of 52% for Ag (47), and falls rapidly to $< 1\%$ for Te (52), disagreeing with Druyvesteyn's theory. N. M. B.

Continuous and discontinuous Compton spectrum of hydrogen. F. Schnaidt (Ann. Physik, 1934, [v], **21**, 89—112).—Theoretical. The intensities of the continuous and discontinuous Compton spectra of H are calc. using the proper function for H. A. J. M.

Structure of the Compton modified band. G. E. M. Jauncey (Physical Rev., 1934, [ii], **46**, 667—668).—The intensity distribution in the Compton band gives directly the component velocity distribution function of the electrons producing the band. N. M. B.

Effect of electron binding on the magnitude of the Compton shift. P. A. Ross and P. Kirkpatrick (Physical Rev., 1934, [ii], **46**, 668—673).—Measurements of Compton shift for 90° scattering of the wave-lengths 0·435, 0·496, and 0·631 Å. by C and Be are $\not< h/mc$, the val. required by the Compton formula, the max. discrepancy being 2·4%, observed for λ 0·631 scattered from C, but agree with a proposed formula (cf. *ibid.*, **45**, 223) and with the results of Bloch (cf. following abstract). N. M. B.

Compton line. F. Bloch (Physical Rev., 1934, [ii], **46**, 674—687).—Mathematical. From Wentzel's theory, formulæ for the intensity distribution in the Compton line are developed. The interaction of the electrons with the at. nucleus gives a broadening of the line and a shift of the position of max. intensity from Compton's val. N. M. B.

Sparking potentials at low pressures. A. J. Dempster (Physical Rev., 1934, [ii], **46**, 728—730).—The no. of electrons set free by the impact of a positive ion on a Ni cathode, calc. from data for the efficiency of ionisation by electrons of various velocities and sparking potentials in air, increases with the velocity of the ion from approx. 4 at 3000 volts to 85 at 30,000 volts, results much $>$ those given by direct observations. An explanation is proposed. N. M. B.

Quartz lamp as pre-ioniser. R. Hellmann (Z. Physik, 1934, **91**, 569—572).—Oscillographic measurements show that light emission from a quartz lamp varies, and care should be taken in using it to illuminate metals to obtain const. photo-emission for ionisation measurements. A. B. D. C.

Coefficient of electron ionisation for nitrogen at low pressures. R. Hellmann (Z. Physik, 1934, **91**, 556—568).—Townsend's coeff. is determined for pressures from 1·6 to 15 mm. A. B. D. C.

Emission of electrons under the influence of chemical action. IV. Reactions of liquid NaK_2 with gaseous $SOCl_2$, S_2Cl_2, SO_2Cl_2, $HgCl_2$, S_2Cl_4, and with mixtures of gases, and a new method of determining the contact potential difference. A. K. Denisoff and O. W. Richardson (Proc. Roy. Soc., 1934, *A*, **146**, 524—564; cf. this vol., 937).—The electron emission from NaK_2 when acted on by $SOCl_2$, S_2Cl_2, SO_2Cl_2, $HgCl_2$, and $(SCl_2)_2$ at very low pressures has been studied, and experiments with the mixtures $COCl_2+COS$, $COCl_2+S_2Cl_2$, and $SOCl_2+S_2Cl_2$ are described. It is proved that the electron currents originating from chemical action possess the additive property and exhibit saturation with true zero applied p.d. A new method is described for determining the contact p.d. between the alloy drop and the surrounding Pt electrode in presence of different gases. A general method of analysis of electronic spectra is given, based on the comparative study of different electronic spectra and on some considerations of the kinetics and the electronic yield of the chemical reactions. The electronic spectra, having been thus analysed, are then applied to test the fundamental relation between the dissociation energy, involved in a certain reaction, and the max. energy of the emitted electrons of the group originating from the reaction with the corresponding mechanism. L. L. B.

Small-angle inelastic scattering of electrons in helium, hydrogen, and mercury. S. N. Van Voorhis (Physical Rev., 1934, [ii], **46**, 480—483).—Measurements for the initial energies range 100—300 volts and 0—15° scattering angles show that scatter-

ing per unit solid angle reaches a max. at a fairly small angle and decreases to a lower val. at zero angle. The position of the max. is a function of energy, and not of momentum as predicted by Born's theory.
N. M. B.

Determination of the variation of the mass of electrons in rapid cathode rays. H. Starke and M. Nacken (Ann. Physik, 1934, [v], **21**, 67—88).—The results obtained for the variation of the mass of the electron with its velocity by Abraham's and Lorentz's theory are compared. A. J. M.

[So-called] **electric moment of the electron.** G. Racah (Atti R. Accad. Lincei, 1934, [vi], **20**, 39—40).—Theoretical. O. J. W.

Activation of nitrogen by electron impacts. J. Ôkubo and H. Hamada (Sci. Rep. Tôhoku, 1934, **23**, 289—295).—The production of active N, as indicated by a sensitive thermopile, increases suddenly when the accelerating potential of the electrons reaches 16 volts, the first ionisation potential of N_2. Above this potential the production of active N increases continuously with the accelerating potential. At pressures of 0·1—10 mm. the primary production of N_2^+ is essential to the formation of active N, and the probability of its formation by single collisions with high-speed electrons is very small. J. W. S.

Approximate phases in electron scattering. F. L. Arnot and G. O. Baines (Proc. Roy. Soc., 1934, **A**, **146**, 651—662).—A no. of phases for Kr have been calc. by Jeffreys' and Born's methods, and these are compared with the exact phases determined by Holtsmark. For the special case of the zero-order phase Jeffreys' expression for a repulsive is $>$ for an attractive field by the term $1/4\pi$, but the error decreases as the order of the phase increases. The cause of the error is discussed. A theoretical scattering curve for 121-volt electrons in Kr has been calc., and is in good agreement with Arnot's experimental curve.
L. L. B.

Scattering of electrons in bromine vapour. F. L. Arnot and J. C. McLauchlan (Proc. Roy. Soc., 1934, **A**, **146**, 662—672).—Theoretical angular distribution curves for elastically scattered electrons of energies from 15 to 339 volts are given for Br. Satisfactory agreement is obtained with the experimental curves (this vol., 577). An approx. Hartree at. field for Br is given. L. L. B.

Production of heavy high-speed ions without the use of high voltages. D. H. Sloan and W. M. Coates (Physical Rev., 1934, [ii], **46**, 539—542).—A tube previously described (cf. A., 1932, 106) is improved to withstand application of 79,000 volts, by decreased heating of electrodes due to lowering their resistance and capacity, and yields Hg ions with energies of 2,850,000 e.v., and beam intensity of the order 10^{-8} amp. N. M. B.

Ionisation of gases by atom beams. A. Rostagni (Nature, 1934, **134**, 626).—Vals. for the effective cross-sections of ionisation of A and He by their own atoms with an energy varying between 50 and 700 e.v. are recorded graphically. The vals. for He are approx. 0·1 those of the corresponding vals. for A. L. S. T.

Production of pairs by collisions of heavy particles. W. Heitler and L. Nordheim (J. Phys. Radium, 1934, [vii], **5**, 449—454).—Mathematical.
N. M. B.

Temperature variation of the total current-carrying elements of air. II. A. Becker and I. Schaper (Z. Physik, 1934, **91**, 422—426; cf. A., 1933, 4).—Potentials up to 6000 volts indicate decrease of the influence of recombination with rise of temp.
A. B. D. C.

Constitution of metallic sodium. II. E. Wigner and F. Seitz (Physical Rev., 1934, [ii], **46**, 509—524; cf. A., 1933, 660).—Mathematical. Correlations between electrons with parallel spin are investigated, and the Fermi zero-point energy is calc. Results show that the electrons behave as if they were entirely free; binding energy is 9 kg.-cal. and lattice const. 4·86 Å., against observed vals. of 26·9 kg.-cal. and 4·23 Å., respectively. Investigation of correlations between electrons with anti-parallel spins leads to binding energy of 23·2 kg.-cal. and lattice const. 4·75 Å. The cause of the discrepancies is discussed.
N. M. B.

Measurement of nuclear spin by the method of molecular beams. Nuclear spin of sodium. I. I. Rabi and V. W. Cohen (Physical Rev., 1934, [ii], **46**, 707—712).—Using a focussed velocity spectrum method, sensitive to very low intensities and slow at. and mol. beams, the angular momentum of the nucleus is measured directly by its effect on the space quantisation of the angular momentum of the extra-nuclear configuration in a magnetic field. The spin of the Na nucleus is 3/2. N. M. B.

Nuclear spin of cæsium. V. W. Cohen (Physical Rev., 1934, [ii], **46**, 713—717).—The spin of the Cs atom was measured by its effect on the Stern–Gerlach pattern of the neutral Cs atom. The val. obtained was 7/2, and from the known magnetic field the hyperfine structure separation for the normal state is $0{\cdot}295\pm0{\cdot}01$ cm.$^{-1}$ N. M. B.

Comparison of some physical and chemical at. wts. G. P. Baxter (J. Chem. Educ., 1934, **11**, 441—444).—A discussion. Ch. Abs. (*e*)

Periodic classification of the elements. M. Lemarchands and M. Jacob (Bull. Soc. chim., 1934, [v], **1**, 1070—1075).—Considering the total chemical energy of an element to be made up of energy of oxidation (or reduction) and "metallic (or non-metallic) energy," it is pointed out that the assignment to the elements of appropriate vals. for these two quantities throws some light on their chemical properties, notably with C. F. L. U.

Investigation of isotopes of oxygen and hydrogen by the mass-spectrograph. H. Muckenthaler (Physikal. Z., 1934, **35**, 851—857).—The ratio $O^{18} : O^{16}$ in ordinary O_2 is about 1 : 1000. H^1 diffuses more rapidly than H^2 through heated Pd. A. J. M.

Systematics of isotopes. J. Mattauch (Z. Physik, 1934, **91**, 361—371).—The selection rule that there are no isobars to isotopes of odd elements and no isobars of odd mass no. gives a scheme of isotopes in agreement with those so far found. A. B. D. C.

Segregation of polonium in bismuth crystals. A. B. Focke (Physical Rev., 1934, [ii], **46**, 623—628).—Geiger counter measurements of no.–distance relations for α-particles emitted normally through cleavage surfaces were made in order to determine the distribution of Po present as an impurity in single Bi crystals. The Po is segregated into small regions having nearly regular spacings, which are unaffected by speed of growth of the Bi crystal and by subsequent heat treatment. The addition of Te suppresses certain layers. N. M. B.

Energy of a β-ray of radium-*B*. F. A. Scott (Physical Rev., 1934, [ii], **46**, 633—640).—The measured energy of the most intense line of the β-ray spectrum of Ra-*B* obtained by magnetic focussing was $(2{\cdot}6145\pm0{\cdot}0001)\times10^5$ e.v., taking e/m as $1{\cdot}760\times10^7$. The val. of $H\rho$ for this line was 1931·8 gauss cm. N. M. B.

Technique of the counter-controlled cloud chamber. P. M. S. Blackett (Proc. Roy. Soc., 1934, **A**, **146**, 281—299; cf. A., 1933, 441).—The breadths of the tracks formed when Geiger counters are used to actuate a cloud chamber can be calc. by taking into account the diffusion of the ions, during the time τ, from the moment of their formation to that of drop formation. The breadth of the track varies as $\tau^{1/2}$. L. L. B.

Neutrons from aluminium and beryllium. R. Jaekel (Z. Physik, 1934, **91**, 493—510).—Energy distributions are given for neutrons excited by Rn, Ra-*A*, and Ra-*C′* α-rays. A. B. D. C.

Induced radioactivity. F. H. Newman and H. J. Walke (Nature, 1934, **134**, 537).—A further discussion of the authors' hypothesis (this vol., 939, 1054). L. S. T.

Disintegration of boron by swiftly-moving protons. M. G. White and E. O. Lawrence (Physical Rev., 1933, [ii], **43**, 304—305).—The yield of α-particles from B for voltages $> 5\times10^5$ is practically the same as that from Li (A., 1933, 205, 1225). The results indicate that for Li and B the effective collision cross-section for disintegration does not increase perceptibly with the speed of the proton above 4 or 5×10^5 volts. L. S. T.

Fermi effect in aluminium. II. I. Kurtschatov, L. Misovski, B. Kurtschatov, G. Schtschepkin, and A. Vibe (Compt. rend. Acad. Sci. U.R.S.S., 1934, **3**, 422—424; cf. this vol., 1152).—The product with a half-period of 12—13 hr., formed on bombarding Al with neutrons, was separated from Al and Mg and shown to be Ra-Na (I) (pptn. with added NaCl with K pyroantimonate). The process is $Al^{27}+n'=\text{Ra-Na}^{24}+He^4$. The disintegration mechanism of (I) is discussed. H. J. E.

Active phosphorus and its β-ray energy spectrum. J. Ambrosen (Z. Physik, 1934, **91**, 43—48).—S bombarded with neutrons gives active P, which was separated from S; the β-ray spectrum was then investigated. A. B. D. C.

Energy spectrum of positrons from radiophosphorus $_{15}P^{30}$ (activated aluminium). Y. Nishina, R. Sagane, M. Takeuchi, and R. Tomita (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, **25**, 1—7).—The energy spectrum of positrons from radio-P from activated Al was investigated by the measurement of 1484 Wilson tracks in a uniform magnetic field, and extended up to about 4×10^6 e.v. Indications of > one intensity max., changing in position with time after activation, were obtained. N. M. B.

Artificial disintegration by radium-*C′* α-particles. Aluminium and magnesium. W. E. Duncanson and H. Miller (Proc. Roy. Soc., 1934, **A**, **146**, 396—419).—An electrical counting method for counting α-particles and protons in the presence of strong β- and γ-radiations is described. Experiments in which Al is bombarded by the α-particles from Ra-*C′* indicate the presence of 3 excited α-particle levels in the resulting nucleus, and 2 resonance levels in the potential barrier at energies > those found by Chadwick and Constable (A., 1932, 318). Similar experiments on Mg indicate 2 excited α-particle levels in the resulting nucleus, and 2 resonance levels in the potential barrier above an energy of $5{\cdot}25\times10^6$ e.v. L. L. B.

Artificial radioactivity produced by neutron bombardment. E. Fermi, E. Amaldi, O. D'Agostino, F. Rasetti, and E. Segrè (Proc. Roy. Soc., 1934, **A**, **146**, 483—500).—Out of about 60 elements investigated, > 40 could be activated by neutron bombardment. No special difference was noted between light and heavy elements. The cross-sections for neutron impact for the elements which can be most intensely activated are of the order of the geometrical cross-section of the nucleus. Thus a high % of the neutrons which hit the nucleus produce an active atom. The active product is sometimes an isotope of the original atom (at. no. Z); in other cases its at. no. is lower by one or two units. Light and heavy elements appear to differ in this respect: for light elements the at. no. of the active product is usually $< Z$, whilst for heavy, non-spontaneously radioactive elements the active product is an isotope of the bombarded element. The emitted electrons always have a negative charge. L. L. B.

Theory of artificial disintegration. K. C. Kar (Current Sci., 1934, **3**, 106—107; cf. this vol., 127, 580). L. S. T.

Nuclear structure and excited radioactivity. G. Guében (Nature, 1934, **134**, 626).—Theoretical. L. S. T.

Gamow's theory of radioactivity. H. Saîni (Arch. Sci. phys. nat., 1934, [v], **16**, 80—101).—A crit. survey of the scope and deficiencies of Gamow's theory. N. M. B.

Mass of the neutron and the constitution of atomic nuclei. A. von Grosse (Physical Rev., 1933, [ii], **43**, 143).—The assumption that the masses of all neutrons are not identical would remove the difficulty of accounting for the difference in energy emission by the same substance during a β-disintegration. L. S. T.

Constitution of nuclei. II. K. Guggenheimer (J. Phys. Radium, 1934, [vii], **5**, 475—485; cf. this vol., 939).—Relations between the abundance of different atoms and the affinity of the nuclei for neutrons, protons, and α-particles, the transformation of neutrons into protons, and the various types of binding in the nucleus are discussed. N. M. B.

Annihilation of electrons and positrons. Y. Nishina, S. Tomonaga, and H. Tamaki (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, **24**, 7—12).—Mathematical. A relativistic calculation is made of the cross-section for the annihilation by recombination of an incident positron and a K, $L_{\text{I, II, III}}$, electron belonging to a bare at. nucleus. N. M. B.

How far do cosmic rays travel? F. Zwicky (Physical Rev., 1933, [ii], **43**, 147—148).—An examination of the two hypotheses of the origin of cosmic rays. L. S. T.

Counter-tube determinations with ultra-ray corpuscles. H. Maass (Physikal. Z., 1934, **35**, 858—861).—Two counter tubes were used with the method of double coincidence, the effect of absorbents placed alternately between and above the two tubes being determined. For thicknesses of Fe $>$ 8 cm. above the tube, an increase in secondary radiation was noted, which was probably due to the existence of an ultra-γ-radiation as a component of the ultra-radiation. A. J. M.

Analysis of cosmic radiation at high altitudes. P. Auger and L. Leprince-Ringuet (Compt. rend., 1934, **199**, 785—787).—High altitude measurements indicate two groups of cosmic rays differing in penetrating power. H. J. E.

Very high altitude survey of the effect of latitude on cosmic-ray intensities, and an attempt at a general interpretation of cosmic-ray phenomena. I. S. Bowen, R. A. Millikan, and H. V. Neher (Physical Rev., 1934, [ii], **46**, 641—652).—Detailed results and conclusions are described in relation to contemporary theory. Energies of cosmic-ray components indicate exclusively an origin in matter-annihilation. N. M. B.

Theory of the origin of the cosmic rays. L. G. H. Huxley (Phil. Mag., 1934, [vii], **18**, 971—983).—A simple mathematical treatment is given. The equations obtained are in agreement with the properties of the cosmic radiation on the assumption that the potential of the earth lies between 6×10^{10} and 10^{11} volts, probably about 7×10^{10} volts, and that the corpuscles all carry charges of similar sign opposite to that of the charge on the earth. Possible agencies by which the earth's charge may be maintained are considered. M. S. B.

Coincidence test of the corpuscular hypothesis of cosmic rays. D. S. Hsiung (Physical Rev., 1934, [ii], **46**, 653—658).—Double and triple coincidences obtained with three Geiger–Müller counters arranged vertically and certain interpositions of Pb absorbers are due to penetrating ionising particles, and not to secondary particles produced by photons which traverse the Pb. N. M. B.

Distribution of photo-electrons of the *M* shell of hydrogen-like atoms. J. Kreisler (Acta phys. polon., 1933, **2**, 7—22; Chem. Zentr., 1934, i, 2397).—Theoretical. H. J. E.

Atomic nuclei and the periodic system. L. Meitner (Naturwiss., 1934, **22**, 733—739).—A lecture.

Investigations on free alkali metals (1930—1933). H. Alterthum and R. Rompe (Physikal. Z., 1934, **35**, 814—836).—A review.

De Broglie theory of photons. J. L. Destouches (Compt. rend., 1934, **199**, 779—781).—Theoretical. H. J. E.

Molecular screening constants. P. Das (Indian J. Physics, 1934, **9**, 35—43).—Using the Hylleraas method the heats of dissociation of LiH, BeH, and Li_2, and the term vals. of H_2, are calc. N. M. B.

Determination of *e/m* and mass of individual charged particles in colloids. K. Krishnamurti (Current Sci., 1934, **3**, 107).—The motion of single colloid particles in a cataphoretic cell under a given p.d. has been observed in the field of the ultramicroscope and the val. of e/m calc. L. S. T.

Interpretation of e^2/mc^2 and h/mc. B. Podolsky (Physical Rev., 1934, [ii], **46**, 734—738).—Equations are re-written on the assumption that m and e need not enter into the electrodynamics and quantum mechanics of electrons, positrons, and photons. Results are discussed. N. M. B.

Method of determining atom form factors. B. von S. Nagy (Z. Physik, 1934, **91**, 105—110).—Theoretical. A. B. D. C.

Approximate wave functions and atomic field for mercury. D. R. Hartree (Physical Rev., 1934, [ii], **46**, 738—743).—Tables of preliminary results are given. N. M. B.

Averages over portions of configuration space. G. Heller and L. Motz (Physical Rev., 1934, [ii], **46**, 502—505).—Mathematical. N. M. B.

Perturbation calculation in many-electron [valency] problem. G. Gelman (Compt. rend. Acad. Sci. U.R.S.S., 1934, **3**, 442—446).—Theoretical. H. J. E.

Approximation treatment for many-electron systems. C. Møller and M. S. Plesset (Physical Rev., 1934, [ii], **46**, 618—622).—Mathematical. A perturbation theory method is developed. N. M. B.

Problems involving permutation degeneracy. R. Serber (J. Chem. Physics, 1934, **2**, 697—710; cf. this vol., 580).—Mathematical. F. L. U.

Application of the Dirac vector model to the d^4 configuration. M. Ostrofsky (Physical Rev., 1934, [ii], **46**, 604—607).—Mathematical. N. M. B.

Nuclear energy levels and the model of a potential hole. H. Margenau (Physical Rev., 1934, [ii], **46**, 613—615).—Mathematical. N. M. B.

Vacuum in Dirac's theory of the positive electron. R. Peierls (Proc. Roy. Soc., 1934, **A**, **146**, 420—441).—Mathematical. The problem of the charge and current induced in the vac. by an electromagnetic field has been studied from the viewpoint of Dirac's theory (where the positive electron is a "hole" in an infinite distribution of electrons in states of negative energy). Essential modifications seem to be needed in the fundamental concepts underlying the theory. L. L. B.

Uncertainty of the electromagnetic field of a particle. G. LEMAITRE (Physical Rev., 1933, [ii], 43, 148).—From Heisenberg's uncertainty principle it is concluded that for instantaneous determinations the field of an electron, proton, or at. nucleus is practically undetermined. Bohr's view, that the field of the nucleus determines the orbit of the electron and that the radiation of a moving electron can be neglected, is supported. L. S. T.

Electron counter and demonstration of Gurwitsch radiation.—See this vol., 1194.

Interpretation of line spectra in crystals. F. H. SPEDDING (Physical Rev., 1933, [ii], 43, 143—144).—The theories of Deutschbein (A., 1932, 983) and Tomaschek (A., 1933, 5) are discussed in relation to the absorption spectra of solids. L. S. T.

Emission spectra of the vapours of the sodium and potassium halides. H. HAMADA (Sci. Rep. Tôhoku, 1934, 23, 296—307).—The emission spectra of NaCl, NaBr, and NaI show a continuous region with max. intensity near the Na *D* line, this continuum being widest for NaCl and narrowest for NaI. This spectrum differs from that of Na vapour in being emitted by quantised mols., held loosely together by polarisation forces, whereas the Na spectrum is emitted by quasi-mols. Similar results are obtained with K halides. J. W. S.

Band spectrum of manganese oxide. A. K. S. GUPTA (Z. Physik, 1934, 91, 471—474).—The energy of dissociation of the lower state is given as 4·4 volts. A. B. D. C.

Test for free radicals of short life. O. OLDENBERG (J. Chem. Physics, 1934, 2, 713—714).—Using a C arc in dry N_2 as source of radiations and high resolving power, the absorption spectrum of H_2O vapour has been photographed after the cessation of an electric discharge through it. Bands due to OH have been observed, their persistence being $> 1/8$ sec. It is not yet known whether the observed decay relates to the average life of OH radicals or to that of combining O and H atoms. F. L. U.

Sensitisation of the photochemical effect in crystals of the alkali halides. A. D. VON LUPKE (Ann. Physik, 1934, 21, [v], 1—14).—The prep. of crystals of KCl showing ultra-violet bands is described. Light absorption in these bands changes the ultra-violet centres into colour centres. The addition of foreign substances (K_2O, KOH, K_2CO_3, KNO_3) causes some photochemical sensitisation. A. J. M.

Ultra-violet bands of beryllium chloride. W. R. FREDRICKSON and M. E. HOGAN, jun. (Physical Rev., 1934, [ii], 46, 454—458).—A band system in the range 3468—3700 Å., using a Be arc in Cl_2, was photographed. Four heads are found for each band; the system is due to a $^2\Pi-{}^2\Sigma$ transition, and only partial rotational analysis was possible. The isotope effect for Cl_2 was observed in -1 and $+1$ sequences and the $^{S}R_{21}$ head of the (0,0) band. From the heats of dissociation electronic extinction appears to be due to the $^1D \longrightarrow {}^1P$ transition in the Be atom. N. M. B.

Spectrophotometric investigation of aqueous cobalt chloride solutions. G. SPACU and J. G. MURGULESCU (Z. physikal. Chem., 1934, 170, 62—70).—The relation of the absorption coeff. of unit thickness of 0·25—1·0*M*-$CoCl_2$ solutions containing KCl for 546 mμ to the Co and Cl concns. may be accounted for by assuming that the reactions $[\mathrm{Co,6H_2O}]^{\cdot\cdot}+\mathrm{Cl}'=\mathrm{D}_1$ and $[\mathrm{Co,6H_2O}]^{\cdot\cdot}+2\mathrm{Cl}'=\mathrm{D}_2$ occur, where the products D_1 and D_2 have different absorption coeffs. R. C.

Spectrophotometric investigation of aqueous cupric chloride solutions. G. SPACU and J. G. MURGULESCU (Z. physikal. Chem., 1934, 170, 71—80).—The absorption coeffs. of 0·25—1·5*M* aq. $CuCl_2$ solutions in which the total [Cl′] is varied up to 4*N* by addition of KCl have been determined at 436, 650, and 680 mμ to find the causes of the deviations from Beer's law. In the red the deviations are ascribed to $[\mathrm{Cu,4H_2O}]^{\cdot\cdot}+\mathrm{Cl}'\rightleftharpoons\mathrm{X}$, where X may be either $[\mathrm{Cu,3H_2O,Cl}]^{\cdot}$ or $\mathrm{CuCl}^{\cdot}$. In the blue $\mathrm{CuCl_4}''$ is responsible. R. C.

Spectra of indium halides. M. WEHRLI and E. MIESCHER (Helv. phys. Acta, 1933, 6, 457—458; Chem. Zentr., 1934, i, 2252).—InCl, InBr, and InI each show 3-band systems, two of which overlap. H. J. E.

Spectra of gallium halides. E. MIESCHER and M. WEHRLI (Helv. phys. Acta, 1933, 6, 458—459; Chem. Zentr., 1934, i, 2252—2253).—The band systems of GaCl, GaBr, and GaI resemble those of the In salts, but are displaced to shorter wave-length. The isotope effect for Ga^{69} and Ga^{71} was observed. H. J. E.

Diffuse band systems in the absorption spectrum of thallous chloride vapour. H. NEUIMIN (Phys. Z. Sovietunion, 1934, 5, 580—585).—13 diffuse bands were observed on the long-wave side of the continuum at 2513 Å.; 4 bands occur on the long-wave side of the continuum at 3113 Å. The dissociation energy of TlCl into Tl and Cl is 109 kg.-cal. TlCl has 2 unstable upper electronic states. CH. ABS. (*e*)

Ultra-violet absorption by potassium nitrate, nitrites, and carbon disulphide at low temperatures. G. RODLOFF (Z. Physik, 1934, 91, 511—532).—Absorption spectra of KNO_3, KNO_2, $NaNO_2$, and CS_2 have been determined to $-250°$ in the region 4400—2400 Å. Near $-180°$ the KNO_2 and CS_2 continuous bands show structure at 600 cm.$^{-1}$ intervals, and at $-250°$ these show further structure; $NaNO_2$ shows this second structure at $-180°$. A. B. D. C.

Optical absorption spectrum of three isomerides of potassium pentachlororuthenite. S. AOYAMA and T. FUKOROI (Sci. Rep. Tôhoku, 1934, 23, 420—425; cf. this vol., 1295).—Curves are given for the absorption spectra between 3400 and 4400 Å. of HCl solutions of K_2RuCl_6 and samples of K_2RuCl_5 and $K_2Ru(H_2O)Cl_5$ prepared in different ways. The existence of three isomerides of K_2RuCl_5 is confirmed, and geometrical models are suggested. J. W. S.

Absorption spectra of the rare earths. W. PRANDTL and K. SCHEINER (Z. anorg. Chem., 1934, 220, 107—112).—Absorption spectra of solutions of the rare earths have been determined between 7000 and 2200 Å. at 5 different concns. The relation between the variations in absorption spectra and at. structure is discussed. M. S. B.

Action of penetrating radium radiation on dissolved substances. G. GUÉBEN (Arch. Phys. biol., 1933, **10**, 292—303; Chem. Zentr., 1934, i, 2555).—The ultra-violet absorption spectra of aq. $KMnO_4$, $K_2Cr_2O_7$, KI,CaI_2, NaOEt, and cinnamic or malonic acid were changed by exposure to rays from radioactive material. Aq. $AgNO_3$, $Na_2C_2O_4$, and fumaric or maleic acid were unchanged. H. J. E.

Rotational and vibrational structure of the fourth positive bands of carbon monoxide. D. N. READ (Physical Rev., 1934, [ii], **46**, 571—575).—The rotational structure of 12 of the fourth positive bands of CO has been measured and analysed. Rotational consts. of the normal state are: $B_0=1\cdot9170$, $\alpha=0\cdot01738$ cm.$^{-1}$, against $B_0=1\cdot84$ by infra-red band measurements. Data for 64 band heads below 2270 Å. are tabulated. N. M. B.

Energy of the C·OH linking and molecular structure in alcohols. Y. HUKUMOTO (Nature, 1934, **134**, 538).—Investigation of a continuous absorption spectrum in the ultra-violet which corresponds with the immediate dissociation of a mol. into its constituents shows that for the normal aliphatic alcohols the energy of the C·OH linking increases as the series is ascended. L. S. T.

Chemical reactivity and light absorption. III. N. R. DHAR and P. K. KAR (J. Indian Chem. Soc., 1934, **11**, 629—634; cf. this vol., 975).—Absorption of light of longer λ by reacting systems involving I than by the reactants, and increased total absorption, are observed in the ultra-violet and visible, but not the infra-red regions. The relative magnitudes of the absorption changes in the several mixtures are in the same order as the respective heats of reaction. J. G. A. G.

Absorption of light in organic compounds. N. Q. CHAKO (J. Chem. Physics, 1934, **2**, 644—653).—An attempt is made to correlate the width and strength of absorption bands with chemical constitution and the nature of the solvent. Examination of data relating to a large no. of substances reveals the present inadequacy of a theoretical basis for such a correlation. F. L. U.

Absorption spectrum of acetylene in the region 2350—2050 Å. A. JONESCO (Compt. rend., 1934, **199**, 710—713).—Approx. 80 bands of C_2H_2 have been examined with a precision 3—5 cm.$^{-1}$ 10—12 of these are represented by $\nu=\nu_0+1034\cdot6V-V^2$ ($\nu_0=43{,}277$, 42,639, and 42,062 cm.$^{-1}$), $V=0$, 1, 2, 3, 4, 5; another frequency interval often appearing is approx. 2700 cm.$^{-1}$ The frequency 1034·6 cm.$^{-1}$ is identified with the vibration ν_1' of the final state of the mol. R. S. B.

Ultra-violet absorption of some aromatic hydrocarbons. AUBERT and T. GHEORGHIU (Ann. Office nat. Comb. liq., 1933, **8**, 451—478; Chem. Zentr., 1934, i, 510).—In the region 2200—2800 Å. selective absorption was observed for C_6H_6, PhMe, PhEt, PhPr, and PhBu. Continuous absorption was observed for $C_6H_4Et_2$, amylbenzene, mesitylene, ψ-cumene, and $C_6H_3Et_3$. H. J. E.

Ultra-violet absorption of some aromatic hydrocarbons. II. Mono-*n*-alkylbenzenes. M. PESTEMER and O. GÜBITZ (Monatsh., 1934, **64**, 426—438).—The extinction–wave no. curves for the series of compounds from PhMe to n-$C_6H_{13}Ph$ have been determined in C_6H_{14} and MeOH and the results compared. The effect of alkyl substitution and of the change from a non-polar to a polar solvent is discussed. M. S. B.

Ultra-violet absorption by aromatic aldehydes and ketones. (MME.) RAMART-LUCAS and J. SÉGAL (Bull. Soc. chim., 1934, [v], **1**, 1049—1054).—Absorption between λ 2200 and 3750 Å. has been measured in EtOH and C_6H_{14} solutions of PhCHO, $C_6H_4Me\cdot CHO$, p-$C_6H_4Pr^\beta\cdot CHO$, o-$C_6H_4(OH)\cdot CHO$, p-$C_6H_4(OMe)\cdot CHO$, p-$C_6H_4Me\cdot COMe$, and p-$C_6H_4(OMe)\cdot COMe$, and in EtOH solutions of semicarbazones of the aldehydes. F. L. U.

Absorption spectra of the nitroanilines and of the corresponding nitroacetanilides. (MLLE.) G. GLOTZ (Bull. Soc. chim., 1934, [v], **1**, 1148—1152).—The absorption of the *o*-, *m*-, and *p*-compounds between λ 2200 and 6000 Å. has been measured, and differences are noted and discussed. F. L. U.

Ultra-violet absorption spectra of derivatives of uracil. J. E. AUSTIN (J. Amer. Chem. Soc., 1934, **56**, 2141—2144; cf. A., 1932, 320).—Ultra-violet absorption spectra curves of EtOH solutions of uracil (I), 1- and 3-methyl-, 1 : 3-dimethyl-, 1 : 3-diethyl-, 1-methyl-3-ethyl-, 3-benzyl-1- and -5-methyl-, 1-benzyl-3-methyl-, and 5 : 6-dihydro-uracil, 2-keto-4-methoxy- and -4-ethoxy-1-methyl- and 2-keto-4-methoxy-1-tetra-acetylglucosido-1 : 2-dihydropyrimidine, and 2 : 4-dimethoxy- and 2 : 4-diethoxy-pyrimidine are given. The 1 : 4-, 1 : 3-, and 2 : 4-derivatives show an absorption max. at 36,400, 37,800, and 38,800 cm.$^{-1}$, respectively, irrespective of the nature of the substituents. The results indicate that (I) (and, by analogy, hydantoin) is predominantly the 2-hydroxy-4-keto-derivative. H. B.

Fluorescence spectrum of ethylamine vapour. A. V. BANOV and N. A. PRILESHAEVA (Compt. rend. Acad. Sci. U.R.S.S., 1934, **3**, 497—499).—Five fluorescence bands between 2700 and 3500 Å. excited by λλ 2300—2800 Å. were observed, the frequency difference between the band max. corresponding with the 1450 cm.$^{-1}$ Raman frequency of NH_2Et. H. J. E.

Photochemical studies. XVIII. Fluorescence of acetone vapour. C. F. FISK and W. A. NOYES, jun. (J. Chem. Physics, 1934, **2**, 654—658; cf. this vol., 852).—The intensity of the fluorescence radiation of $COMe_2$ vapour free from O_2 has been studied as a function of the incident intensity and of the pressure. The results are discussed with reference to the mechanism of photochemical decomp. F. L. U.

Displacement of absorption spectra of azo-compounds. M. HORIO and S. YAMASHITA (J. Soc. Chem. Ind. Japan, 1934, **37**, 491—497B).—The absorption spectrum of azobenzene (non-polar) is nearly the same as vapour, as liquid, or as solute in polar or non-polar liquids. For the polar substances hydroxy-, amino-, and trihydroxy-azobenzene the spectra in the liquid state or dissolved in polar solvents differ from those of the solid or of solutions in non-polar solvents. A. G.

Relation between absorption spectra and constitution of dyes. VI.—See this vol., 1344.

Spectra and latent energy of flame gases. W. T. David (Nature, 1934, **134**, 663).—Mainly a discussion. In CO–air combustion the latent energy in const.-pressure combustion is > in closed-vessel explosions. It appears that the greater is the latent energy in the CO flame gases the greater is the relative intensity of the ultra-violet radiation. L. S. T.

Halogen molecules and their spectra. *J–J*-like coupling. Molecular ionisation potentials. R. S. Mulliken (Physical Rev., 1934, [ii], **46**, 549—571).—Relations and rules, with comparisons with observed vals., for mol. and at. ionisation potentials are discussed. Electron configurations of N_2, CO, X_2, HX (X=halogen), and O_2 are examined. New low-energy states of X_2 and XY are predicted, and observed absorption spectra of XY and X_2 mols. are interpreted, with suggestions for interpreting observed fluorescence and emission spectra. Indications of *J–J*-like coupling from the vac. ultra-violet (λλ 1600—1950) bands of XY are examined. N. M. B.

Photographic method for the study of mechanical models of vibrating molecules. D. H. Andrews and J. W. Murray (J. Chem. Physics, 1934, **2**, 634—636).—The method and some of its applications are described. F. L. U.

Nature of the red shift in the infra-red emission bands in flame spectra. V. N. Kondratev (J. Exp. Theor. Phys., Russia, 1933, **3**, 265—272).—The shift is explained by means of the superposition of single bands, which correspond with the oscillation quanta emitted by the mols. when strongly oscillating as a result of the reaction taking place. The magnitude of the shift is related to the energy of oscillation; hence analysis of infra-red flame spectra can be used to determine the chemical processes proceeding in the burning zone. Ch. Abs.

Structure of the ozone molecule and its infra-red bands. G. Hettner, R. Pohlman, and H. J. Schumacher (Z. Physik, 1934, **91**, 372—385).—The spectrum was investigated to 27 μ. The 7·6 μ band is ascribed to N_2O_5, and a new intense band is given at 14·1 μ. The mol. is an isosceles triangle of vertical angle 19·5°. A. B. D. C.

Infra-red spectrum and the molecular structure of ozone and sulphur dioxide. R. M. Badger and L. G. Bonner (Physical Rev., 1933, [ii], **43**, 305—306).—Disagreement with the views of Gerhard (A., 1933, 208) on the structure of O_3 and with those of Bailey and co-workers (A., 1931, 144) on SO_2 is expressed. L. S. T.

Infra-red absorption spectrum of silane. W. B. Steward and H. H. Nielsen (J. Chem. Physics, 1934, **2**, 712).—Positions and intensities of 4 bands are given. The spectrum appears to be similar to that of CH_4. F. L. U.

Near infra-red absorption of solutions of hydroxides and hydrolysing salts. W. Gordy (J. Chem. Physics, 1934, **2**, 621—623; cf. this vol., 1154).—Observations were made on aq. solutions of KOH, NaOH, LiOH, NaOAc, Na_2CO_3, $ZnCl_2$, and $ZnBr_2$ in the region 0·60—2·80 μ. Bands at 2·60 and 1·81 μ are characteristic of the hydroxide mol., and that at 2·30 μ of OH′. The remaining bands are accounted for as harmonics of 2·30, 3·65, and 5·20 μ. F. L. U.

Near infra-red absorption spectrum of mono-deutero-acetylene. A. McKellar and C. A. Bradley, jun. (Physical Rev., 1934, [ii], **46**, 664—666).—Using absorbing columns up to 20 ft. in length at atm. pressure, the spectrum, photographed for the range 6000—10,500 Å., showed a band with origin at 10,302 Å., attributed to $C_2H^1H^2$. The calc. interat. distances are $C–C=(1{\cdot}247\pm0{\cdot}008)\times10^{-8}$, $C–H^1=C–H^2=(0{\cdot}940\pm0{\cdot}036)\times10^{-8}$ cm. N. M. B.

Rotation–vibration spectrum of acetylene (C_2H_2). G. Herzberg and J. W. T. Spinks (Z. Physik, 1934, **91**, 386—399).—A C_2H_2 band at 1·174 μ and two weak bands at 1·016 and 1·037 μ have been photographed and the lines measured; this gives variation of inter-nuclear separation with rotation, and also a new allocation of band frequencies. A. B. D. C.

Infra-red and Raman spectra of methyl compounds. A. Adel and E. F. Barker (J. Chem. Physics, 1934, **2**, 627—629).—The appearance of an intense extra band in the infra-red and Raman spectra of the Me halides is explained by resonance interaction between the ν_1 and $2\nu_4$ levels. Comparison of a no. of Me compounds indicates that the phenomenon is characteristic of the Me group. F. L. U.

Influence of temperature on the absorption of organic liquids in the region of the near infra-red. B. Bloch and J. Errera (Compt. rend., 1934, **199**, 713—715).—Absorption bands in the region 1·5 μ due to C·H, C:O, C·Cl, and N·H in org. compounds are not influenced by temp. With alcohols the band due to O·H at 1·6 μ decreases in intensity as temp. rises, and a band at 1·4 μ appears at approx. 20°, and becomes well marked at approx. 90°. MeOH, EtOH, Bu^aOH, $C_5H_{11}OH$, and $C_7H_{15}{\cdot}OH$ have been examined. $OH{\cdot}CH_2{\cdot}CH_2Cl$ (I) behaves like an alcohol, which disagrees with the quantum resonance supposed by Zahn to exist between (I) and $^-O{\cdot}CH_2{\cdot}CH_2Cl^+$. The C·H band of (I) at 1·74 μ is not influenced by temp. R. S. B.

Infra-red spectra of the chlorine derivatives of ethylene. T. Y. Wu (Physical Rev., 1934, [ii], **46**, 465—469).—Data for regions of absorption and band envelopes are given for the infra-red absorption spectra of $CH_2{:}CHCl$, *cis*- and *trans*-$C_2H_2Cl_2$, C_2HCl_3, and C_2Cl_4 in the region 2—25 μ. Analysis and the Raman spectra are considered. N. M. B.

Vibrational spectrum of water vapour. L. G. Bonner (Physical Rev., 1934, [ii], **46**, 458—464).—Mathematical. From a treatment of the non-linear triat. XY_2 type mol. the vibrational energy expression is obtained. Application of the results to the H_2O mol. gives the primary binding consts. and vibration frequencies for infinitesimal amplitudes. A prediction of the infra-red vibration spectrum of the symmetrically substituted H^2_2O mol. is given. N. M. B.

Electric moments and infra-red spectra. A correction. R. S. Mulliken (J. Chem. Physics, 1934, **2**, 712—713; cf. this vol., 942). F. L. U.

Infra-red absorption of cellulose esters. Cellulose acetate. O. B. Orlov and D. A. Fedorov (J. Tech. Phys., Russia, 1933, **3**, 1124—1131).—By addition of plasticisers, cellulose acetate films equiv. in absorptive properties to glass can be obtained. Ch. Abs.

Plotnikov effect or longitudinal light scattering in liquids. R. S. Krishnan (Proc. Indian Acad. Sci., 1934, **1**, 44—47).—The effect (halo produced around a pencil of transmitted light) was more conspicuous in liquids not free from dust than in pure liquids, and disappeared completely when the AcOH, EtOH, MeOH, H_2O, petrol–Et_2O, $[\cdot CH_2\cdot OH]_2$, and castor oil had been purified by repeated distillation in vac., indicating that the effect is not a mol. phenomenon, but is due to the presence of dust. N. M. B.

Normal frequencies of vibration of symmetrical pyramidal molecules AB_3 with application to the Raman spectra of trihalides. J. B. Howard and E. B. Wilson, jun. (J. Chem. Physics, 1934, **2**, 630—634).—Theoretical. Interat. distances are calc. for trihalides of P, As, Sb, and Bi. F. L. U.

Raman spectrum of sulphur in the solid and liquid states. C. S. Venkateswaran (Proc. Indian Acad. Sci., 1934, **1**, 120—121).—No difference could be detected between the structure or positions of the Raman lines for the liquid state and the rhombic form of S. Hence the liquid state seems to differ from the solution state, for which small shifts in the frequencies have been recorded. J. W. S.

Intensity of Raman effect in water. A. Carrelli and F. Cennamo (Nuovo Cim., 1933, [ii], **10**, 329—332; Chem. Zentr., 1934, i, 2095).—In the band groups of H_2O excited by λλ 3665, 4047 Å., three max. occur. at 3230, 3450, and 3560 cm.$^{-1}$ H. J. E.

Raman spectra and molecular constants of phosphorus trifluoride and phosphine. D. M. Yost and T. F. Anderson (J. Chem. Physics, 1934, **2**, 624—627).—Raman lines for liquid PF_3 were found at 890, 531, 840, and 486 cm.$^{-1}$, and for liquid PH_3 at 2306, 979, and 1115 cm.$^{-1}$ A regular pyramidal structure is indicated for PF_3. Entropies are calc. F. L. U.

Raman spectra of sulphuric acid solutions. R. M. Bell and M. A. Jeppeson (J. Chem. Physics, 1934, **2**, 711—712).—The Raman spectrum of aq. H_2SO_4 at different concns. shows a gradual shift of frequency with concn. among two groups, rather than a shift among three different frequencies as reported by Woodward and Horner (this vol., 473). F. L. U.

Raman spectrum of nitrosylsulphuric acid. W. R. Angus and A. H. Leckie (Nature, 1934, **134**, 572).—The Raman spectrum of a solution of this acid in H_2SO_4 shows in addition to displacements due to H_2SO_4 a line corresponding with a displacement of 2340 cm.$^{-1}$ together with a no. of faint lines. L. S. T.

Raman and ultra-violet absorption spectra of metal carbonyls and alkyls. A. B. F. Duncan and J. W. Murray (J. Chem. Physics, 1934, **2**, 636—643; cf. this vol., 10).—Raman lines, and the limits of absorption at −78° and room temp., are given for $Ni(CO)_4$, $PbMe_4$, and $PbEt_4$. The results are discussed. The calc. symmetry no. for $Ni(CO)_4$ is 6·3, indicating a plane square rather than a tetrahedral configuration. F. L. U.

Multiplicity of some Raman frequencies of the nitrate group in nitrates with more than one valency. Z. Ollano and G. Frongia (Nuovo Cim., 1933, [ii], **10**, 306—315; Chem. Zentr., 1934, i, 1451—1452).—The frequencies, 1440, 1030, 980, and 720 cm.$^{-1}$, are simple for aq. solutions of Na, K, NH_4, and $Hg^{\cdot}$ nitrates; in those of Mg, Mn, Ba, and Al, $Ce^{\cdot\cdot\cdot}$, La, and Bi, 1440 cm.$^{-1}$ is broad and complex, probably double, and 720 cm.$^{-1}$ is double with an interval of 30—40 cm.$^{-1}$ between the components. The doublet structure of this frequency, which corresponds with vibrations perpendicular to the symmetry axis of the NO_3 pyramid, is attributed to the presence of $[M(NO_3)]^{\cdot}$ or $[M(NO_3)_2]^{\cdot}$ and $[M(NO_3)]^{\cdot\cdot}$ ions in conc. solutions in spectroscopically detectable amounts. L. S. T.

Raman spectrum of deuteriobenzene. J. W. Murray, C. F. Squire, and D. H. Andrews (J. Chem. Physics, 1934, **2**, 714—715).—The Raman spectrum of $C_6H^2_6$ obtained by polymerisation of $C_2H^2_2$ shows a line at 943 cm.$^{-1}$ This agrees with the frequency (945 cm.$^{-1}$) calc. from the shift of the 992 line of $C_6H^1_6$ due to substituting six H^2 atoms for the H^1 atoms. F. L. U.

Influence of high temperature on the Raman bands of benzene. S. C. Sirkar (Current Sci., 1934, **3**, 113—114).—The changes which many of the lines in the Raman spectrum of C_6H_6 undergo between 35° and 160° are described and discussed. L. S. T.

Raman effect of furan and three derivatives. L. Médard (Bull. Soc. chim., 1934, **1**, [v], 934—942; cf. this vol., 830).—The characteristic olefinic C:C frequency, 1600 cm.$^{-1}$ approx., is absent from the Raman spectrum of furan (I), doubtful in the case of furfuraldehyde (II), but present in those of 2-methylfuran and furfuryl alcohol. The frequencies characteristic of the (I) ring are 610, 745, 880, 1150, 1390, 1500, 3126, and 3160, and are not found in tetrahydromethylfuran. (I) has no frequencies at 919—930, 1220—1237, and 1458—1476, possibly owing to its symmetry or the absence of side-chain–nuclear vibrations. The frequencies of the C:O in (II) are modified. J. G. A. G.

Application of the Raman effect to organic chemistry. III. Tetramethylethylene. IV. Configuration of anethole, *iso*safrole, and *iso*eugenol. T. Hayashi (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, **25**, 31—35, 36—45).—III. The following frequencies, in cm.$^{-1}$, have been found in the Raman spectrum of $CMe_2{:}CMe_2$ at 18°: 1665, due to tetra-substituted C:C, 1378 (corresponding with 1342 for C_2H_4), 1447, due to substituted CH_2; 2997, 2903, 2853, 1017, 954, and 894, all analogous to frequencies appearing in Raman spectra of saturated and unsaturated hydrocarbons. It is inferred that substitution of the H atoms of C_2H_4 by Me increases the strength of the double linking.

IV. The Raman spectra of anethole (I), *iso*safrole (II), and *iso*eugenol (III) have been determined at approx. 20°. The C:C frequencies, in $cm.^{-1}$, are 1644 (I), 1641 (II), and 1646 (III). The influence of the OMe has been studied with *p*-methoxystyrene, for which the C:C frequency is 1620, as against 1636 for styrene. From this effect, and from the influence of OMe on the CO frequency of PhCHO, it is inferred that the C:C frequencies of (I), (II), and (III) correspond not with the frequency 1645 of *cis*-CHPh:CHMe, but with the frequency 1663 of *trans*-CHPh:CHMe. It is supposed that (I), (II), and (III) exist in the *trans*-form. Other frequencies observed are: 3046 (I), 3056 (II), and 3060 (III), due to aromatic CH; 2991, 2904, 2820 (I), 2995, 2902, 2855 (II), and 2990, 2916, 2850 (III), due to aliphatic CH; 1492, 1432 (I), 1483, 1434 (II), and 1452, 1430 (III), due to CH_2.

R. S. B.

Raman effect. Raman spectrum of organic substances. XXIII (Poly-substituted benzenes. IV). XXIV. (Benzoyl, phenylacetyl, and cinnamoyl compounds.) K. W. F. Kohlrausch and A. Pongratz (Monatsh., 1934, **64**, 361—373, 374—384).—XXIII. Data have been obtained for a no. of compounds $C_6H_3Me_2X$ (X=Cl, Br, I, or CN). The results are discussed.

XXIV. The frequency ω of the CO has been determined for a no. of derivatives $CH_2Ph{\cdot}COX$, BzX, and CHPh:CH·COX. In the Cl-derivative a duplication of the CO ω takes place, but not in the only Br-derivative, BzBr, examined. Association of the CO group with the C:C linking increases intensity, but lowers ω.

M. S. B.

Line emission and absorption of chromium phosphors. III. Behaviour at low temperatures and in a magnetic field. O. Deutschbein (Ann. Physik, 1934, [v], **20**, 828—842; cf. A., 1932, 1076).—Between 78° and 14° abs. there is no marked change in the sharpness and position of the lines emitted by Cr phosphors. The intensity ratio of some of the lines, however, varies considerably between these temp. The variation of the intensity with temp. makes possible an arrangement of the terms, and the term scheme of the Al_2O_3–Cr phosphor has been accurately derived. The principal lines (I) and some of the secondary lines (II) are split in a magnetic field, (I) into more components than (II). (I) are more strongly degenerate than (II).

A. J. M.

Natural fading in single crystals of phosphorescent zinc compounds. V. V. Antonov-Romanovski (Compt. rend. Acad. Sci. U.R.S.S., 1934, **3**, 432—435).—The dependence of the decay of phosphorescence on the crystal size (approx. size 10—100 μ), temp., and intensity of the exciting light has been measured. The decay was slower in small than in large crystals.

H. J. E.

Radiation damping and the polarisation of fluorescence radiation. G. Breit and I. S. Lowen (Physical Rev., 1934, [ii], **46**, 590—597).—Mathematical. The case in which the distance between two or more energy levels is comparable with their natural breadth is considered in a systematic treatment of emission, absorption and fluorescence, and the calculation of the polarisation of fluorescence radiation. Results are given for the polarisation of H_α excited by absorption of the second line of the Lyman series.

N. M. B.

Behaviour of calcite in ultra-violet light. A. Köhler and H. Leitmeier (Zentr. Min., **A**, 1933, 401—411; Chem. Zentr., 1934, i, 2103—2104).—Observations on the luminescence phenomena are recorded for 300 specimens.

H. J. E.

Phosphorescence of glass solarised by soft *X*-rays. H. Kersten and C. H. Dwight (J. Opt. Soc. Amer., 1934, **24**, 285—286; cf. this vol., 40).—The variation of the intensity of the phosphorescence with time of excitation, and the rate of its decay have been investigated by measurement of blackening produced on a photographic film.

J. W. S.

Ionisation potentials of formaldehyde and halogen derivatives of methane. T. N. Jewitt (Physical Rev., 1934, [ii], **46**, 616—617).—Vals. measured by a mol.-ray method for CH_2O, MeCl, MeBr, and MeI were 11·3, 10·7, 10·0, and 9·1 volts, respectively.

N. M. B.

Electrolytic valve action in molten salts. H. Grünert (Z. Physik, 1934, **91**, 49—69).—Valve action has been investigated for Ta and Al electrodes in molten $NaNO_3$, KNO_3, their eutectic mixture, and $K_2Cr_2O_7$.

A. B. D. C.

Emission of electrons from cold metal surfaces. C. C. Chambers (J. Franklin Inst., 1934, **218**, 463—484).—By repeating Del Rosario's work it is found that the cold electron current did not commence until voltages much > those found by others because of extremely good vac. conditions and freedom from impurities. The formula of Fowler and Nordheim is applicable in the measurable regions in form directly, and in magnitude only if irregularities in the surface are such as to raise the field at the surface to a sufficiently high val.

W. R. A.

Surface photo-electric effect in metals. I. K. Mitchell (Proc. Roy. Soc., 1934, **A**, **146**, 442—464).—Theoretical. The theories of the surface photo-electric effect in metals proposed by Wentzel and Fröhlich are shown to be incorrect. The photo-electric emission due to a single surface is calc. by two methods which lead to the same result. The theoretical spectral distribution curves for K are compared with experiment.

L. L. B.

Effect of out-gassing potassium on the selective photo-electric effect. F. Klauer (Ann. Physik, 1934, [v], **20**, 909—918).—The K was submitted to seven-fold distillation in vac. The sensitivity is very small for freshly prepared layers, but increases on keeping, gas probably being taken up from the walls. The introduction of a very small pressure of intensively dried H_2 has no effect on the sensitivity. The selective photo-effect with the alkali metals is to be ascribed to the fact that the ordinary metals always contain H_2.

A. J. M.

Semi-conductors. G. Déchêne (Ann. Physique, 1934, [xi], **2**, 241—345).—The discontinuities of potential at the junction of a semi-conductor

(HgO, $PbCl_2$, ZnO, Na_2CO_3), and a metallic electrode when a current passes, are attributed to the formation of a space charge in the thin layer of semiconductor; this hypothesis allows an explanation of the influence of temp., illumination, pressure, and modifications with time. From the capacity of the contact the order of magnitude of the layer in which the potential variation takes place is deduced as 10^{-2} or 10^{-3} cm. Evidence is given that the complex ionising electromagnetic radiation emitted above a crit. potential, when the electrode is in grid form, originates in the adjacent air, and not in the semiconductor. The intensity of the radiation varies with time, with the resistivity of the substance, and with the voltage at the grid. N. M. B.

Effects produced on illuminating cuprous oxide in a magnetic field. I. K. Kikoin (Compt. rend. Acad. Sci. U.R.S.S., 1934, **3**, 418—421).—When a plate of Cu_2O with its surface parallel to the magnetic field is illuminated perpendicularly, an e.m.f. of the order of 20 volts is set up in the plate in a direction perpendicular to that of illumination and to the field. Measurements under varied conditions are recorded. H. J. E.

Voltaic and thermal potential of cuprous oxide. G. Mönch (Z. Physik, 1934, **91**, 124—130).—These are independent, the voltaic being a surface and the thermal a vol. effect. A. B. D. C.

Crystal photo-effect. G. Mönch and R. Stühler (Z. Physik, 1934, **91**, 253—263; cf. A., 1933, 1230). A. B. D. C.

Crystal photo-effect. G. Mönch (Z. Physik, 1934, **91**, 264—271).—Theoretical. Classical and quantum-mechanical theories are discussed; Frenkel's theory (A., 1933, 1103) agrees best with absence of photo-effect in synthetic Cu_2O crystals.

A. B. D. C.

Behaviour of the normal cathode fall at the m.p. of the metal. A. Wehnelt and H. Kurzke (Ann. Physik, 1934, [v], **20**, 919—920).—Sn, Pb, and Hg in A were used. Sn and Pb show a sudden increase in the cathode fall at the m.p. For Hg there is a decrease. A. J. M.

High-voltage polarisation in crystals of saltpetre. H. M. Bryevich and B. M. Hochberg (J. Exp. Theor. Phys. U.S.S.R., 1933, **3**, 545—554).—The temp. dependence of the vol. charge from 30° to 74° and the effect of added $AgNO_3$ on the vals. have been measured. Ch. Abs. (*e*)

Electronic and lattice conduction of heat in metals. E. Grüneisen and H. Reddemann (Ann. Physik, 1934, [v], **20**, 843—877).—The thermal conductivity of Ag, Cu, Pd, and the alloys Au–Ag, Au–Cu, Cu–Pd, and Au–Pd was determined at −183°, −195°, and −255°. The rule of the linear isotherm, and Norbury's relationship, hold only up to a certain degree of lattice distortion, above which the heat-resistance increases more slowly than is indicated by the rule. The addition to another metal of metals which cause the same change of resistance does not alter the heat-resistance by the same amount. The results may be explained by assuming that the conductivity is made up of two parts, one being the electronic, the other the lattice, conduction, the latter being not so greatly affected by deformation of the lattice as the former. A. J. M.

Electrical conductivity of amber at different pressures. F. Seidl (Z. Physik, 1934, **91**, 318—322).—This conductivity was determined at atm., low and high vac. pressures. A. B. D. C.

Conductivity of compressed mercuric sulphate. W. Ścisłowski (Acta phys. polon., 1932, **1**, 457—463; Chem. Zentr., 1934, i, 515).—When $HgSO_4$ is pressed between a Zn and a Pt electrode a current passes more feebly in the direction $Zn \longrightarrow HgSO_4$ than in the reverse direction. A resistant layer forms near the Zn–$HgSO_4$ interface. H. J. E.

Electrical conductivity of semi-conductors. A. N. Arseneva and B. V. Kurchatov (J. Exp. Theor. Phys. U.S.S.R., 1933, **3**, 149—152).—The electrical conductivity of pure MoO_3 is $6{\cdot}1\times10^{13}$ ohm^{-1} cm.$^{-1}$ at room temp.; vals. increase rapidly with increase in concn. of Mo_2O_5. Farkas' theory is preferred to that of Wilson and Bronstein. Ch. Abs.

Elucidation of the form of zwitter ions by dielectric measurements. W. Kuhn and H. Martin (Ber., 1934, **67**, [*B*], 1526—1529).—Approx. calculation of the dipole moment of hexaglycylglycine leads to $3{\cdot}4\times10^{-18}$, which is too small to permit the conception that the mol. is rod-like (cf. Wyman *et al.*, A., 1933, 459). Reasons are advanced in favour of the view that measurements of the dielectric const. do not afford evidence in favour of a stiff, stretched form of the mols. of NH_2-acids. H. W.

Ionic polarisation in solid bodies. I. V. Kurchatov (J. Exp. Theor. Phys., U.S.S.R., 1933, **3**, 133—135).—Vals. of γ in Errera's formula and in $\gamma = \{[(\varepsilon-1)/(\varepsilon+2)] - [(n_0^2-1)/(n_0^2+2)]\}/[(\varepsilon-1)/(\varepsilon+2)]$, in which ε is the dielectric const. for a frequency $n_0=10^6$ hertz, are tabulated for LiF, NaF, KF, RbF, MgF_2, CaF_2, SrF_2, BaF_2, LiCl, NaCl, KCl, RbCl, LiBr, NaBr, KBr, RbBr, LiI, NaI, KI, and RbI. The former vals. are the less trustworthy. Ch. Abs.

Variation of the dielectric constant of Rochelle salt crystals with frequency and applied field strength. A. Zeleny and J. Valasek (Physical Rev., 1934, [ii], **46**, 450—453).—Measurements perpendicular to the *a* axis at 0° over the frequency range 30—30×10^6 cycles per sec. show uniform decline from 62,000 at 30 cycles to 220 at 10^7 cycles and an abrupt fall to negative vals. (inductive reactance) at 14×10^6 cycles, independently of the size and mounting of the crystal. N. M. B.

Polarity of chemical compounds. VII. K. Higasi (Bull. Inst. Phys. Chem. Res. Japan, 1934, **13**, 1167—1175).—Theoretical. Müller's rule for the influence of solvent on observed dipole moment (μ) disagrees with experiment with EtOH, $Bu^{\beta}OH$, $C_5H_{11}{\cdot}OH$, $C_{16}H_{33}{\cdot}OH$, α-$C_{10}H_7{\cdot}OH$, and NH_2Ph in polar and non-polar solvents. The influence of the solvent is correlated with the shape of the solute mol., and ε for the solvent. μ observed for mols. with small or negative Kerr consts. (K) should increase with increasing ε, but should decrease with increasing ε for mols. with large positive K. This explains the anomalies to Müller's rule. R. S. B.

Dielectric properties of acetylenic compounds. IV. Arylhalogenoacetylenes. Positive iodine. C. J. Wilson and H. H. Wenzke (J. Amer. Chem. Soc., 1934, **56**, 2025—2027; cf. this vol., 717).—The dipole moments of several arylhalogenoacetylenes (I) have been determined. The C to I moment has the + end towards the I atom; the C to Br moment and the C to Cl moment in (I) are < the corresponding moments in substituted C_6H_6. The Br and Cl are less negative than in derivatives of paraffins, ethylenes, or benzenes. E. S. H.

Effect of the solvent in dipole moment measurements: moment of ethylene bromide. M. A. G. Rau and B. N. Narayanaswamy (Proc. Indian Acad. Sci., 1934, **1**, 14—27).—Data for the polarisations of $C_2H_4Br_2$ in C_6H_6, PhMe, CCl_4, and *cyclo*hexane at infinite dilution and over the temp. range 10—40° are tabulated. The calc. moments vary widely with the solvent, and increase by about 0·08—10^{-18} e.s.u. over the temp. range. Potential energies between the rotating parts of the mol. are calc. N. M. B.

Index of refraction of water and its thermal history. V. K. La Mer and M. L. Miller (Physical Rev., 1933, [ii], **43**, 207—208).—No difference in the val. of n for H_2O dependent on thermal treatment has been detected. L. S. T.

Refractivity of cellulose and its derivatives. I. Influence of non-cellulosic impurities on refractivity of cellulose fibres. II. Influence of oxidation and hydrolysis on [refractivity of] cellulose fibres. K. Kanamaru (Helv. Chim. Acta, 1934, **17**, 1047—1066, 1066—1072).—I. Measurements of n_D, both parallel to (n_γ) and perpendicular to (n_α) the fibre axis have been made with ramie, hemp, jute, Manila hemp, straw, and bamboo fibres, at each stage of a process of purification consisting of extraction by EtOH, Et_2O, H_2O, and 1% NaOH, and of chlorination. Vals. of n_γ increase, and of n_α decrease, with purification, the latter converging to 1·524 at 21° for all varieties, whereas the former varies with the material. Purified hemp cellulose has $n_\gamma - n_\alpha$ 0·071. Measurement of the double refraction can be used as a criterion of purity for a given variety of cellulose fibre.

II. Oxy- and hydro-cellulose behave similarly to the above, in that with progressive degradation first n_γ, and later n_α, increases. Only the former reaches the val. characteristic of the cellulose micelle. This indicates that n_γ may depend on the configuration of the main chain, n_α being influenced by chemical changes in the side-chains. F. L. U.

Refractive dispersion of organic compounds. V. Oxygenated derivatives of *cyclo*hexane. Inadequacy of the Ketteler–Helmholtz equation. C. B. Allsopp. **VI. Refractivities of the oxygen, carbonyl, and carboxyl radicals. Origin of optical rotatory power and of the anomalous rotatory dispersion of aldehydes and ketones.** T. M. Lowry and C. B. Allsopp (Proc. Roy. Soc., 1934, **A**, **146**, 300—312, 313—326).—V. The refractive indices of C_6H_{11}·OH at 25° and of *cyclo*hexanone and C_6H_{11}·CO_2Et at 20° have been determined for 6708—2366 Å. It is found that, although the rotatory dispersion of optically active ketones is largely dominated by the ketonic absorption band, the contribution of this band to the refractive dispersion is extremely small. At wave-lengths covered by, or near to, the absorption bands, the Ketteler–Helmholtz equation is inadequate.

VI. Using the above data, vals. are deduced for the refractivities of the :O, :C:O, and ·CO·O radicals over the range 6708—2400 Å. :C:O exhibits an anomalous dispersion in the region covered by the absorption band with max. 2880 Å. :O also shows a slight anomaly, in a region of complete transparency. The refractivity of ·CO·O is of a normal type. The rotatory dispersion of *sec.*-BuOH can be accounted for by means of the term $R_A R_B R_C R_D/\lambda^2$, where R_A, R_B, R_C, R_D are the refractivities of the four radicals. The experimental vals. for the primary alcohols and for the *sec.* alcohols with branched chains are beyond the range of the formula, even when multiplied by Boys' factor $(\mu^2+2)(\mu^2+5)$. The origin of the anomalous rotatory dispersion of aldehydes and ketones is discussed. L. L. B.

Molecular refraction of crystallised organic compounds and its applicability to questions of constitution. A. Neuhaus (Ber., 1934, **67**, [*B*], 1627—1636).—From consideration of the different forms of the α-follicular hormone (I) it is shown that the refraction increments (Eisenlohr, von Auwers, *et al.*) for C, H, O, and the double linking deduced from org. liquids are valid in high degree for the cryst. condition. The empirical and constitutional formulæ of the (I) have thus been confirmed. Consideration of available data shows that the relationships and possibilities developed above are generally applicable to cryst. org. compounds containing C, H, and O or C, H, O, and N. Several homogeneous hydrocarbons present exceptions, obviously of an ordered type. The constitution of the hormones of the corpus luteum is discussed. H. W.

Remarkable properties of a doubly-refracting liquid. G. van Iterson (Proc. K. Akad. Wetensch. Amsterdam, 1934, **37**, 367—376).—Bands are observed when Cd phosphoglycerate (I) in presence of NaOAc in a capillary is viewed between crossed nicols. Other examples of double refraction with this gelatinous liquid, especially after mechanical agitation, have been studied. It is inferred that fibrils of (I) align themselves in the direction of flow of the liquid. R. S. B.

Surface of double refraction and fringes with certain crystalline plates. C. Gaudefroy (Compt. rend., 1934, **199**, 731—734).—Theoretical. The author's equation of double refraction is discussed. When the angle between the two optic axes of a crystal is 90° or nearly so, and a crystal plate cut parallel to these axes is placed perpendicular to the incident convergent beam, the whole field is uniformly lit. With parallel rays the retardation of the plate is const., whatever the inclination to the incident beam. Diaspore obeys these conditions. R. S. B.

Stereochemical structure. VII. Rotatory powers and racemisations of the optically active benzoins. R. Roger and A. McGregor (J.C.S., 1934, 1545—1550; cf. this vol., 476).—Rotatory powers of the optically active benzoins in (*a*) $COMe_2$, EtOH, $CHCl_3$, CS_2, CCl_4, dioxan, and (*b*) NH_2Ph, C_5H_5N, piperidine, $NHEt_2$, NEt_3, are given. The vals. in (*a*) satisfy the Rupe and Lowry–Dickson criteria. *D*-Benzoin is lævorotatory between λ 6563 and 4358 in group (*a*) solvents and in NH_2Ph and C_5H_5N, but dextrorotatory in the others. The rotatory powers are not directly ∝ to the dipole moment of the solvent. Vals. in $CHCl_3$ and dioxan decreased with rise of temp. It is suggested that the optically active benzoins contain a centre of fixed asymmetry (the mandelyl complex) and a centre of induced asymmetry (the PhCO group) the relative contributions of which to the optical rotation may be altered by the solvent. The influence of the material of the containing vessel, various solvents, and catalysts on the rate of racemisation has been studied. R. S.

Rotatory dispersion curves. II. Configuratively related substituted fatty acids. P. A. Levene and A. Rothen (J. Chem. Physics, 1934, 2, 681—688; cf. this vol., 12).—Rotatory dispersion curves of acids of the types $SH{\cdot}CHR{\cdot}CO_2H$ and $SO_3H{\cdot}CHR{\cdot}CO_2H$ and of their Na salts have been measured in the visible and ultra-violet regions. The results agree with the rule previously reported, that in members of homologous series the total rotation of consecutive members may differ in sign, but the signs of the partial rotations remain const. F. L. U.

Extent of the validity of the "rule of shift." P. A. Levene, A. Rothen, and G. M. Meyer (Science, 1934, **80**, 101—102).—Max. mol. rotations of correlated *p*-nitrophenyl esters of α-substituted AcOH and $EtCO_2H$ in the homogeneous state and in C_7H_{16} are recorded. The need for the exercise of caution in using the "rule of shift," which postulates that in configuratively related substances an identical substitution brings about a shift of rotation in the same direction, to correlate the configurations of substances the two-component partial rotations of which are of opposite sign is pointed out. L. S. T.

Effect of concentration, temperature, and wave-length of light on the Verdet constant of cerous chloride solutions. F. G. Slack, R. L. Reeves, and J. A. Peoples, jun. (Physical Rev., 1934, [ii], **46**, 724—727).—Data are tabulated for a concn. range up to almost saturated solution, for the temp. range 10—45°, and for wave-lengths 5893, 5461, and 4481 Å. Curves for the Verdet const. as a function of temp. and concn. are given. N. M. B.

Kerr effect in solutions. V. A. Joffe (Compt. rend. Acad. Sci. U.R.S.S., 1934, **3**, 491—496).—Vals. are recorded for $PhNO_2$ (up to 30%) in paraffin oil, C_6H_6, CCl_4, and C_7H_{16}. The mol. const. for $PhNO_2$ remains const. in each solvent up to a crit. concn., and then decreases, owing to association. H. J. E.

Dispersion of the electro-optical Kerr effect in carbon dioxide. G. G. Quarles (Physical Rev., 1934, [ii], **46**, 692—694).—Data for the range 4000—7500 Å. are given. The abs. val. of the Kerr const. *B* for CO_2 is $(0{\cdot}249 \pm 0{\cdot}003) \times 10^{-10}$ at 17·5°, 5890 Å., and 1 atm. pressure. N. M. B.

Magnetic circular dichroism of solutions of cuprammonium hydroxide and the corresponding salts (nitrate and sulphate). R. Cordonnier (Compt. rend., 1934, **199**, 667—668; cf. A., 1933, 765).—Data are tabulated. The effects ∝ mol. concns. H. J. E.

Dependence of polarisation on the strength of the electric field for seignetto-electrics outside the region of spontaneous orientation. I. V. Kurchatov (J. Exp. Theor. Phys., U.S.S.R., 1933, **3**, 181—188). Ch. Abs.

Physico-chemical test for mitogenetic (Gurwitsch) rays. M. Heinemann (Nature, 1934, **134**, 701).—The coagulation of unstable inorg. sols, *e.g.*, Au sol, is used to detect these rays. L. S. T.

Structure hypotheses for the heteropoly-compounds. A. Rosenheim [with E. Brauer and (Frl.) E. Materne] (Z. anorg. Chem., 1934, **220**, 73—95).—Recent work on poly- and heteropoly-anions indicates that there is no reason to discard the views on the structure of these anions based on Werner's co-ordination theory. M. S. B.

Stereochemistry of the free triarylmethyl radical. Total asymmetric synthesis. G. Karagunis and G. Drikos (Z. physikal. Chem., 1934, B, **26**, 428—438).—A more detailed account of an investigation, the principal results of which have been recorded (A., 1933, 1041). R. C.

Significance of chemical linking energies. C. T. Zahn (J. Chem. Physics, 1934, 2, 671—680).—A general theoretical discussion in which energies associated with linking interaction are taken into account. F. L. U.

Multiple linkings in organic substances. V. S. Gutiria (J. Gen. Chem. Russ., 1934, **4**, 408—419).—Theoretical. R. T.

Merkel diagram for secondary valency compounds and its technical application. H. Bräuer (Z. ges. Kälte Ind., 1933, **40**, 167—170; Chem. Zentr., 1934, i, 2326).—The relation between the heat content and concn. of the more volatile component is represented graphically. The method is illustrated for $CaCl_2,nNH_3$ (n=1, 2, 4, or 8) at 0·5—16 atm. Technical applications are discussed. H. J. E.

Vibrations of tetrahedral pentatomic molecules. III. Comparison with experimental data. IV. Isotopic shifts. (Miss) J. E. Rosenthal (Physical Rev., 1934, [ii], **46**, 730—733; cf. A., 1934, 719).—III. From data for 9 mols. of the type XY_4 the vibrations may be explained on the basis of valency forces only in the case of CH_4; for the others an additional repulsive force must be postulated.

IV. Certain relations between the frequencies of the isotopic mols. are independent of the vals. of the force consts. N. M. B.

Diamagnetism of organic liquid mixtures at different temperatures. S. R. Rao and P. S. Varadachari (Proc. Indian Acad. Sci., 1934, **1**, 77—97).—The vals. of χ for C_6H_6–, $CHCl_3$–, and $PhNO_2$–$COMe_2$ mixtures at 15—50°, as measured by the Quincke method with intense magnetic fields, obey the additivity law. χ for the pure liquids shows no variation between 15° and 50°. It is concluded that association produces no change in the sp. susceptibility of org. liquids, and that the additive law holds unless chemical combination occurs. J. W. S.

Paramagnetic saturation in a single crystal. W. J. de Haas, J. van den Handel, and C. J. Gorter (Physical Rev., 1933, [ii], **43**, 81).—The magnetisation of a mono-axial single crystal of Dy Et sulphate has been determined as a function of temp. and field strength in the directions of the optical axis and a secondary axis perpendicular to it. L. S. T.

Dependence of the magnetic susceptibility of water and potassium iodide solutions on temperature. G. Tammann (Z. Physik, 1934, **91**, 410—412).—Cabrera and Fahlenbrach's results (cf. this vol., 841) are explained by variation of the mol. aggregation of H_2O with temp. A. B. D. C.

Magnetochemical investigations. X. Manganous chalcogenides. H. Haraldsen and W. Klemm. **XI. Magnetic behaviour of some rhenium compounds.** W. Schüth and W. Klemm (Z. anorg. Chem., 1934, **220**, 183—192, 193—198).—X. Magnetic susceptibilities of MnO, MnS, MnSe, and MnTe have been determined between 90° and 728° abs. and the effective magneton nos., $\mu_{\text{eff.}}$, calc. $\mu_{\text{eff.}}$ increases with rise of temp. and approaches the val. for aq. Mn^{II} salts or for salt hydrates. The vals. for the different compounds vary in the order MnSe>MnS>MnO>MnTe, which is unexpected, since the metallic character increases in order of increasing mol. wt. from MnO to MnTe. It is suggested that the behaviour is due, not to the interaction of cation and anion only, but also to the influence of the cations on one another.

XI. Compounds of Re^{VII} have a very slight paramagnetism varying with temp. The metallic character of the compounds ReO_3, ReO_2, and ReS_2 practically suppresses the ionic paramagnetism, whilst in the trihalides the absence of paramagnetism is probably due to the formation of larger mols. At higher temp. $\mu_{\text{eff.}}$ for $ReOCl_4$, $ReCl_5$, and the complex halogen compounds of Re^{IV} approximates to the val. to be expected if the magnetism is due to electronic spin only. At room temp. and at low temp., however, the magnetism is < this val. M. S. B.

Magneto-chemical characteristics of the oxides of nickel. S. S. Bhatnagar and G. S. Bal (J. Indian Chem. Soc., 1934, **11**, 603—616).—Pure NiO is green; black samples owe their colour, in part, to adsorbed O. Magnetic susceptibility determinations at 25—366° show that the high vals. recorded in the lit. are due to traces of Ni formed by reduction during the prep. of the NiO. The val. of χ for NiO is $9{\cdot}56\times10^{-6}$. The existence of other Ni oxides was not confirmed. J. G. A. G.

Classical model of ferromagnetism and its additional quantising at low temperatures. G. Heller and H. A. Kramers (Proc. K. Akad. Wetensch. Amsterdam, 1934, **37**, 378—385).—Theoretical. Quantising the classical model leads to the theory of Bloch and Møller. R. S. B.

Discussion on energy distribution in molecules in relation to chemical reactions. (Proc. Roy. Soc., 1934, A, **146**, 239—271).—C. N. Hinshelwood. Attention was directed to the independent modes of activation of the mols. taking part in a reaction. Sp. linkings in a compound undergoing decomp. may be activated to a high vibrational level. Experiments support the hypothesis that mols. with activation energy differently located may behave as virtually independent entities kinetically; in a mol. like CH_2O the chance that the activation energy is communicated to the mol. so as to cause rapid decomp. is relatively > in a substituted mol. such as EtCHO. Bimol. reactions in solution where the observed rate is nearly equal to the rate of encounter of the appropriate activated mols., and reactions of the same order where the reaction velocity is many powers of ten < the activation rate, were discussed.

J. E. Lennard-Jones discussed the problem with reference to the electronic structure of mols. and electronic orbitals.

M. W. Travers criticised previous results obtained by Hinshelwood and Hutchinson on the pyrolysis of MeCHO (A., 1926, 804). Investigation by a different experimental method leads to other conclusions.

M. Polanyi discussed the accumulation of energy in a mol. and its transfer into elongation of a certain linking.

C. Zener dealt with the factors which may greatly reduce the probability that a mol. should dissociate following collision with a second mol., if the combined energies of the two mols. are sufficient for this dissociation.

E. J. Bowen directed attention to the difficulty of satisfactory chemical analysis in the experimental investigation of this subject.

R. G. W. Norrish emphasised the importance of investigating every possible photochemical and spectroscopic aspect of this problem: the absorption spectrum, fluorescence, products of decomp., and the quantum yield at different wave-lengths. The photochemical decomp. of certain aldehydes and ketones was discussed.

H. W. Thompson spoke on the correlation of certain spectroscopic results with the corresponding photochemical data. The conditions for the occurrence of a dissociation process were discussed. The absorption spectra of several metal-alkyl compounds and compounds containing the chromophoric group SO_2 were considered.

C. J. M. Fletcher described the experimental results supporting the hypothesis of the association of the energy of activation with different parts of the mol., for the different activated states which exist for the aldehydes.

E. K. Rideal directed attention to the connexion between the no. of squared terms (S) involved in a reaction and E, the energy of activation, and showed how these magnitudes could be correlated with constitutional factors. The effect of increasing chain length in a series of compounds containing a const. end-reacting group on the relation between E and S was described.

A. R. Ubbelohde discussed the physical tests used to check the chemical equations. L. L. B.

Molecular rotation in ice at 10° abs. Free energy of formation and entropy of water. W. F.

Giauque and M. F. Ashley (Physical Rev., 1933, [ii], **43**, 81—82).—Preliminary vals. calc. are $H_2+0\cdot5O_2=H_2O(g)$, $\Delta F_{298\cdot1}-54,670$ g.-cal. per mol.; $H_2+0\cdot5O_2=H_2O(l)$, $\Delta F_{298\cdot1}-56,720$; $H_2O(g)$, $S_{298\cdot1}$ 45·17 (abs. 47·92) g.-cal. per degree per mol.; and $H_2O(l)$ $S_{298\cdot1}$ 16·9. A comparison of vals. indicates a lack of equilibrium between *o*- and *p*-H_2O in ice, and rotation of *o*-H_2O in ice. L. S. T.

Budde effect in halogens. T. S. Narayana (Indian J. Physics, 1934, **9**, 91—109).—The effect was absent in pure super-dried Cl_2; it was observed in moist Cl_2 and Br, but decreased with drying; it was absent in Cl_2 and Br above 500 and 550 mμ, respectively. The effect was shown by dry Cl_2 when heat losses from the walls of the Pyrex bulb were arrested, and by dry air–halogen mixtures. The effect ∝ pressure and the square root of light intensity. Theories are reviewed and a mechanism is proposed. N. M. B.

Effect of temperature on the rotational heat of methane. R. Renner (Physikal. Z., 1934, **35**, 811—814).—Theoretical. A. J. M.

Intramolecular forces in octahedral models, particularly sulphur hexafluoride, on the basis of normal frequencies. A. Eucken and F. Sauter (Z. physikal. Chem., 1934, **B**, **26**, 463—472).—Theoretical. From the observed normal frequencies of SF_6 (this vol., 1055) and a calculation of the normal frequencies of an octahedral model, an attempt has been made to determine the nature of the intramol. forces in SF_6. As a first approximation, the intramol. force system may be regarded as a combination of a Coulomb central force system with an angular force system. In so far as the intramol. forces can be regarded at all as central forces, they behave in respect of sign and magnitude like Coulomb forces effective between the centres of the atoms, considered fully ionised. R. C.

Rotational wave equation of tetramethylmethane for zero potential and a generalisation. L. J. B. La Coste (Physical Rev., 1934, [ii], **46**, 718—724).—Mathematical. The exact solution is similar to that for the rigid spherical top. N. M. B.

Determination of parachor in solution. I. S. K. Ray (J. Indian Chem. Soc., 1934, **11**, 671—679).—The surface tension and *d* of solvent and solution have been determined in the systems $C_{10}H_8$–C_6H_6, –CCl_4, –$CHCl_3$, α-$C_{10}H_7\cdot OH$–C_5H_5N, –EtOAc, coumarin–C_6H_6, –$CHCl_3$, –C_5H_5N, 8-hydroxyquinoline–C_6H_6, –CCl_4, xanthone–$CHCl_3$, –C_5H_5N, phenanthrene–C_6H_6, –CCl_4, –$COMe_2$, anthracene–$PhNO_2$, dithiolthiodiazole–EtOH, and the parachors of the solutes have been calc. on the assumption that they obey the straight-line mixture law. E. S. H.

Parachor of benzyl alkyl ethers. T. C. Huang and K. P. Sung (Sci. Rep. Nat. Tsing Hua Univ., 1934, **2**, 303—306).—The parachors of benzyl Me, Et, Pr^a, Pr^β, Bu^a, Bu^β, and *iso*amyl ethers have been determined and appear to be normal. H. N. R.

Molecular organic compounds. V. Parachors of the phenol–amines in solution. C. A. Buehler and E. H. Spreen (J. Amer. Chem. Soc., 1934, **56**, 2061—2062; cf. A., 1932, 841).—The parachors of the 1 : 1-compounds (f.p. quoted after base) of PhOH with NH_2Ph, 30·4° (corr.), *o*-$C_6H_4Me\cdot NH_2$, 34·7° (corr.), *m*-$C_6H_4Me\cdot NH_2$, −3·5±0·5°, and *p*-$C_6H_4Me\cdot NH_2$, 28·8° (corr.), determined (method: Hammick and Andrew, A., 1929, 638) in solutions of either component, are const. for a given temp., but increase with rise in temp. (cf. *loc. cit.*). Mol. wt. determinations (in PhOH) indicate that the compounds are generally undissociated. H. B.

Theory of liquids. II. T. S. Wheeler (Proc. Indian Acad. Sci., 1934, **1**, 105—114; cf. this vol., 1159).—Formulæ are deduced relating the attractive force coeff. to the parachor and giving the force between mols. at the distance of closest approach. Expressions for surface tension and internal latent heat of vaporisation are developed to include attractive and repulsive forces, and the force consts. calc., from the equations of state of certain gases by the Lennard-Jones method applied to these formulæ. J. W. S.

Variation of refractive index for *X*-rays with angle of incidence. F. Jentzsch (Z. Physik, 1934, **91**, 151—166; cf. this vol., 125).—Data are given for glass. A. B. D. C.

Effect of pressure on the intensity of *X*-rays scattered from nitrogen at small angles. G. G. Harvey (Physical Rev., 1934, [ii], **46**, 441—445).—Scattering curves at 60, 80, and 100 atm. resemble those for a solid or liquid, and this is due to the closeness of the scattering centres. At small angles the scattering from a "permanent" gas diminishes owing to intermol. interference. N. M. B.

Absorption spectrum of *X*-rays. S. Aoyama and T. Fukuroi (Sci. Rep. Tôhoku, 1934, **23**, 405—418).—No difference could be detected in the *X*-ray absorption spectra of α-K_2RuCl_5 and α-K_2RuCl_5,H_2O, but marked difference was observed between β-K_2RuCl_5 and β-$K_2Ru(H_2O)Cl_5$. This is attributed to the co-ordination of the H_2O to the Ru in the β-salt, but not in the α-salt. Differences can be observed between the Debye–Scherrer photographs of the α- and β-salts, but not between those of the β- and γ-salts. The latter also give the same absorption spectra. J. W. S.

Crystallite orientation in a polycrystalline metal during plastic flow. R. E. Gibbs and N. Ramlal (Phil. Mag., 1934, [vii], **18**, 949—956).—*X*-Ray measurements on Cd wire show that, when a polycryst. metal flows, the β-flow, which gradually diminishes with time, is connected with a rotation of the axes of the crystallite, thus confirming the conclusions of Andrade *et al.* (A., 1933, 14). M. S. B.

Complete *X*-ray diagram of fibre structures. K. Hutino (Bull. Inst. Phys. Chem. Res. Japan, 1934, **13**, 1187—1197).—Intensity distributions are treated theoretically for various planes of the Debye–Scherrer sphere. R. S. B.

Obtaining monocrystals with a given axial orientation. P. A. Polibin and A. I. Freuman (J. Exp. Theor. Phys., U.S.S.R., 1933, **3**, 162—164).—Bridgman's method was applied to Zn, Cd, and Sn. Ch. Abs.

Suggested form of crystallographic presentation. M. A. Peacock (Amer. J. Sci., 1934, [v],

28, 241—254).—The two-circle presentation is combined with an improved conventional presentation.
C. W. G.

Change in the properties of (I) deformed polymorphic crystals, (II) monocrystals, when subjected to a period of rest. M. O. Kornfeld (J. Exp. Theor. Phys. U.S.S.R., 1933, 3, 563—566, 567—570).—I. Rest does not restore completely the properties of deformed polycryst. Al. Laue photographs show overlapping of the grain boundaries (I). During rest changes occur at (I).

II. Data are recorded for the relative limits of fluidity before and after rest for deformed mono- and poly-crystals.
Ch. Abs. (*e*)

Complexity of the solid state. A. Smits and N. F. Moerman (Nature, 1934, **134**, 698—699).—Irradiation by *X*-rays accelerates the establishment of the inner equilibrium in SO_3. The v.p.–time of irradiation curve increases linearly to a const. val. at 76·0 mm. after 598 min. at 24·8°. The thermal reaction taking place is different from the reaction produced by *X*-rays, which is of zero order. *X*-Rays appear to split up polymerised mols. in the solid phase.
L. S. T.

Distortion of the crystal lattice of α-brass. W. A. Wood (Nature, 1934, **134**, 572).—*X*-Ray spectra of cold-rolled α-brass show that deformation of the alloy is accompanied by changes in the average size and shape of the unit cell, and in the latent energy of the crystal lattice.
L. S. T.

Absorption of *X*-rays and chemical linkings. A. Soltan (Acta phys. polon., 1932, 1, 317—326; Chem Zentr., 1934, i, 1609).—Absorption measurements on H_2O and gaseous or liquid O_2 showed no deviation from the additive law attributable to an effect of chemical linking.
H. J. E.

Inertness and chemical activity of the rare gases. IV. Differences in the properties of the platinum–helium compound and pure platinum: action of aqua regia on both substances. V. *X*-Ray spectrogram of the cathodic deposit of the platinum–helium compound with excess of platinum. H. Damianovich (An. Inst. Invest. cient. tech., 1931, 2, 15—23, 24—32; Chem. Zentr., 1934, i, 2543—2544).—IV. The solubility of the Pt–He compound in dil. aqua regia increases with the He content. With 20 c.c. of He per g. of Pt the material is 74% sol. The insol. residue is different from the He-containing material. A definite compound is probably formed.

V. *X*-Ray photographs for the Pt–He compound show a ring characteristic of amorphous material. It disappears after heating. Colloidal PtS_2 or Bi_2S_3 give a similar ring.
H. J. E.

Crystal structure of Tl_7Sb_2. F. R. Morral and A. Westgren (Svensk Kem. Tidskr., 1934, **46**, 153—156).—A slight distortion of the previously proposed structure leads to a much better agreement with the intensities of the powder photograms. Each Sb atom is surrounded by four Tl atoms distant 3·10 Å., one distant 3·38 Å., and four distant 3·48 Å. R. P. B.

Crystal structure of copper sulphate pentahydrate. C. A. Beevers and H. Lipson (Proc. Roy. Soc., 1934, A, **146**, 570—582).—$CuSO_4,5H_2O$ has *a* 6·12, *b* 10·7, *c* 5·97 Å., 2 mols. per unit cell. The Cu atoms lie on the special positions (000) and ($\frac{1}{2}\frac{1}{2}0$), and the S on the general position (0·01, 0·29, 0·64). Four of the H_2O mols. are arranged in squares around the Cu atoms, and the 2 O make approx. octahedra with these. The fifth O is not co-ordinated, but is in contact with 2 O atoms and 2 H_2O mols. All the H_2O mols. show 2 O linkings each, in agreement with the theory proposed by Bernal and Fowler (A., 1933, 1106). The cryst. structure of $CuSO_4,5H_2O$ explains the existence of the three successive stages of dehydration.
L. L. B.

Filiform sulphur and its structure. K. H. Meyer and Y. Go (Helv. Chim. Acta, 1934, **17**, 1081—1093).—If a thread of plastic S is repeatedly stretched to 12—15 times its initial length it becomes microcryst. and no longer contracts. The resulting filiform S is found by *X*-ray analysis to have an elementary cell with *a* 26·4±0·1, *b* 9·26±0·05, *c* 12·32±0·05 Å., β 79° 15′, space-group C_{2h}^2, containing 112 atoms. Filiform S retains its structure up to 50°, above which it becomes non-cryst. and contracts to 1/10 of its initial length. Both *X*-rays and light convert it rapidly into rhombic S. The analogy between the physical properties of S and rubber is noted.
F. L. U.

***X*-Ray study of a long *X*-cut quartz crystal vibrating under the transverse piezoelectric effect.** M. Y. Colby and S. Harris (Physical Rev., 1934, [ii], 46, 445—450; cf. A., 1933, 557).—Analysis of Mo *Kα* reflexion for the crystal non-oscillating, oscillating at its fundamental frequency under the transverse piezoelectric effect, and oscillating at its second harmonic frequency shows that there is no elastic deformation of the spacing of the (110) planes $> 1{\cdot}45 \times 10^{-5}$ per unit dimension, and that any increase in intensity of reflected *X*-rays produced by piezoelectric oscillations of the crystal is due to a reduction of secondary extinction.
N. M. B.

Crystal structure of thallium cyanide. M. Strada (Atti R. Accad. Lincei, 1934, [vi], 19, 809—811).—TlCN is body-centred cubic. If the CN group is considered as a single entity the unit cell contains 1 mol. with *a* 3·82 Å., but if the C and N are assumed to occupy distinct positions in the lattice the unit cell then contains 8 mols. with *a* 7·64 Å. The CN′ ion has an apparent radius 1·81 Å.
O. J. W.

Structure of heteropoly-acids. R. Signer and H. Gross (Helv. Chim. Acta, 1934, **17**, 1076—1080).—12-Silico-, 12-boro-, and meta-tungstic acids are shown by powder diagrams to have the same structure as 12-phosphotungstic acid (this vol., 479). Both the pentahydrates and higher hydrates were examined. The chemical properties are shown to be simply related to the structure in each case.
F. L. U.

Crystal structure of some phosphates and arsenates of tervalent metals. I. Phosphate and arsenate of aluminium. M. Strada. **II. Arsenate and phosphate of yttrium.** M. Strada and G. Schwendimann (Gazzetta, 1934, **64**, 653—662, 662—674).—I. $AlPO_4$ and $AlAsO_4$ have a tetragonal structure of the SiO_2 type, space-group S_4^2, with *a* 4·85±0·005, 4·90±0·005, *c* 6·60, 6·64 Å., *c*/*a* 1·362, 1·355, respectively, and 2 mols. per unit cell. The P and As atoms have an S_4, and the O atoms a C_1, symmetry. The calc. radius of the As^{5+} ion is 0·518 Å.; the distances Al–O, P–O, and As–O are 1·91, 1·80, and 1·878 Å., respectively.

II. *Anhyd.* $YAsO_4$ was prepared by heating to 500° the dihydrate obtained by pptg. a solution of the nitrate with Na_2HAsO_4. It belongs to the tetragonal system, space-group D_{4h}^{19}, 4 mols. per unit cell, *a* 6·890, *c* 6·269 Å., d_{calc} 5·053, $d_{obs.}^{20}$ 4·561. YPO_4 has the same structure as xenotime, with *a* 6·862, *c* 6·174 Å., $d_{calc.}$ 4·174, $d_{obs.}$ 3·785. The following ionic radii have been calc.: Y 1·027, O 1·216, As^{5+} 0·521, P^{5+} 0·422, AsO_4 1·738, PO_4 1·638 Å. O. J. W.

X-Ray analysis of the structure of dibenzyl. J. DHAR (Indian J. Physics, 1934, 9, 1—20; cf. this vol., 948).—The C_6 rings have a plane hexagonal structure, and lie in parallel planes separated by about 0·23 Å. Full data and discussions are given. N. M. B.

X-Ray analysis of the crystal structure of dibenzyl. I. Experimental and structure by trial. J. M. ROBERTSON (Proc. Roy. Soc., 1934, A, **146**, 473—482).—$[CH_2Ph]_2$ has *a* 12·77, *b* 6·12, *c* 7·70 Å., β 116°; space-group C_{2h}^5 ($P\,2_1/a$), 2 mols. per unit cell, each possessing a centre of symmetry. Quant. intensity measurements have been made of the reflexions from about 100 crystal faces. The mol. extends in 3 dimensions, instead of being planar as in the aromatic compounds previously examined. The planes of the C_6 rings, although parallel, are at right angles to the plane containing the zig-zag of the connecting CH_2 groups. L. L. B.

Shape of the dibenzyl molecule. J. M. ROBERTSON (Nature, 1934, **134**, 381).—A double Fourier analysis confirms previous views (see above) as opposed to those of Dhar (this vol., 948). L. S. T.

Determination of the atomic positions in *p*-dinitrobenzene by the Fourier analysis method. K. BANERJEE (Phil. Mag., 1934, [vii], **18**, 1004—1008).—*X*-Ray measurements have been made on crystals of $p\text{-}C_6H_4(NO_2)_2$. Structure factors for the different planes have been calc. on certain assumptions and compared with the observed structure factors. A rough agreement has been observed. The planes of the NO_2 groups are inclined to the plane of the C_6 ring. M. S. B.

X-Ray studies on choleic acids. Y. GO and O. KRATKY (Z. physikal. Chem., 1934, B, **26**, 439—452).—Of a no. of compounds of deoxycholic acid (I) with fatty acids, almost all give the same *X*-ray diagram, indicating the presence of the same basic lattice, composed of (I) mols., in each. Apparently the fatty acid mols. are arranged one behind another, forming canals extending through the basic lattice. Choleic acids containing EtOH of crystallisation have also been obtained. R. C.

X-Ray crystallographic measurements on derivatives of cardiac aglucones.—See this vol., 1354.

X-Ray diagram of ring-thread structure and orientation of micelles in films. I. SAKURADA and K. HUTINO (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, **24**, 193—210). A. J. M.

Cybotactic condition in the region of the critical point. I. Ethyl ether. R. D. SPANGLER. **II. *iso*Pentane.** C. A. BENZ and G. W. STEWART (Physical Rev., 1934, [ii], **46**, 698—703, 703—706).—I. *X*-Ray diffraction–ionisation curves are given for 37 combinations of vals. of pressure, temp., and sp. vol. in the neighbourhood of the crit. point. Results, interpreted on the cybotactic theory, show that groups are very sensitive to changes in sp. vol., but show less dependence on temp. and pressure; that groups disappear at approx. the same sp. vol. at various temp. and pressures; that groups may appear in the gaseous state, and that beyond a certain sp. vol. no groups appear and the curves are of the gas type.

II. Curves for *iso*pentane, obtained similarly to the above, show that the sp. vol. is unique in determining the extent of cybotactic groups; the sp. vol. at which these groups disappear is 90% > the crit. vol.; above the crit. pressure the formation of groups increases with decrease in sp. vol.; the internal description of liquefaction above the crit. pressure, passing from gas to liquid, is the same for Et_2O and *iso*pentane. N. M. B.

Explosive antimony. I. Microscopy of polished surfaces. C. C. COFFIN and S. JOHNSTON (Proc. Roy. Soc., 1934, A, **146**, 564—570).—Details are given of the microscopical examination of polished surfaces of explosive Sb, before and after explosion. L. L. B.

Molecular structure as determined by a new electron diffraction method. I. Experimental. II. Halogen–carbon linking distance in some simple benzene derivatives. H. DE LASZLO (Proc. Roy. Soc., 1934, A, **146**, 672—689, 690—700).—I. An apparatus is described for obtaining photographic records of the scattering of fast electron beams by the vapour of any substance which will vaporise in a vac. up to 1000° without decomp. It is possible to record many more interference max. than were previously observed; these new high-order max. are particularly sensitive to changes in chemical structure, hence making possible more accurate determinations of inter-at. distances and mol. spatial configurations.

II. The electron diffractions of C_6Cl_6, C_6Br_6, $s\text{-}C_6H_3Br_3$, $s\text{-}C_6H_3I_3$, $p\text{-}C_6H_4Br_2$, and $p\text{-}C_6H_4I_2$ have been measured. The results agree with the theoretical scattering curves based on a model of C_6H_6 as a regular flat hexagonal ring with C–C distance 1·41 Å. The halogen–C distances are C–Cl $1·69\pm0·01$, C–Br $1·88\pm0·01$, C–I $2·05\pm0·01$ Å. These distances are independent of the no. of similar atoms substituted at the same time in the C_6H_6 ring, and all the atoms lie in the plane of the ring. The C–halogen distances are about 0·06 Å. < those generally accepted for aliphatic compounds. L. L. B.

Structure of carbon. Investigation by electron diffraction. F. TRENDELENBURG [with E. FRANZ and O. WIELAND] (Z. tech. Physik, 1933, **14**, 489—495; Helv. phys. Acta, 1933, **6**, 477—478; Chem. Zentr., 1934, i, 2249).—Specimens of graphite (I) and soot gave results characteristic of the (I) lattice. Intensity variations with crystal size were studied. H. J. E.

Electron diffraction investigations of the aluminium silicates and other substances of the layer lattice type. F. Trendelenburg and O. Wieland (Wiss. Veröff. Siemens-Konz., 1934, **13**, No. 3, 31—41).—A comparison of *X*-ray and electron diffraction photographs of kaolin, pholerite, pyrophyllite, agalmatolite, talc, $Mg(OH)_2$, and PbI_2 shows, as with graphite, a difference in the intensities in the lines corresponding with the same indices in the photographs taken with the two types of rays. This intensity variation depends on the condition of the surface. Surfaces which are parallel to the cleavage planes are smooth towards electrons, and intense, sharp interferences are not found. Crystals which show good cleavage (*e.g.*, calcite), and those which have no decided cleavage (*e.g.*, quartz), show little or no difference in the intensities of the electron and *X*-ray interference. A. J. M.

New method of investigating the diffraction of slow electrons by crystals. W. Ehrenberg (Phil. Mag., 1934, [vii], **18**, 878—901).—A rapid visual method, requiring the use of a fluorescent screen, for determining the scattering of slow electrons by a crystal, is described. The results obtained with a Cu crystal are compared with those obtained by Farnsworth (A., 1933, 761). M. S. B.

New method for determining electron diffraction patterns produced by thin films. W. Cochrane (Phil. Mag., 1934, [vii], **18**, 956—970).—Instead of using the photographic method, small parts of the diffracted electron beam were allowed to pass successively into a Faraday cylinder and were measured with an electrometer. Films of celluloid, Au, Al, and Ag were used and the experimental vals. for the intensities of the diffracted rays were found to agree with those given by Born's theory. Methods for the prep. of the very thin films used are described. M. S. B.

Drift of magnetic permeability at low inductions after demagnetisation. R. L. Sanford (J. Res. Nat. Bur. Stand., 1934, **13**, 371—376).—To obtain consistent results a period of 18—24 hr. should elapse after demagnetisation before the test is made. E. S. H.

Magnetisation of the permanent oxide magnet at high temperatures. Y. Kato, T. Takei, N. Kawai, and H. Aikawa (J. Chem. Soc. Japan, 1934, **55**, 584—589).—$CoO–Fe_2O_3$ and the solid solution of $CoO–Fe_2O_3$ and Fe_3O_4 are more strongly magnetised at 300° than at room temp. Ch. Abs. (*e*)

Structural demagnetising field of ferromagnetics. T. Kahan (J. Phys. Radium, 1934, [vii], **5**, 463—470).—A new method for investigating the structural demagnetising factor is described. Applied to the thermal variation of the factor for specimens of Ni and Co marked decrease in the factor with rise of temp. is found, thereby confirming the existence of the factor, since the geometrical demagnetisation factor is independent of temp. N. M. B.

Magnetic Hall effect in crystalline media. M. Kohler (Ann. Physik, 1934, [v], **20**, 878—890).—Theoretical. The compatibility of the dependence of the magnetic Hall effect on the crystallographic orientation of the crystal used with the symmetry of the crystal is examined. A. J. M.

Magnetic resistance changes in crystalline media. M. Kohler (Ann. Physik, 1934, [v], **20**, 890—908).—Theoretical. Assuming that the resistance change (I) $\propto$ the square of the field strength, the dependence of (I) on the crystallographic orientation of the current and the magnetic field is investigated. A. J. M.

Magneto-caloric effect and other magnetic phenomena in iron. H. H. Potter (Proc. Roy. Soc., 1934, A, **146**, 362—387).—The magneto-caloric effect and other magnetic phenomena in Fe have been studied in the region of the Curie point. The results demand that the intramol. field factor N is independent of σ, but shows a rapid increase with increasing T near the Curie temp. The Weiss magneton nos. of Ni and Fe in the paramagnetic state are discussed. L. L. B.

Large Barkhausen discontinuities and their propagation in Ni–Fe alloys. II. R. E. Reinhart (Physical Rev., 1934, [ii], **46**, 483—486; cf. this vol., 588).—Relationships between longitudinal field, intensity of magnetisation, and velocity of propagation were investigated. The behaviour of propagation phenomena for pure Ni is the reverse of that for 10% Ni–Fe alloy, the difference being related probably to differences in magnetostrictive properties. N. M. B.

Anomalous case of magnetic viscosity. A. V. Mitkevitsch (Compt. rend. Acad. Sci. U.R.S.S., 1934, **3**, 426—431).—Data are recorded. The relation between magnetic viscosity and lag due to eddy currents is discussed. H. J. E.

Electric strength of rock-salt exposed to *X*-rays. A. Vorobev (Compt. rend. Acad. Sci. U.R.S.S., 1934, **3**, 424—425).—Resistance to sparking through the crystal was lowered 30—40% during exposure to *X*-rays, indicating that electrons are important in the sparking mechanism. H. J. E.

Optical constants of polished and sputtered molybdenum surfaces. R. D. Summers (J. Opt. Soc. Amer., 1934, **24**, 261—263).—The refractive index, index of absorption, and reflectivity of opaque films of Mo, sputtered in air and in H_2, as measured by Drude's method at λλ 5780, 5460, and 4360 Å., vary with the conditions of sputtering and are $\ll$ for the metal in mass. The optical consts. for massive Mo polished under kerosene are the same as for the metal polished in air. The low vals. for sputtered films are attributed to lattice distension by occluded gas. J. W. S.

Optical constants of thin metal films in the long-wave infra-red. W. Woltersdorff (Z. Physik, 1934, **91**, 230—252).—Reflexion and transmission curves are given for Al, Ag, Sb, and Bi between 21 and 91 μ. A. B. D. C.

Effect of temperature on the reflectivity of copper, silver, and gold. Y. Fujioka and T. Wada (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, **25**, 9—19).—The reflectivities (r) of Cu, Ag, and Au have been measured for λ 2500—6500 Å. at

—180°, 0°, and 100°. r for Ag agrees with the val. calc. from dispersion theory. R. S. B.

Total radiation of iron in the region of temper colours. R. Hase (Arch. Eisenhüttenw., 1934—1935, 8, 93—96).—The emissivity (E) of clean Fe remains const. below 300° in spite of the formation of a dark-coloured film on the surface, and then increases rapidly with increasing oxidation to a const. max. at 450° and higher, E being then 80—90% of black-body radiation. Above 1400° the oxide film goes into solid solution in the Fe, and E then falls, since the surface becomes clean again. The oxide film in the region of temper colours has an effect on E when it exceeds 0·5 μ in thickness. A. R. P.

Oscillation energy of particles in a crystal lattice. S. Franchetti (R. Ist. lombardo Sci. Lett. Rend., 1933, [ii], 66, 731—742; Chem. Zentr., 1934, i, 2249).—Theoretical. H. J. E.

Metallic binding. H. Bomke (Z. Physik, 1934, **91**, 400—409).—Binding forces between metal atoms, liquid or solid, are electrostatic; a positive ionic lattice with distributed electron cloud gives a min. potential for the crystal, and gives the heat of sublimation in terms of the lattice energy. On this scheme, metals fall into two groups. A. B. D. C.

Plasticity and mosaic structure of cast and recrystallised metals. U. Dehlinger and F. Gisen (Physikal. Z., 1934, **35**, 862—864).—The mosaic structure of Al is often as stable in the pure metal as in the impure. Recryst. Al shows stronger mosaic structure than the cast metal. The results of this and previous work (this vol., 16) are summarised. A. J. M.

Elastic constants of single crystals of iron. R. Kimura and K. Ohno (Sci. Rep. Tôhoku, 1934, **23**, 359—364).—The results are not in agreement with Cauchy's relation. The compressibility calc. is in fairly good agreement with Bridgman's experimental val. J. W. S.

Photo-electric determination of the elastic limit of rock-salt crystals. M. N. Podaschevski (Z. Physik, 1934, **91**, 97—104).—Sensitivity of the primary internal photo-electric current of X-irradiated NaCl to plastic deformation is used to determine the elastic limit. A. B. D. C.

Effect of salt on the hardness of rock-salt crystals. V. D. Kuznetzov and A. A. Borobeva (J. Exp. Theor. Phys. U.S.S.R., 1933, 3, 555—562).—Hardness determinations are recorded for NaCl, dry, and after wetting with saturated aq. NaCl (I) or (I)+AcOH. H_2O alters the hardness of tempered, but not of untempered, crystals. Ch. Abs. (e)

Torsional modulus of nickel at high temperatures with simultaneous magnetisation. II. W. Möbius (Physikal. Z., 1934, **35**, 806—811; cf. A., 1932, 683).—At field strengths about 20—30 gauss there are min. in the isotherms of the torsional modulus, for all temp. almost up to the Curie point. Probably the orientation of elementary circuits caused by the field is partly destroyed by the torsion of the wire; vibrational energy being used up in this way, the modulus thus becomes smaller. A. J. M.

Allotropy of liquid benzene. H. W. Deinum (Rec. trav. chim., 1934, **53**, 1061—1063).—The conclusions of Menzies and Lacoss (A., 1932, 452) are criticised. A formula for the v.p. of C_6H_6 between 0° and 100° is given. F. L. U.

Little-known properties of metals. E. Raub (Mitt. Forsch. Probieramts. Edelmetall. Schwäb-Gmünd, 1933, 7, 51—64; Chem. Zentr., 1934, i, 1601—1602).—I. The toxic and bactericidal action of metals is discussed. The amounts of metals which go into solution during use of eating utensils are too small to produce hygienic disturbances; they exert a favourable effect by killing bacteria. No bacterial cultures could be developed in the remnants of food from a Ag cover.

II. [With H. Nann.] The cause of metallic odour has been sought in the different phases of production. Ag alloys with additions of Se and Te are odourless. Treatments with electrolytic baths, with purifying, burnishing, and cleansing media produced a slight odour. S compounds [*e.g.*, allyl sulphide, mustard oil (I), onion, leek, and mustard juices] produce the characteristic "Ag odour." The action of these substances, with phenylallylthiocarbamide instead of (I), on Cu, Ni, Zn, Al, Fe, alpakka, brass, Cr, Au, Pd, and Pt is quite different; the odour produced varies in strength and in nature. After Ag, alpakka, brass, and Cu react the strongest. Direct Cr-plated brass smells strongly, but Ni- and Cr-plated brass remain odourless. Treatment with dil. HCl, or nascent H, or heating to 300° removes the odour. L. S. T.

Pressure coefficients of acoustic velocity for organic liquids. J. C. Swanson (J. Chem. Physics, 1934, 2, 689—693).—Acoustic velocities have been determined at 22·7—25·5° and at pressures up to 300 kg. per sq. cm. for EtBr, CCl_4, $CHCl_3$, Et_2O, C_5H_{12}, CS_2, C_6H_6, PhMe, and NH_2Ph. F. L. U.

Interpretation of the anomalous sound absorption in air and oxygen in terms of molecular collisions. H. O. Kneser (J. Acoustical Soc. Amer., 1933, 5, 122—126).—Knudsen's results (*ibid.*, 112) are discussed. Ch. Abs.

Electric resistance of magnesium and its alloys. K. Takahashi and W. Eda (Kinz. no Kenk., 1933, **10**, 127—136).—8% Al added to Mg increases the resistivity (I) from 4 to 14 ohm^{-6} per c.c. Addition of Cu increases (I) only slightly; the order is Al, Sn, Zn, Ag, Cd, Ni, Cu. Ch. Abs.

Superconductivity and Fermi–Dirac statistics. J. A. Kok (Nature, 1934, **134**, 532—533).—Theoretical. L. S. T.

Superconductivity of alloys and its magnetic destruction. W. J. de Haas and J. Voogd (Comm. Kamerlingh Onnes Lab. Leiden, Suppl. 73, 1—21; Chem. Zentr., 1934, i, 668).—The properties of the crystal lattice are of paramount importance for superconductivity (I). In general, alloys with a lattice of superconducting components show only a relatively small displacement of the transition point (II), whilst in those which possess a lattice other than that of superconducting components (II) is markedly displaced. The superconducting compound Au_2Bi has a lattice different from those of its non-superconducting components. The magnetic field necessary for destroying (I) increases with a fall in temp. more markedly in alloys than in the pure components. L. S. T.

Determination of the magnitude of motion of conductivity electrons. E. Patai (Physikal. Z., 1934, **35**, 837).—Apparatus for this determination makes use of the superconductivity of Pb, and its disappearance at a definite temp. A. J. M.

Effect of temperature on electrical resistance. W. J. de Haas and J. Voogd (Comm. Kamerlingh Onnes Lab. Leiden, Suppl. 73, 22—34; Chem. Zentr., 1934, i, 668).—A summary of measurements of the electrical resistance of pure metals at low temp. Vals. of R/R_0 at 4·5—1·13° abs. are given for many metals. L. S. T.

Resistance of liquid metals. N. F. Mott (Proc. Roy. Soc., 1934, *A*, **146**, 465—472).—The fact that the electrical resistance of most normal metals in the liquid state just above the m.p. is about twice that of the solid metal just below the m.p., whilst with certain abnormal metals, such as Bi, Ga, and Sb, the conductivity increases on melting, is discussed from the point of view of the wave-mechanical theory of electronic conduction. The change of resistance on melting can be accounted for by the change in at. frequency, for normal metals. The behaviour of abnormal metals is explicable qualitatively. L. L. B.

(A) Theory of heat conduction by liquids. (B) Conductivity number of chemically related substances in the liquid state. A. Kardos (Forsch. Ingenieurwes., *A*, 1934, **5**, 14—24; Z. tech. Physik, 1934, **15**, 79—80; Chem. Zentr., 1934, i, 2099—2100).—A. A method of calculating the thermal conductivity of liquids is developed.

B. The above theoretical vals. are compared with observed vals. for series of related liquids. H. J. E.

Heat-capacity curves of the simpler gases. VI. H. L. Johnston and E. A. Long (J. Chem. Physics, 1934, **2**, 710).—A correction (cf. this vol., 951). F. L. U.

Specific heat of liquids at the b.p. N. A. de Kolosovski (J. Gen. Chem. Russ., 1934, **4**, 269—272).—Sp. heat at the b.p., T, is given by $MC=kT^3$, where M is the mol. wt. of a member of a homologous series, for which k is a characteristic const. R. T.

Specific heats of silver and zinc at liquid helium temperatures. W. H. Keesom and J. A. Kok (Proc. K. Akad. Wetensch. Amsterdam, 1934, **37**, 377—378).—The influence of surface on the sp. heat of a Zn block with increased ratio surface/vol. is insufficient to explain the rapid fall in $\theta=7{\cdot}745TC^{-\frac{1}{3}}$ (C=at. heat) below the crit. temp. of He. The sp. heat of Ag cooled without admission of He is identical with the val. determined in presence of He. The fall in θ is not due to adsorbed He, and is attributed to the heat capacity of free electrons. For Ag, agreement with Sommerfeld's formula for the heat capacity of free electrons is obtained, but with Zn no definite conclusion results. R. S. B.

Thermodynamic functions of nitrous oxide and carbon dioxide. L. S. Kassel (J. Amer. Chem. Soc., 1934, **56**, 1838—1842).—The free energy, heat content, and sp. heat of N_2O have been calc. up to 1500° abs. and of CO_2 up to 1000° abs., from spectroscopic data. Equilibrium consts. of the water-gas and producer-gas reactions and the thermal decomp. of CO_2 have been calc. for a wide range of temp. E. S. H.

Latent heat of vaporisation [of ethyl alcohol]. S. Oguri, S. Anjo, and Y. Kuwabara (Bull. Waseda Appl. Chem. Soc., 1934, **22**, 1—4).—The val. for EtOH at the b.p. is 207·74 g.-cal. Ch. Abs.

General rule for the determination of b.p. at different pressures. Y. H. Li (J. Chinese Chem. Soc., 1934, **2**, 108—116).—From Trouton's rule and the Clausius–Clapeyron equation an expression is derived which permits the b.p. of a liquid to be calc. at any required pressure, if its b.p. at another pressure and the b.p. of another liquid at the two different pressures are known. The expression is more trustworthy than Trouton's rule because the ratio of the Trouton consts. of the two liquids remains const. throughout the whole range of pressures, whereas the individual vals. may vary separately. J. W. S.

B.p. of divinyl ether. W. A. Lott and W. G. Christiansen (Pub. Chem. Pharm. Res. Labs. E.R. Squibb and Sons, 1934, 12 pp.).—Discrepancies in recorded vals. are discussed. The b.p. is 28·3±0·2°. A distillation apparatus is described. Ch. Abs. (*e*)

B.-p. correction. C. S. Hoyt (J. Chem. Education, 1934, **11**, 405).—For all normal liquids the correction of the b.p. for each mm. deviation of the barometer from 760 mm. equals the abs. b.p. divided by 8000 (or another const. in the case of certain groups of related mols. and polar liquids). Ch. Abs. (*e*)

Entropy of polyatomic molecules. J. O. Halford (J. Chem. Physics, 1934, **2**, 694—696).—The calc. entropies of 7 org. compounds having 4—7 rotational degrees of freedom agree well with experimental vals. F. L. U.

Temperature variation of the second virial coefficient of helium. N. G. Whitelaw (Physica, 1934, **1**, 749—751).—Vals. calc. from the Joule–Thomson effect (cf. A., 1933, 218) are compared with direct determinations. H. J. E.

Properties of real gases according to the thermodynamic equation of state. I. Dependence of the Joule–Thomson effect of helium on pressure and temperature. V. Jacyna (Z. Physik, 1934, **91**, 349—352).—The Joule–Thomson effect for He is tabulated between −150° and 500° and from 0 to 100 kg. per sq. cm. A. B. D. C.

Limits of validity of the theorem for preliminary choice of arbitrary functions in the thermodynamic equation of state. V. Jacyna (Z. Physik, 1934, **91**, 353; cf. this vol., 1070). A. B. D. C.

Phenomenon of fusion in relation to a new equation of state and the lattice structure of solids. II. S. Franchetti (Atti R. Accad. Lincei, 1934, [vi], **19**, 800—803; cf. this vol., 1062).—Theoretical. O. J. W.

***n*-Paraffin hydrocarbons of high mol. wt.** L. Ivanovszky (Petroleum, 1934, **30**, No. 42, 1—3).—From vals. reported in the lit. for the physical properties of *n*-paraffins of high mol. wt. (particularly C_{20} to

C_{40}), an attempt has been made to correlate the latter (as represented by the no. of C atoms in the mol.) with d_4^{90}, n_D^{90}, m.p., and mol. vol. In the last case only is the relation linear; curves for d and n against no. of C atoms are coincident. C. C.

Rhenium fluorides. A correction. O. Ruff and W. Kwasnik (Z. anorg. Chem., 1934, **220**, 96; cf. this vol., 1083).—A corr. val. for the v.p. of ReF_6 is : $\log p = -1507{\cdot}9/T - 7{\cdot}5818$. Hence the heat of vaporisation is 6893 g.-cal., Trouton's const. 21·5, and crit. temp. 208·8° approx. B.p. by extrapolation is 47·6° and v.p. at m.p. 261·4 mm. M. S. B.

Vapour pressure of metals with high b.p. E. Baur and R. Brunner (Helv. Chim. Acta, 1934, **17**, 958—969).—V.p. of Zn, Mg, Pb, Ag, Mn, Al, Cu, Si, Sn, Cr, Au, and Be have been measured. Their logs. in every case $\propto 1/T$. The b.p. at 760 mm. are calc. The results agree generally with those of other workers. The b.p. of Al is, however, 2270°, not 1800° as reported by Greenwood (A., 1909, ii, 720). F. L. U.

Viscosity law. K. H. Meyer and H. Mark (Z. Elektrochem., 1934, **40**, 728; cf. this vol., 952).—Polemical. E. S. H.

Mechanism of viscosity of liquids. A. D. Goldhammer (Compt. rend. Acad. Sci. U.R.S.S., 1934, **3**, 484—490).—Theoretical. H. J. E.

Gold–manganese phase diagram. H. Bumm and U. Dehlinger (Metallwirt., 1933, **13**, 23—25; Chem. Zentr., 1934, i, 2238).—X-Ray observations show a small two-phase region between the cubic face-centred mixed crystals and tetragonal γ-Mn. A new body-centred tetragonal phase (50 at.-% Mn; a 3·28, c 3·14 Å.) has been detected below 700°. H. J. E.

Crystal structure of thallium–bismuth solutions. A. Ölander (Z. Krist., 1934, **89**, 89—92).—The powder photographic method has been used and the hexagonal phase (34—46 at.-% Tl) has received special attention. B. W. R.

Modification of aluminium–silicon alloys. J. A. Klajatschko (Kolloid-Z., 1934, **69**, 215—218).—A discussion, directing attention to the possible stabilising influence on the disperse system of small amounts of a third constituent. E. S. H.

Equilibria in alloyed bronzes. III. Copper-rich copper–manganese–tin alloys. J. Verö (Mitt. berg-hütt. Abt. kgl. Hochschule Berg-Forstw., 1933, **5**, 128—155; Chem. Zentr., 1934, i, 1703; cf. Veszelka, A., 1933, 1111).—Mn (up to 4%) produces a lowering of the crystallisation and transition temp. of binary Sn bronzes. With $>$ 4% Mn a new Mn-rich phase (X) is formed by separation from the γ mixed crystals. The phase relations for Cu-rich alloys with 0—15% Mn are discussed. H. J. E.

Magnetic study of mixed crystals of the system sulphur–selenium. S. S. Bhatnagar and P. L. Kapur (J. Indian Chem. Soc., 1934, **11**, 701—705).—The magnetic susceptibility of solid solutions containing $\not<$ 10% Se in S has been determined. The composition curve does not follow the mixture rule. E. S. H.

"Meta-alite," a metastable form of alite. S. Solacolu (Zement, 1934, **23**, 587—591).—Chemical, microscopical, and X-ray analysis of the product of the reaction $3CaO,SiO_2 \rightleftharpoons 2CaO,SiO_2 + CaO$ at 1900° shows the existence of a metastable solid solution of CaO and $2CaO,SiO_2$. T. W. P.

Refractivity and density of binary and ternary mixtures of water, acetaldehyde, and paraldehyde, and their analytical application. M. Strada and A. Macri (Giorn. Chim. Ind. Appl., 1934, **16**, 335—341).—Vals. of d and n for the ternary and three binary systems are recorded. The ternary diagram (which contains a large heterogeneous area) may be employed for the rapid and accurate analysis of mixtures by physical measurements. H. F. G.

Anomalies in the molecular polarisation of acetone and dichloroethane. M. Kubo (Bull. Inst. Phys. Chem. Res. Japan, 1934, **13**, 1221—1233).—The mol. polarisations of $COMe_2$ and $C_2H_4Cl_2$ have been measured in mixtures of CCl_4 and C_6H_6, and are abnormally large. The results seem to show that $COMe_2$ combines with $2CCl_4$, and that $C_2H_4Cl_2$ combines with C_6H_6 to give a complex $C_2H_4Cl_2,C_6H_6$ which is much more polar than free $C_2H_4Cl_2$. R. S. B.

Binary mixtures. II. Diminution of viscosity by tetrahydronaphthalene. L. Piatti (Angew. Chem., 1934, **47**, 732—733).—Addition of 30 vol.-% of tetrahydronaphthalene reduces the curvature of the viscosity–temp. graph of partly resinified cresol. H. W.

Constitution of solutions of aldehydes in alcohols. Phenylacetaldehyde in benzyl alcohol. A. Müller (Helv. Chim. Acta, 1934, **17**, 1231—1239).—Measurements have been made of the thermal change on mixing $CH_2Ph{\cdot}CHO$ with $CH_2Ph{\cdot}OH$, and of the viscosity and capillary spreading of the mixtures. The results, in conjunction with existing data on the refractive index, support the view that a semi-acetal $CH_2Ph{\cdot}CH(OH){\cdot}O{\cdot}CH_2Ph$ is formed in equilibrium with unchanged aldehyde, probably in the enolic form. The reaction is probably general. F. L. U.

Equilibria in liquid mixtures and solutions. B.p. and composition of the vapours of (A) aqueous ethylene glycol and ethylene oxide; (B) the system ethyl alcohol–ether. V. A. Kireev (J. Appl. Chem. Russ., 1934, 7, 489—494, 495—496).—A. [With A. A. Popov.]—B.-p. data are given for the systems $[{\cdot}CH_2{\cdot}OH]_2$–H_2O and $(CH_2)_2O$–H_2O, and the composition of the vapour phases is determined at the b.p.

B. [With E. M. Chatschadurova.]—B.p. and composition of the vapour phase are determined for $EtOH$–Et_2O. R. T.

Theory of concentrated solutions. XI. Thermodynamic properties of concentrated solutions of organic nitrogen compounds of the aliphatic series. N. I. Joukovsky (Bull. Soc. chim. Belg., 1934, **43**, 397—446).—The v.-p. curves and mol. heats of fusion of MeCN and CS_2, the mol. heats of fusion of EtCN, $Pr^{a}CN$, and $Bu^{a}CN$, and the v.-p. curves of NEt_3, $MeNO_2$, $CH_2{:}CH{\cdot}CH_2{\cdot}NCS$, Et_2O, and MeOH have been determined. F.-p. data are given for the following binary mixtures: $MeCN–EtCN$, $–Pr^{\alpha}CN$, and $–Bu^{\alpha}CN$; $EtCN–Pr^{\alpha}CN$ and $–Bu^{\alpha}CN$; $Pr^{\alpha}CN–Bu^{\alpha}CN$ (ideal solutions); $C_6H_6–MeCN$ and $–EtCN$ (non-ideal), $–Pr^{\alpha}CN$, $–Bu^{\alpha}CN$ (ideal), $–MeNO_2$ (non-ideal), $–CH_2{:}CH\cdot CH_2\cdot NCS$, and $–NEt_3$ (ideal); $PhNO_2–MeCN$ and $–MeNO_2$ (approaching ideality), $–CH_2{:}CH\cdot CH_2\cdot NCS$ (almost ideal), and $–NEt_3$ (abnormal); $HCO_2H–MeCN$ (ideal), $–MeNO_2$ (non-ideal), $–CH_2{:}CH\cdot CH_2\cdot NCS$ [crit. solution temp. (T) 39·8°], $–NEt_3$ (compound formation); $HCO\cdot NH_2–Et_2O$ ($T >$ 195°), $–MeOH$ (almost ideal), $–CS_2$ ($T >$ 120°), $–HCO_2H$ (equimol. compound), $–PhNO_2$ (T 108·2°), $–C_6H_6$ ($T >$ 150°); $CS_2–NEt_3$ (ideal solution). Miscibility data for $CS_2–MeCN$, $CS_2–MeNO_2$, $HCO_2H–CH_2{:}CH\cdot CH_2\cdot NCS$, $PhNO_2–HCO\cdot NH_2$, and $HCO_2H–NEt_3$ are recorded. Compositions of vapour and liquid phases are given for Et_2O with $MeCN$, $MeNO_2$, $CH_2{:}CH\cdot CH_2\cdot NCS$, NEt_3 (almost ideal); CS_2 with $MeCN$, $MeNO_2$, $CH_2{:}CH\cdot CH_2\cdot NCS$, NEt_3 (ideal); $MeOH$ with $MeCN$ (azeotrope at 30% $MeCN$ and 30°), $MeNO_2$ (azeotrope at 10% CH_3NO_2 and 30°), $CH_2{:}CH\cdot CH_2\cdot NCS$ (almost ideal) and vals. of n for $Et_2O–MeCN$ (which shows a max.), $MeOH–MeCN$, and $MeOH–MeNO_2$. Activity coeffs. have been calc. for all the mixtures studied, and the results are discussed in relation to the dielectric const. of the components and to previous work R. S.

Critical opalescence of binary mixtures. A. Rousset (Compt. rend., 1934, **199**, 716—718).—The apparent absorption coeffs. of the following mixtures have been measured within approx. 0·2° of the crit. temp.: $H_2O–Pr^{\beta}CO_2H$ (I), NH_2Ph–*cyclo*hexane (II), $H_2O–NEt_3$ (III), $C_6H_{14}–PhNO_2$ (IV). The absorption, and hence the intensity of diffusion of light, $\propto \lambda^{-n}$, where $n=4$ for (III) and (IV) up to the crit. temp. (T_c); for (I) and (II) $n=4$ when $T-T_c \gg 0·15°$, but decreases when $T-T_c$ approaches 0. Diffusion intensities have been measured in two opposite directions equally inclined to the incident beam for (I)-(IV), and for $CS_2–MeOH$ (V), NH_2Ph–turpentine (VI). (III), (IV), and (V) show complete symmetry, but in the case of (I), (II), and (VI) forward is > backward diffusion, and this dissymmetry increases as $T-T_c$ decreases. Ornstein and Zernicke's theory does not hold for (I)—(VI), but results with (III), (IV), and (V) agree with Rocard's theory. R. S. B.

Striæ in chemical processes. VI. Striæ formed by mixing liquids of the same refractive index. E. Schally and F. Nagl (Monatsh., 1934, **64**, 385—398).—If one solution is allowed to flow into another stationary solution of the same high n val., striæ may be observed by the striæ microscope. If there is a reversal in the alternation of light and dark shades due to the striæ, when the stationary and flowing solutions are interchanged, they are called D-striæ. Pairs consisting of aq. inorg. salts or of aq. salt+aq. sugar, $CO(NH_2)_2$, or $CS(NH_2)_2$ solutions have been examined for varying differences of n. There are essential changes in the D-striæ when the two solutions no longer have equal n. A third internal shadow is obtained if the more rapidly diffusing substance flows into the more strongly refracting. Observations have also been made with org. solutes in CCl_4, using monochromatic light to obviate colour disturbances. Between isomeric solutes in solutions of equal n there are no D-striæ, or feeble ones only. For homologues the shadows vary in accordance with the increasing mol. wt. D-striæ are always to be expected where the two solutes have different rates of diffusion. M. S. B.

Equilibria in tetrahalide systems. P. A. Pond and E. B. Crone (J. Amer. Chem. Soc., 1934, **56**, 2028—2031).—The solubility–temp. curves have been determined for $TiBr_4$ and $GeCl_4$, respectively, in liquid SO_2. $PbCl_4$ does not form such a partly miscible system. There is no evidence of compound formation. E. S. H.

Mutual solubility and surface tension. V. V. Sementschenko and E. A. Davidovskaja (J. Gen. Chem. Russ., 1934, **4**, 632—646).—The rule that substances which lower (raise) the tension at liquid–liquid interfaces increase (reduce) the mutual solubility of the liquids is verified for the systems $MeOH–C_6H_{14}$ and nicotine–H_2O in presence of alkali chlorides and aliphatic acids. R. T.

Solubility of hydrogen in water under pressure and at high temperatures. V. Ipatiev, jun., and V. P. Teodorovitsch (J. Gen. Chem. Russ., 1934, **4**, 395—399).—Deviations from Henry's law are observed above 200° at 100 atm. R. T.

Solubility of calcium carbonate. J. Pia (Int. Rev. ges. Hydrobiol. Hydrog., 1933, **29**, 84).—Lit. data have been recalc. and the results tabulated. Ch. Abs.

Solubility of ammonium chromate in water. J. I. Gerasimov (J. Gen. Chem. Russ., 1934, **4**, 721—722).—Solubility data are given for the range 0—75°. R. T.

Solubility of stereoisomerides of cystine.—See this vol., 1381.

Polytherm of $CoCl_2–H_2O$. H. Benrath (Z. anorg. Chem., 1934, **220**, 142—144).—The solubility curve of $CoCl_2$ in H_2O indicates the existence of the *hydrate* $CoCl_2,4H_2O$ at 46—48° approx. It forms hard, bluish-red, monoclinic crystals which, unlike $CoCl_2,6H_2O$, show no pleochroism. M. S. B.

Permeability of palladium to hydrogen. III. Fractionation of electrolytic hydrogen. IV. V. Lombard and C. Eichner (Bull. Soc. chim., 1934, **1**, [v], 945—954, 954—967; cf. this vol., 250, 497).—III. Full details are given of results already published (*ibid.*, 977).

IV. Progressive changes in the permeability of Pd to H_2 have been investigated. Traces of O_2 increase the rate of diffusion, D, of H_2. D of H_2 from admixture with N_2 through Pd into a vac. is given by $D=KP_{H_2}^{\cdot8}$, and the D of H_2 into N_2 increases with rate of flow of N_2. J. G. A. G.

(A) Passage of active hydrogen through a mercury column. C. Reczyński and B. Skorobohatyj. **(B) Sorption of gas in the mercury arc at high vapour pressure.** B. Skorobohatyj (Acta phys. polon., 1932, **1**, 413—418, 419—426; Chem. Zentr., 1934, i, 498).—(A) When a Hg arc has been maintained in H_2 for a short time, H_2 diffuses from the apparatus through a Hg column 1 m. long (after the arc is extinguished). The process probably occurs at the Hg–glass interface.

B. Sorption of N_2 in a Hg arc, attributed to Hg nitride formation, has been studied. H_2 is taken up more rapidly than N_2. H. J. E.

Diffusion of vapours through gas films. T. K. Sherwood and E. R. Gilliland (Ind. Eng. Chem., 1934, **26**, 1093—1096).—The gas film coeff. ∝ (diffusivity × total pressure)$^{0·56}$, to (Reynold's no.)$^{0·83}$, and to the mol. wt. of the diffusing vapour, and inversely ∝ the mean pressure of the non-diffusing gas. Hence the performance of a packed tower for any sol. vapour can be calc. from its known performance with another vapour. Equations are given connecting the absorption coeff. with the height of packing equiv. to a theoretical plate, but this method of calculation is not recommended. A. G.

Diffusion in liquids. VI. Micro-diffusion apparatus for coloured and colourless liquids. R. Fürth and R. Zuber. **VII. Zuber's micro-diffusion method applied to diffusion measurements at very low concentrations.** K. Sitte (Z. Physik, 1934, **91**, 609—616, 617—621). A. B. D. C.

Distribution of H^1_2O and H^2_2O in various systems. H. Erlenmeyer and H. Gärtner (Helv. Chim. Acta, 1934, **17**, 970—973).—When anhyd. Na_2SO_4 is mixed with H_2O containing H^2_2O and allowed to crystallise at 0° the resulting crystals contain the same proportion of H^2_2O as does the solution. Et_2O, shaken in bulk with H_2O, effects no change, but when droplets of Et_2O are caused to rise through H_2O there is a small increase of $[H^2_2O]$ in the Et_2O phase, indicating adsorption of H^2_2O at the interface. Rapid and complete exchange occurs between the H atoms of H_2O and H_2O_2, whilst none is detectable between those of H_2O and KH_2PO_2. F. L. U.

Hydration of salts with heavy water; constitution of salt hydrates. J. N. E. Day, E. D. Hughes, C. K. Ingold, and C. L. Wilson (J.C.S., 1934, 1593—1599).—Using heavy H_2O with a known H^2 content corresponding with an excess *d* over that of normal H_2O of about $2000/10^6$ the following salt hydrates were formed from the anhyd. salt: $SrCl_2,6H_2O$; $CuSO_4,5H_2O$; Li_2SO_4,H_2O; $Na_2CO_3,10H_2O$; $K_2C_2O_4,H_2O$. Measurements were made of the *d* of the H_2O recovered from the cryst. hydrate and from the solution. The results for the five salts, which illustrate the cation, anion, and carbonyl types of hydration, show that the differences of selectivity for light and heavy H_2O in the formation of cryst. hydrates are negligibly small, if real. This result is to be expected on the physical theory of hydration (Fajans, Born, Magnus, Garrick), but not on the structural theory (Werner, Sidgwick). It would seem, therefore, that any structure involved in the linking of hydrate H_2O can at best have but a loose and evanescent character. O. J. W.

Adsorption of oxygen and hydrogen on bright platinum. H. Reischauer (Z. physikal. Chem., 1934, B, **26**, 399—412).—H is not appreciably adsorbed at 20—700° at pressures below 5×10^{-2} mm. O is not adsorbed below about 120°, but at higher temp. there are two kinds of activated adsorption, with differing heats of activation and different temp. ranges. The total amount adsorbed in the two ways together is 5 O_2 mols. for each atom of the Pt surface, but the partition of the surface between the two kinds of adsorption depends on the previous treatment of the Pt. The rate of adsorption is effectively independent of the pressure, which may be explained by supposing that adsorption proper occurs on only a limited no. of the surface atoms, from which the O diffuses over the surface. In the adsorption with the smaller heat of activation, the O_2 adsorbed first is taken up more rapidly than that adsorbed later and reacts particularly readily with H. Heating in knallgas increases the no. of active Pt atoms. The true surface of the Pt foil used was apparently about 2·5 times as great as the apparent surface. R. C.

Adsorption of vapours of mutually soluble liquids. V. Kirejev and N. D. Solugub (Kolloid-Z., 1934, **69**, 222—225).—The adsorption of mixed vapours of EtOH and Et_2O in air by active C and SiO_2 gel at partial pressures of the vapours 2—30 mm. has been studied in respect of amount and composition. The composition of the adsorbed mixture is influenced by a selective adsorption factor, which is greatest at small concns. of vapour. Temp. has little influence when the amount of vapour mixture is const., but the degree of saturation is important in determining the amount of mixture adsorbed. E. S. H.

Adsorption of salol and aspirin from alcoholic solutions by active carbon. M. Péronnet and P. Crété (J. Pharm. Chim., 1934, [viii], **20**, 359—367).—Salol (I) and aspirin are rapidly adsorbed from EtOH solutions by active C and in neither case is hydrolysis evident. (I) is the more readily adsorbed and Freundlich's law is followed. S. C.

Adsorption. Silica gel and its applications. A. Travers (Bull. Soc. Ind. Mulhouse, 1934, **100**, 485—522).—A lecture. E. S. H.

Desorption of ether from active-charcoal powder by water vapour in relative motion. E. Boye (Kolloid-Z., 1934, **69**, 218—222; cf. this vol., 1066).—Et_2O is desorbed from highly-active C by superheated H_2O vapour more slowly than from less active C. The amount of desorbed Et_2O corresponding with a given amount of H_2O vapour varies inversely as the activity of the C; the relations between this quantity, max. adsorption, and surface are worked out. The technical significance of the results is discussed. E. S. H.

Theory of ionic adsorption. H. Muller (Cold Spring Harbor Sympos. Quant. Biol., 1933, **1**, 34—38).—Data for NaCl, $CaCl_2$, and Na_2SO_4 with glass, graphite, and collodion have been studied mathematically. Ch. Abs.

Theory of a unimolecular adsorption layer. N. Fooks (J. Phys. Chem. U.S.S.R., 1933, **4**, 562—566).—An adsorption isotherm equation is developed statistically. Ch. Abs. (*e*)

Solvation of molecules and the equation of state of an adsorbed layer. S. E. Bresler, B. A. Talmud, D. L. Talmud, and Y. B. Khariton (J.

Phys. Chem. U.S.S.R., 1934, **5**, 107—115).—The effect of cations and anions on the dehydration (I) of insol. layers of cetyl alcohol and oleic acid adsorbed on aq. electrolytes and glucose is in the order of the lyotropic series. (I) is related to the electrostatic effects of polar groups in the adsorbed layer. Ch. Abs. (*e*)

Two-dimensional equation of state and structure of surface layers. B. Tamamushi (Bull. Chem. Soc. Japan, 1934, **9**, 363—393).—Mathematical. E. S. H.

Relation between surface tension of solutions and solubility of physiologically important fatty acids. F. Erödi (Biochem. Z., 1934, **273**, 273—278).—The influence of p_H on the solubility and on the surface tension of solutions of stearic, oleic, linoleic, linolenic, and arachidic acids has been examined. The micelles formed by the unsaturated acids are smaller, and these are consequently more easily resorbed in the animal system. W. McC.

Interference colours of thin films of oxides, sulphides, or iodides on metals. U. R. Evans (Kolloid-Z., 1934, **69**, 129—137).—Published work is reviewed in the light of optical theory. E. S. H.

Friction and adhesion. IV. Theory of adhesion of small particles. B. Derjaguin (Kolloid-Z., 1934, **69**, 155—164; cf. this vol., 1169).—A mathematical treatment for deformable and non-deformable particles. E. S. H.

Influence of time of contact between mineral and air bubbles on flotation. I. Sven-Nilsson (Kolloid-Z., 1934, **69**, 230—231).—A certain induction time is necessary to enable an air bubble to adhere to a mineral surface. The time may be < 0.1 sec. or > 1 day, depending on the size of the bubble, treatment of surface, and presence of other reagents. E. S. H.

Effect of salts on the electric charge of surfaces in liquids. H. A. Abramson and H. Müller (Cold Spring Harbor Sympos. Quant. Biol., 1933, **1**, 29—33).—For graphite, glass, quartz, cellulose, collodion, and paraffin oil with ions which do not produce reversal of sign of charge, concn. : p.d. is complex, but concn. : surface *d* of electric charge gives a simple curve resembling the adsorption curve. Ch. Abs.

Surface phenomena at the boundary between solid and solution. Change in the heat of wetting in surface-active materials by the introduction of an electrolyte. V. Iljin, V. V. Semenschenko, and V. I. Ivanov (J. Exp. Theor. Phys. U.S.S.R., 1933, **3**, 571—578).—The heat of wetting (*H*) of C with aq. NaCl and $Pr^{\beta}OH$ and with an EtOH solution of *sec.*-BuOH has been measured. The electrolyte increases *H*. Ch. Abs. (*e*)

Theory of the diffuse double layer. H. Müller (Cold Spring Harbor Sympos. Quant. Biol., 1933, **1**, 1—8).—A discussion. Ch. Abs.

Surface conductance. K. S. Cole (Cold Spring Harbor Sympos. Quant. Biol., 1933, **1**, 23—28).—A mathematical discussion of Smoluchowski's diffuse layer and ionic concept of surface conductance. Ch. Abs.

Theory of electrophoretic migration. H. Müller (Cold Spring Harbor Sympos. Quant. Biol., 1933, **1**, 9—13).—The validity of Smoluchowski's formula is discussed. Ch. Abs.

Streaming potential measurements. D. R. Briggs (Cold Spring Harbor Sympos. Quant. Biol., 1933, **1**, 14—22).—A formula has been developed. The variation in streaming potential (I) of ovalbumin has been measured; the (I) equation is invalid for very low pore diam. and for low hydrostatic potentials. Ch. Abs.

Electro-osmosis. IV. S. Imai (Bull. Inst. Phys. Chem. Res. Japan, 1934, **13**, 1198—1220).—The electrokinetic potential (ζ) of electrolytes has been measured using a diaphragm of sintered powdered SiO_2. For acid solutions, $\zeta=\zeta_0e^{-\beta c}-(\zeta_0-\zeta_\omega)e^{-\gamma c}$, where ζ_0 is the val. obtained by extrapolating the log ζ–c curve to $c=0$, ζ_ω is the val. of ζ for conductivity H_2O, and β and γ are consts. For alkaline solutions, $\zeta=\zeta_0'+k\log c-\alpha e^{\delta\log c}$, where α, k, and δ are consts., and for salt solutions, $\zeta=\zeta_0'+k\log 1/c+\alpha e^{-\delta\log 1/c}$. R. S. B.

Liesegang stratification developed in the diatomaceous gyttia from Lake Haruna, and problems related to it. K. Sugawara (Bull. Chem. Soc. Japan, 1934, **9**, 402—409).—A periodic structure is shown by the $Fe(OH)_3$ formed by diffusion of atm. O_2 through the lake deposits, which were stored in glass tubes. The deposits contained about 63% SiO_2, and Fe^{II} salts in the capillary-bound H_2O. E. S. H.

Physico-chemical properties of solutions in condensed gases. V. Determination of the mol. wt. of substances dissolved in liquid ammonia at room temperature. A. I. Schattenstein and A. M. Monoszon (J. Phys. Chem. U.S.S.R., 1933, **4**, 691—695).—Vals. for $CO(NH_2)_2$ (I), *d*-glucose (II), quinhydrone (III), NH_4Cl, and NH_4NO_3 are recorded. The degree of association of (I) is independent of temp. NH_4Cl is strongly associated, (II) unassociated, and (III) dissociates into benzoquinone and quinol. Ch. Abs. (*e*)

Properties of electrolytic solutions. XIII. F.p. of solutions in benzene. F. M. Batson and C. A. Kraus (J. Amer. Chem. Soc., 1934, **56**, 2017—2020; cf. this vol., 486).—The f.-p. const. of C_6H_6 is 5·075°. The f.p. of solutions of tri*iso*amylammonium picrate, $AgClO_4$, and tetra*iso*amylammonium picrate and thiocyanate in C_6H_6 have been determined. At very low concns. the f.-p. curves approach those based on the formula wt. of the electrolyte. At higher concns. the deviations increase, especially for electrolytes having electrically symmetrical ions. E. S. H.

Compressibility of aqueous solutions. II. W. G. Thomas and E. P. Perman (Proc. Roy. Soc., 1934, **A**, **146**, 640—650).—The compressibility coeffs. of aq. solutions of KCl, KBr, KI, $CaBr_2$, $SrBr_2$, $BaBr_2$, AcOH, and CH_2O have been measured at 30° at pressures up to 100 atm., using an improved form of Perman and Urry's method (A., 1930, 154). Results (obtained by W. D. Urry) are also given for solutions of glucose, sucrose, and raffinose. L. L. B.

Dilatometric study of complex formation in solutions of chlorides. A. V. Titov (J. Gen. Chem.

Russ., 1934, 4, 567—576).—The complex salts Na_2ZnCl_4, $NaCoCl_3$, $NaHgCl_3$, and Na_2CdCl_4 are indicated by max. increase in vol. on mixing solutions of the constituent salts; solutions of the individual salts exhibit a decrease in vol. on dilution. Complex formation does not take place appreciably in the systems $MgCl_2$–NaCl, $CaCl_2$–NaCl, $CaCl_2$–NH_4Cl, and NH_4Cl–NaCl. R. T.

Constitution of iodic acid and its salts. I. M. R. Nayar and T. R. Gairola. **II. [Raman spectra.]** M. R. Nayar and P. Sharma (Z. anorg. Chem. 1934, **220**, 163—168, 169—171).—I. F.-p. determinations in aq. solution indicate that HIO_3 is polymerised in conc. solutions. In dil. solutions the mols. are simple. KIO_3 does not polymerise. Electrical conductivity measurements do not support the view that HIO_3 is dibasic.

II. Raman spectral data support the above conclusions. M. S. B.

Anionic weight of some sulpho-salts in aqueous solution. H. Brintzinger and H. Osswald (Z. anorg. Chem., 1934, **220**, 172—176).—From measurements of the dialysis coeff. in aq. solution the following anionic formulæ have been deduced: $[As(H_2O)_2S_4]'''$, $[Sb(H_2O)_2S_4]'''$, $[Sn(H_2O)_2S_4]''''$, $[Mo(H_2O)_2S_4]''$, $[GeS_3]''$, $[V(HS)_2SO]'$, $[W(WS_3)_3S_4]''$, $[As(AsS_3)S_3]''''''$. M. S. B.

Anionic weights of complex cyanides in aqueous solution. H. Brintzinger and H. Osswald (Z. anorg. Chem., 1934, **220**, 177—179).—The formulæ of complex cyanides of Fe, Co, Ni, Cu, Ag, Zn, Cd, and W have been determined by measurements of the dialysis coeffs. The ferro- and cobalto-cyanide ions are abnormally large and the following alternative formulæ are suggested: $[Fe(or\ Co)(CN)_6]_2''''''''$ or $[Fe(or\ Co)(CN)_6(H_2O)_{12}]''''$. M. S. B.

Mobility of small selenium spheres in air at high speeds. A. S. Berkowitsch (Helv. phys. Acta, 1934, 7, 170—202; Chem. Zentr., 1934, i, 3171).—The velocity ∝ applied force. The particles also obey the Millikan law of fall. H. J. E.

Sedimentation equilibrium in colloidal suspensions. S. Levine (Proc. Roy. Soc., 1934, **A**, **146**, 597—623).—An expression is derived for the distribution in the sedimentation equilibrium. Departure from Perrin's law is indicated, varying, according to the charges on the particles and the concn. of the electrolyte, from $n=1\cdot6\times10^{13}$ to $n=4\cdot0\times10^{14}$, with corresponding limiting concns. lying between $n=2\cdot1\times10^{14}$ and $n=5\cdot5\times10^{15}$. L. L. B.

Dispersion analysis of fine suspensions. N. N. Zaprudski (Tzvet. Met., 1933, No. 5, 15—23).—A review and discussion. Electrical methods give promising results. Ch. Abs.

Physico-chemical state of silicate dusts in salt solutions. I. Stability of dust suspensions. II. Solubility of silicate dusts. E. A. Nauman (Arch. Sci. biol. U.S.S.R., 1933, **33**, 533—550, 551—557).—I. The influence of electrolytes on the stability of suspensions of porcelain dust is examined.

II. Solubility data are recorded. Ch. Abs. (*p*)

Electrophoresis of cholesterol suspensions. L. S. Moyer (Biochem. Z., 1934, **273**, 122—131).—Cholesterol (I) sols possess very different electrokinetic properties according to their method of prep. Suspensions of powdered (I) crystals gave the best results, and curves showing the electrophoretic velocity at varying p_H are given. Addition of glucose does not alter the electrophoretic behaviour. P. W. C.

Preparation of colloidal solutions through the silent electric discharge. II. S. Miyamoto (Kolloid-Z., 1934, **69**, 179—181; cf. this vol., 841).—Sols of As, Sb, and Hg_2Cl_2 in H_2O, EtOH, $Bu^{\beta}OH$, and amyl alcohol can be prepared by the method previously described. E. S. H.

Preparation of hydrosols of sparingly-soluble metal salts by electrolysis. N. Peskov and B. Saprometov (Kolloid-Z., 1934, **69**, 181—185).—When a very dil. salt solution is electrolysed under certain conditions, an insol. compound of the salt anion and the cathode metal is dispersed. When the medium is a gelatin gel periodic pptn. structures are formed. E. S. H.

Formation of emulsions in definable fields of flow. G. I. Taylor (Proc. Roy. Soc., 1934, **A**, **146**, 501—523).—Experiments have been made on the deformation and bursting under controlled conditions of a drop of one liquid suspended in another. Measurements of the interfacial tension of the liquids, their viscosities, and the rate of deformation of the outer fluid are described. An expression is found for small distortions from the spherical form which occur at slow speeds. L. L. B.

Relation between particle size of highly-polymerised substances and viscosity of their solutions. R. Obogi and E. Broda (Kolloid-Z., 1934, **69**, 172—178).—The results of measurements of the viscosity and osmotic pressure, at 25° and 40°, of fractionated, homogenised solutions of cellulose acetate show that up to a particle wt. about 60,000 the variation of viscosity with mol. wt. is in fair agreement with Staudinger's relation. Experimental difficulties prevent the confirmation of the rule at higher mol. wt. E. S. H.

Colloid chemistry of metal soaps. I. Dipole moment. Wo. Ostwald and R. Riedel (Kolloid-Z., 1934, **69**, 185—199).—The dielectric polarisation, *n*, and *d* of solutions of Al, Mg, and Cd soaps in C_6H_6 and the solubilities of the soaps have been measured. *n* ∝ concn. and decreases with increasing no. of C atoms. The dielectric mol. polarisation and dipole moment increase with the no. of C atoms, the increase being linear except for myristate and laurate. E. S. H.

Anomalous osmotic pressures of colloid solutions at equilibrium. D. R. Briggs (Cold Spring Harbor Sympos. Quant. Biol., 1933, **1**, 152—165).—Anomalous osmotic pressures of aq. gum arabic against NaCl at varying pressure, p_H, and concn. of EtOH, $Na^{\cdot}$, and Cl' are found. The sign of the charge carried by the colloid appears to be the determining factor. Ch. Abs.

Colloidal nature and related properties of clays. W. W. Meyer (J. Res. Nat. Bur. Stand., 1934, **13**, 245—258).—Weathering tends to produce a compound of isoelectric p_H equal to the p_H of the weathering solution, and therefore to reduce the content of fine particles; the sp. surface thus varies inversely with the p_H of the weathering solution and with the degree of weathering. A low $SiO_2 : M_2O_3$ ratio causes a min. ion concn. at the surface of the particles, and therefore also influences the particle size and activity, since the colloidal properties of a clay are due to the ionic atm. surrounding the particles. Coagulation and deflocculation are discussed in terms of the difference of ionic charge between the particles and their atms.; in coagulated clay the imbibed H_2O film is thin and mol. attraction occurs, whereas in the deflocculated condition the film is sufficiently thick to prevent such attraction. This view is in accord with the relative ease of deflocculation of different clays, and the differences in behaviour of deflocculating agents. The plasticity, shrinkage on drying, and transverse strength when dry of ceramic clays are discussed. H. F. G.

Stability of colloids and the theory of rapid coagulation. H. Müller (Cold Spring Harbor Sympos. Quant. Biol., 1933, **1**, 60—64).—A discussion. Smoluchowski's theory is supported.
Ch. Abs.

Bound water in hydrophilic colloid systems. A. V. Dumanski, A. G. Kulman, and O. N. Golosova (J. Appl. Chem. Russ., 1934, **7**, 585—591).—The capacity for binding H_2O increases in the series potato$<$soft wheat$<$hard wheat$<$maize$<$rye$<$soya meal. The colloids of flour, dough, and bread are highly hydrated; their affinity for H_2O varies during the process of baking, and falls rapidly in bread with time after baking. R. T.

" Bound " water of biological colloids.—See this vol., 1246.

Lyophilic colloids. IV. " Disintegration-sheath " theory and stability of hydrophilic colloids. S. M. Liepatov (Kolloid-Z., 1934, **69**, 199—202; cf. A., 1934, 1069).—The adsorption of the easily-sol. fraction of the colloid at the surface of the micelle brings about an orientation of lyophilic groups, which strengthens the binding between the solvent and the micelle surface. The sheath thus formed weakens the attraction field between the mols. The theory is applied to the mechanism of gelation.
E. S. H.

Effect of movement on the electrical conductivity of hydrosols. W. S. Urbański (Acta phys. polon., 1933, **2**, 181—192; Chem. Zentr., 1934, i, 835).—The electrical resistance of a V_2O_5 hydrosol increases when it flows past an electrode. A limiting val. is reached. The effect decreases on dilution. A well-dialysed Fe_2O_3 sol behaves similarly.
H. J. E.

Influence of light on hydrophobic sols in relation to their natural stability. W. Heller (Compt. rend., 1934, **199**, 723—724).—The velocity of growth of particles (v), at 20°, of dialysed $Fe(OH)_3$ sol, which was kept in the dark for approx. 200 days, has been studied by means of magnetic double refraction. v decreases with time in the dark, but increases if the sol is then exposed to diffused daylight, especially for the sols dialysed for the longest time (least stable). The mechanism is discussed. R. S. B.

Changes in charge, conductivity, stability, and composition of colloidal arsenious oxide on exposure to light. C. B. Joshi, P. M. Barve, and B. N. Desai (Current Sci., 1934, **3**, 105).—The charge on the colloidal particles decreases and the conductivity increases with an increase in the period of exposure to electric light. The amount of free H_3AsO_3 increases, whilst the total S decreases. The flocculation vals. with KCl at first increase and then decrease; those with $MgCl_2$ decrease continuously. On exposure to light the As_2S_3 hydrolyses to H_3AsO_3 and H_2S which is photochemically oxidised to SO_2. L. S. T.

Interpretation of dielectric constant anomalies in emulsions. A. Piekara (Acta phys. polon., 1933, **2**, 225—228; Chem. Zentr., 1934, i, 1628; cf. Urbański, this vol., 1171).—Polemical. H. J. E.

Application of quantitative filtration analysis to the study of the transformation of aluminium hydroxide suspension into the jelly state. V. A. Pokrovski (Kolloid-Z., 1934, **69**, 202—205).—By Ostwald's method (A., 1925, ii, 198) the ripening of gel-like suspensions of $Al(OH)_3$ and the effect of temp. thereon can be studied. E. S. H.

Colloidal behaviour of sericin. V. H. Kaneko (Bull. Chem. Soc. Japan, 1934, **9**, 409—421; cf. this vol., 1069).—The rate of gelatinisation of sericin depends on p_H and is greatest at the isoelectric point (p_H 4·5). Syneresis occurs over the region p_H 3·5—4·8. The variation of setting point with concn. has been determined. When the sol is frozen, sericin is pptd. in the form of fibres, which are incompletely sol. on thawing. Sericin gel has been used as a medium for the prep. of periodic pptn. structures of several substances, and the rate of diffusion of inorg. salts and org. dyes in the gel has been determined.
E. S. H.

Nephelometric investigation of protein solutions. E. M. Mystkowski (Biochem. Z., 1934, **273**, 161—169).—The passage from the sol to the gel condition does not run parallel with changes of Tyndall effect, considerable increase in turbidity occurring without conversion into gel. Tables and curves summarise the effect of NaCl, $CaCl_2$, Na_2SO_4, $MgCl_2$, and $MgSO_4$ at varying p_H on the degree of turbidity. P. W. C.

Theory of dominating forms. I. Chemical equilibria as electrostatic phenomena. II. Theory of hydrides. J. V. Chodakov (J. Gen. Chem. Russ., 1934, **4**, 328—358, 359—371).—Theoretical. R. T.

Third law of thermodynamics. W. H. Rodebush (J. Chem. Physics, 1934, **2**, 668—670).—Theoretical. F. L. U.

Thermodynamics of hydrocarbon reactions. A. V. Frost (Khim. Tverd. Topl., 1933, **4**, 171—185).—Equilibrium consts. for the following reactions have been calc. from experimental data: $C_6H_6+3H_2 \rightleftharpoons C_6H_{12}$; $PhMe+3H_2 \rightleftharpoons C_6H_{11}Me$; $2C_6H_6 \rightleftharpoons Ph_2+H_2$; C (graphite)$+2H_2 \rightleftharpoons CH_4$; C (amorphous)$+2H_2 \rightleftharpoons CH_4$; 2C (graphite)$+2H_2 \rightleftharpoons C_2H_4$; $C_2H_4+H_2 \rightleftharpoons C_2H_6$; 2C (graphite)$+3H_2 \rightleftharpoons C_2H_6$.
Ch. Abs. (*e*)

Equilibria in a chemical system. Hydrogen sulphide–propylene–*iso*propyl mercaptan–*n*-propyl mercaptan. F. T. Barr and D. B. Keyes (Ind. Eng. Chem., 1934, **26**, 1111—1114).—The standard free energy changes for the reaction $H_2S+C_3H_6=PrSH$ are $-14{,}600+28{\cdot}80T$ (Pr^{β}) and $-14{,}600+30{\cdot}00T$ (Pr^{α}). Dynamic measurements have been made with NiS on kieselguhr as catalyst. The total mercaptan formation decreases with rising temp., but at 250—300° the equilibrium ratio of the two is nearly const. at 65 Pr^{β} to 35 Pr^{α}. A. G.

Bivalent dissociating systems. M. Gex (Arch. Phys. biol. Chim.-Phys. Corps organ., 1933, **10**, 257—291; Chem. Zentr., 1934, i, 827).—Mathematical. L. S. T.

Factors determining electrolytic dissociation and energy of dissociation of salt molecules. W. J. C. Orr and J. A. V. Butler (Phil. Mag., 1934, [vii], **18**, 778—792).—Theoretical. A method of calculating energies of dissociation of salt mols. in the vapour state is given. Experimental vals. for the alkali metal halides are generally in agreement with those calc. The origin of the difference in electrolytic behaviour between these and salts of metals of the transitional series is to be sought in the homopolar nature of the latter. F. L. U.

Thermodynamic dissociation constant of benzoic acid at 25°, from conductivity measurements. G. H. Jeffery and A. I. Vogel (Phil. Mag., 1934, [vii], **18**, 901—909).—Conductivity data have been obtained for BzOH and NaOBz. A method of applying the solvent correction is given. The thermodynamic dissociation const. is $6{\cdot}373\times10^{-5}$. M. S. B.

Ionisation constant of *n*-butyric acid from 0° to 60°. H. S. Harned and R. O. Sutherland (J. Amer. Chem. Soc., 1934, **56**, 2039—2041).—Determinations have been made at 5° intervals by measuring the e.m.f. of the cells $H_2|HX(m_1),NaX(m_2),NaCl(m_3)|AgCl|Ag$. The max. val. is $1{\cdot}575\times10^{-5}$ at 8°. The heat of ionisation has been calc. E. S. H.

Classical dissociation constant of bromophenol-blue in aqueous salt solutions. M. Kilpatrick (J. Amer. Chem. Soc., 1934, **56**, 2048—2050).—Data have been obtained for the yellow–purple colour change in solutions of different salts up to $3M$. The application of various equations is discussed. E. S. H.

Ionisation of calcium, magnesium, and strontium citrates. A. B. Hastings, F. C. McLean, L. Eichelberger, J. L. Hall, and E. Da Costa (J. Biol. Chem., 1934, **107**, 351—370).—Determination of Ca^{++} by the frog's heart method (cf. this vol., 1422) and by equilibration experiments with $CaCO_3$ as the solid phase indicate that the dissociation of Ca citrate (I) takes place in two stages, viz., $Ca_3Cit_2 \rightleftharpoons Ca^{++}+2CaCit^-$ (complete dissociation); and $CaCit^- \rightleftharpoons Ca^{++}+Cit^{---}$ (partial dissociation). In logarithmic form, $pCa^{++}+pCit^{---}-pCaCit^-=pK_{CaCit^-}=3{\cdot}22\pm0{\cdot}025$ at 22° and p_H 7·4. Mg and Sr citrates behave similarly, the corresponding vals. for pK_{MgCit^-} and pK_{SrCit^-} being 3·22 and 2·70±0·06, respectively. A structure is suggested for the Ca salt. A. E. O.

Complexes formed by mercuric chloride and alkali metal chlorides in aqueous solution. C. Tourneux (Bull. Soc. chim., 1934, [v], **1**, 1043—1049).—Equilibrium consts. for the reactions $KCl+2HgCl_2 \rightleftharpoons KHg_2Cl_5$ and $2KCl+HgCl_2 \rightleftharpoons K_2HgCl_4$ are calc. for temp. between 0° and 100°. The variations of K with temp. are in accordance with van 't Hoff's law. F. L. U.

Solutions containing zwitterions: erratum. J. G. Kirkwood (J. Chem. Physics, 1934, **2**, 713; cf. this vol., 962). F. L. U.

Activity in mixtures of strong electrolytes. I. L. Brüll (Gazzetta, 1934, **64**, 607—614).—The activity coeffs. of $ZnCl_2$ in aq. solutions of alkali chlorides have been determined from e.m.f. measurements of the cell $Hg,Zn|ZnCl_2+MCl|Hg_2Cl_2|Hg$, where M=Li, Na, or K. The results are compared with the vals. calc. by the theory of Bonino (this vol., 254). O. J. W.

Apparent and true activity coefficients in solutions of electrolytes. L. Brüll (Gazzetta, 1934, **64**, 615—623).—The true activity coeffs. for dil. solutions of $CdCl_2$ are calc. assuming the existence of $CdCl^+$ ions. O. J. W.

Principles involved in the phase rule. F. J. Tromp (J. Chem. Met. Soc. S. Africa, 1934, **35**, 34—40).—In place of the usual equation $F=C+2-P$ it is proposed to substitute $F=V-E$, in which V, the no. of intensive properties, is defined as 2+the total no. of mol. fractions of every constituent of every phase in which it occurs. E is the total no. of independent equations relating to the constituents, including mol. fraction, arbitrary, and free energy equations. Examples are given. F. L. U.

System PbO–SiO₂. R. F. Geller, A. S. Creamer, and E. N. Bunting (J. Res. Nat. Bur. Stand., 1934, **13**, 237—244).—Three compounds exist, viz., $4PbO,SiO_2$ (m.p., incongruent, 725±1°), which occurs in three forms, transitions occurring at 720±2°, and at 120—155°; $2PbO,SiO_2$ (m.p., congruent, 743±3°); and PbO,SiO_2 (m.p., congruent, 764±3°). Eutectics occur at 714±3° and 25 mol.-% SiO_2; 716±3° and 40·5 mol.-% SiO_2; and 732±3° and 61 mol.-% SiO_2. H. F. G.

System silica–alumina. II. Reactivity of kaolinite and a new group of silicates. O. Rebuffat (Giorn. Chim. Ind. Appl., 1934, **16**, 433—435).—The eutectic point of the system tridymite (I)–hydrated kaolinite (II), $Al_2O_3,2SiO_2,2H_2O$, is at 1620° with 10% Al_2O_3. As suspected from the m.-p. diagrams, (I) reacts with (II) slowly at 600—700°, forming the *compound* $Al_2O_3,3SiO_2$. Similarly, (II) reacts at 1000° with β-stannic acid, forming the *compound* $Al_2O_3,2SiO_2,SnO_2$, and with TiO_2, forming a compound which is probably analogous. D. R. D.

Equilibria in the system KBr–KBrO₃–H₂O. J. I. Gerasimov (J. Gen. Chem. Russ., 1934, **4**, 723—727).—Equilibrium data at 0—80° are given. R. T.

Equilibrium diagrams of salts for salt baths. IV. Barium chloride–calcium chloride–sodium chloride system. T. Satô and T. Amano (Kinzoku no Kenkyu, 1934, **11**, 305—316).—The eutectoid

points in the systems $BaCl_2$–$CaCl_2$, $BaCl_2$–NaCl, and $CaCl_2$–NaCl correspond with 617° ($CaCl_2$ 54 mol.-%), 656° ($BaCl_2$ 40 mol.-%), and 501° (NaCl 54 mol.-%), respectively. The system $CaCl_2$–NaCl affords no indication of the compound $4NaCl,CaCl_2$. The eutectoid in the ternary system corresponds with 453° ($BaCl_2$ 16, $CaCl_2$ 47, NaCl 37 mol.-%).
Ch. Abs. (*e*)

Polytherms of the ternary system $MnCl_2$–$(LiCl)_2$–H_2O. H. Benrath (Z. anorg. Chem., 1934, **220**, 145—153; cf. A., 1932, 697).—The following ternary *compounds* are formed: $MnCl_2,4LiCl,10H_2O$, stable from $< 0°$ to approx. 28°; $MnCl_2,LiCl,2H_2O$, above 53°; $MnCl_2,2LiCl,2H_2O$, above 73°; $MnCl_2,LiCl,5H_2O$, at $< 0°$ to 26°; $MnCl_2,2LiCl,4H_2O$, at 23—76° approx. In addition, the following occur as stable solid phases in the system at 0—100°: $MnCl_2,4H_2O$, $MnCl_2,2H_2O$, $LiCl,2H_2O$, $LiCl,H_2O$, and LiCl. M. S. B.

Double decomposition in the absence of a solvent. XXV. Irreversible mutual system $TlCl+KI \longrightarrow TlI+KCl$. E. M. Tschernomordik (J. Gen. Chem. Russ., 1934, **4**, 456—465).—The phase diagrams indicate limited solid solution formation, and absence of compound formation. R. T.

Equilibrium of sulphides of metals with hydrogen chloride. I. System zinc sulphide–hydrogen chloride. II. System manganese sulphide–hydrogen chloride. E. V. Britzke, A. F. Kapustinski, and B. K. Veselovski (J. Phys. Chem. U.S.S.R., 1934, **5**, 77—84, 103—106).—I. Vals. of log Kp determined by a static method are 1·14 and 1·67 at 565° and 635° abs., respectively.

II. The dissociation pressure of MnS derived from the MnS–HCl reaction at 680—1000° and from the MnS–H_2 reaction at 1373° abs. give the heat of formation of MnS as 44,900 g.-cal. Ch. Abs. (*e*)

Heat of formation of iron carbide, Fe_3C. G. Naeser (Mitt. Kaiser-Wilh.-Inst. Eisenforsch., 1934, **16**, 1—7; Chem. Zentr., 1934, i, 3181–3182).—The val. varies from +8 to −3·9 kg.-cal. per mol. according to the state of the C. H. J. E.

(A) **Affinity of metals for sulphur.** E. V. Britzke and A. F. Kapustinski. (B) **Heat of formation of disulphides and trisulphides of arsenic.** (C) **Heat of formation of double compounds of pentoxide and trioxide of arsenic, and the heat of formation of arsenic sulphate.** E. V. Britzke, A. F. Kapustinski, and L. G. Chentzova (J. Phys. Chem. U.S.S.R., 1934, **5**, 85—90, 91—96, 97—102).—A. With increase in the radii of the metal ions the electrolytic dissociation consts. of the sulphides decrease, whilst the thermal dissociation consts. increase.

B. The heats of formation (I) of solid As_2S_2 and As_2S_3 from solid As and rhombic S are calc. as 28·9 and 34·7 kg.-cal.

C. The val. of (I) for As_2O_3,SO_3 from solid As_2O_3 and gaseous SO_3, and of solid As_2O_3,As_2O_5 from solid As_2O_3 and solid As_2O_5 are 23·03 and −24·5 kg.-cal., respectively. The heats of dissolution of As_2O_3 and As_2O_5 in 0·83*N*-NaOH are 9·61 and 63·23 kg.-cal., respectively. Ch. Abs. (*e*)

Affinity. LXI. Construction and use of a high-temperature calorimeter with closed reaction space. W. Biltz, G. Rohlffs, and H. U. von Vogel (Z. anorg. Chem., 1934, **220**, 113—141).—A calorimeter for the determination of heats of dissolution in a sealed glass bomb is described. By measuring the heats of dissolution of Zn and ZnO, and also of CaO and $CaCO_3$, in aq. HCl at 90°, the heats of formation of ZnO from Zn and of $CaCO_3$ from CaO, respectively, have been calc. and found to be in good agreement with other determinations. The calorimeter has been employed in the determination of the heats of formation (kg.-cal. per g.-mol.) of the following compounds: AuSn $8·_2$; $AuSn_2$ $5·_5$; $AuSb_2$ approx. $3·_5$; Au_3Zn 24; AuZn 11; $AuZn_3$ 22; CuO 36·4; Cu_2O 39·4. The val. of the heat of dissociation of 4CuO into $2Cu_2O$ and O_2, calc. from the heats of formation of the oxides, is 66·8 kg.-cal. at 20°. M. S. B.

Heats of combustion and formation of the normal aliphatic alcohols in the gaseous and liquid states, and the energies of their atomic linkings. F. D. Rossini (J. Res. Nat. Bur. Stand., 1934, **13**, 189—202).—Existing data are reviewed and correlated with the author's val. (157·0 kg.-cal.) for the increase of the heat of combustion caused by the addition of the CH_2 group, and "best" vals. for the heats of evaporation, combustion, and formation are selected. The energy of dissociation, at 0° abs., of $C_nH_{2n+1}·OH$ into its constituent atoms $\propto n$, when n is >6; the deviations, which correspond with lower stability, for $n<6$, are attributed, as in the case of the paraffin hydrocarbons, to the presence of different types of C·C, C·H, and C·O linkings. H. F. G.

Electrolytic transport of water in normal lanthanum chloride solutions. J. Baborovský and O. Viktorin (Chem. Listy, 1934, **28**, 257—258).—Higher vals. are found at p_H 3·12 than at p_H 1·92. R. T.

Conductance of solutions of electrolytes. T. Shedlovsky, A. S. Brown, and D. A. MacInnes (Trans. Electrochem. Soc., 1934, **66**, 237—250).—The equiv. conductance of KCl and NaCl solutions at 25° has been redetermined up to 0·12 and 0·22*M*, respectively, and the results are shown to be accurately represented by Shedlovsky's modified Debye–Hückel–Onsager equation (A., 1932, 699). The application of the theory to the dissociated part of weak and intermediate electrolytes is discussed and illustrated by new data for $CH_2Cl·CO_2H$ at 25°, the thermodynamic dissociation const. of which is found to be $1·39(5) \times 10^{-3}$. H. J. T. E.

Ionic radius in aqueous solutions of electrolytes. L. Brüll (Gazzetta, 1934, **64**, 624—634).—The ionic radii obtained from mobility data are compared with the parameter *a* in the theory of Bonino (this vol., 254). This quantity is identified with the diameter of the hydrated ion. The following hydration vals. are derived: Li^+ 7·5, Na^+ 3·0, K^+ 1·0, Ca^{++} 8·0, Sr^{++} 4·5, Ba^{++} 3·5, Zn^{++} 8·0. O. J. W.

Estimation of limiting equivalent conductivity from the streaming currents. K. Gostkowski (Acta phys. polon., 1933, **2**, 215—218; Chem. Zentr., 1934, i, 827).—Electrokinetic potential V and Λ_∞ are connected by the equation $\Lambda_\infty/\Lambda'_\infty=KV/V'$. Λ_∞ for HCl calc. from known data for KCl and HCl is 444, and by comparison with $Pb(NO_3)_2$ instead of KCl, 446; using Λ_∞ for NaOH (204·5) it is 409. This val. for NaOH is too small, and when the new val. of 222 is used Λ_∞ for HCl is 444. L. S. T.

Behaviour of aqueous solutions in a high-frequency electric field. P. V. Zimakov (Compt. rend. Acad. Sci. U.R.S.S., 1934, **3**, 450—453).—Observations have been made on the effect of high-frequency discharges in aq. $CH_2Cl·CH_2·OH$, NaOAc, NaI, $Al_2(SO_4)_3$, and other solutions contained in a glass tube with a H_2O-vapour cloud (I) over the solution. The discharge is accompanied by chemical change (*e.g.*, aq. NaI forms I). The solution must first be warmed to 70—90° to produce (I). H. J. E.

Salt error of the quinhydrone electrode and the activity coefficient of the hydrogen ion in concentrated neutral salt solutions. A. Urmánczy (Magyar chem. Fol., 1933, **39**, 124—137; Chem. Zentr., 1934, i, 3322).—Data are recorded for aq. KCl, NaCl, $BaCl_2$, $CaCl_2$, $MgCl_2$, KNO_3, $NaNO_3$, $Ca(NO_3)_2$, $Mg(NO_3)_2$, K_2SO_4, Na_2SO_4, and $MgSO_4$ at 25°. At salt concn. $> N$ the salt error (I) $\propto$ the equiv. salt concn. For NO_3' and Cl′, (I) is negative. For SO_4'' it is positive. The activity coeff. of H˙ in 0·01*N*-HCl containing neutral salts is calc. Its logarithm $\propto$ the salt concn. H. J. E.

Effect of certain substances used in photography on the potential of the silver bromide electrode. V. A. Veidenbach (J. Appl. Chem. Russ., 1934, **7**, 339—342).—The potential *E* at a AgBr electrode in the cell Ag|AgBr–*x*KBr|saturated NH_4NO_3|saturated KCl–$HgCl_2$|Hg is unaffected by gelatin, Na_2SO_3, and Na_2SO_4; these substances can hence influence only the developer, its oxidation–reduction potential, or the process of formation of the image. KBr lowers *E*, and thus retards development. R. T.

Physico-chemical properties of solutions in condensed gases. VI. Electrode potentials in liquid ammonia. V. A. Pleskov and A. M. Monoszon (J. Phys. Chem. U.S.S.R., 1933, **4**, 696—702).—Referred to Pb|0·1*N*-$Pb(NO_3)_2=0$ at −50°, the observed electrode potentials, ϵ, are Zn −0·848; Cd −0·510; H_2 −0·331; Cu 0·103; Ag 0·472, and Hg 0·414. Activity coeffs. in 0·1*N* solution, based on $\epsilon=0$ for Pb and also on $\epsilon=0$ for Pb in aq. solution, are recorded. Ch. Abs. (*e*)

Phenomena at the contacts between electrodes and electrolytes. I. So-called electrode–electrolyte resistance to the passage [of a current]. E. Denina (Gazzetta, 1934, **64**, 527—563).—A crit. summary of the various methods used for the measurement of the so-called "transfer resistance" at an electrode–electrolyte interface during the passage of an electric current. Experimental data and the theories of the nature of this resistance are discussed. O. J. W.

A. **Influence of electrolytes on the electrification of water forced through a capillary tube.** T. Malarski and K. Gostkowski. B. **Relation between electrokinetic potential and equivalent conductivity.** K. Gostkowski (Acta phys. polon., 1932, **1**, 465—482, 483—486; Chem. Zentr., 1934, i, 520).—A. The effect of 1-, 2-, 3-, and 4-valent cations and anions on the potential has been measured.

B. The electrification of electrolyte solutions on passing through a capillary [measured by the potential (*V*) of a Pt plate in the issuing liquid] is related to the equiv. conductivity (λ_∞) by $\lambda'_\infty/\lambda''_\infty=K(V''/V')$, where $K=1$ approx. H. J. E.

Diffusion in liquids. VIII. Theory of the "boundary layer" of dilute electrolyte solutions. IX. Diffusion of dilute electrolytes into one another. X. Potential difference between dilute electrolytes in contact. K. Sitte (Z. Physik, 1934, **91**, 622—641, 642—650, 651—659).—VIII. The theories of Planck and Henderson are discussed, and formulæ representing first approximations are obtained.

IX. Experiment shows no essential difference between diffusion of electrolytes into one another and their separate diffusion into H_2O; the formation of a "boundary layer" as postulated by Planck could not be observed. Both colourless and coloured electrolytes were used.

X. Chang's observed time variation of potential difference (cf. A., 1933, 468) can be explained by ordinary diffusion processes. A. B. D. C.

Electric boundary layer disturbance. IV. Effect of an alternating electric field on the permeability potential of a membrane. M. Shikata and K. Kitao (Bull. Agric. Chem. Soc. Japan, 1934, **10**, 90—91).—The p.d. between the sides of a collodion membrane (I) separating KCl solutions of different concn. almost disappears when (I) is placed for 10—30 sec. in a 220-volt a.c. field of 60 cycles. In 5—10 min. it returns to the normal val. Ch. Abs. (*e*)

Electrolytic metal potentials in pure buffer solutions. S. Bodforss (Kungl. Fysiogr. Sällskapets I Lund Förhandl., 1933, **3**, 33 pp.; Chem. Zentr., 1934, i, 829).—The slip potentials (I) of different metals have been measured in various salt and buffer solutions (*e.g.*, phosphate, tartrate, acetate, sulphate) in an atm. of H_2. Renewal of the metal surface by rotation causes the potential to become negative with increasing velocity of rotation, and this potential tends towards a limiting val. (II). (II) for Sn, Bi, Cd, and Pb is reached at 600—1000 r.p.m. With Cu, Ag, W, and Ni, (II) is reached at such a high rotation ($>$ 2000 r.p.m.) that (I) is quickly destroyed. For most metals (II) is a linear function of p_H and is independent of the nature of the anion concerned. It is improbable that the metals function in the sense of a Pt–H_2 electrode. The stationary potentials can generally be satisfactorily determined. They are more noble than (I) and are dependent on p_H and the anions present. L. S. T.

Acidity of substituted phenols and thiophenols. G. Schwarzenbach and H. Egli (Helv. Chim. Acta, 1934, **17**, 1176—1182).—Normal acidity potentials (A., 1930, 1526) of PhOH and PhSH with Cl, Br, I, Me, OH, and OMe as substituents have been determined at 20° in 48·95 and 95 vol.-% EtOH. F. L. U.

Influence of a substituent on the acidity of an organic acid. I. G. Schwarzenbach and H. Egli (Helv. Chim. Acta, 1934, **17**, 1183—1196).—The question of the extent to which the influence of a substituent on acidity is purely electrostatic is discussed. From the results recorded (preceding abstract) it appears that the acidity of thiophenols with *m*-substituents is 200 mv., and with *p*-substituents 205 mv., $>$ that of the corresponding phenols. The relation of acidity to the composition of the solvent depends on the nature and position of the substituent. These facts are best interpreted by assuming that the influence of a substituent is partly electrostatic, but that another effect is superimposed whereby the electronic structure of the atom carrying the acid H is modified, thus altering the energy of expulsion of a proton. F. L. U.

Reduction potential of organic compounds. J. Hirade (J. Biochem. Japan, 1934, **20**, 161—191).—The reduction potential (I) of various org. compounds in $0{\cdot}05M$ aq. solution at p_H 7—12 at 38° has been determined colorimetrically and electrometrically with plain (II) and platinised Pt electrodes (III). (I) attains an equilibrium or " limit " val. (IV) only after a long time, and the use of a " quasi-equilibrium " point (V) is advocated; (V) is generally attained more rapidly with (III) than with (II). Concn. of the substance has little effect on the time necessary for attainment of (IV). The vals. of (V) are significantly influenced by p_H and, unlike those of (IV), are dependent on the nature of the electrode. F. O. H.

Reversible oxidation–reduction potentials in dye systems. B. Cohen (Cold Spring Harbor Sympos. Quant. Biol., 1933, **1**, 195—204).—Chemical consts. of a series of indophenols, aminoindophenols, indamines, thiazines, oxazines, indigotinsulphonates, safranines, neutral-red, rosindulines, and rosindones are presented. Ch. Abs.

Reversible two-step oxidation. L. Michaelis (Cold Spring Harbor Sympos. Quant. Biol., 1933, **1**, 224—229).—Electrometric titration curves are given for pyocyanine and a series of " viologens." Ch. Abs.

Effect of animal charcoal on oxidation–reduction processes. F. Johne and H. Weden (Biochem. Z., 1934, **273**, 147—153).—Animal C at neutral and faintly acid p_H in presence of O_2 oxidises $K_4Fe(CN)_6$ almost completely to $K_3Fe(CN)_6$, but in strongly alkaline ($0{\cdot}2N$-NaOH) solution the reverse reaction occurs quantitatively, whilst at p_H between these limits equilibrium mixtures of the two compounds are formed. The potentials of the various mixtures at alkaline, neutral, and faintly acid p_H agree accurately with those of the O_2 electrode at the same p_H. In more strongly acid solution, however, partial reduction occurs. P. W. C.

Titration curves of some phosphoric esters containing three carbon atoms and of inosinepyrophosphoric acid. M. Kiessling (Biochem. Z., 1934, **273**, 103—108).—p_K vals. for α- and β-glycerophosphoric, phospho- and diphospho-glyceric, dihydroxyacetone-, pyruvic acid-, synthetic glyceraldehyde-, and hexosedi-phosphoric, and phosphoric acid are recorded. The 3-carbon phosphoric esters are always stronger acids than H_3PO_4 in the first stage, and frequently but not always in the second stage of dissociation. Titration curves for Lohmann's inosinepyrophosphoric acid (I) and adenylpyrophosphoric acids before and after hydrolysis and the analogy between free adenylic and inosinic acids provide fresh evidence for the existence of (I). P. W. C.

Liquid potential and the activity coefficients of the ions. Z. Szabó (Magyar chem. Fol., 1933, **39**, 145—153; Chem. Zentr., 1934, i, 3036).—A graphical method for calculating the potential at the liquid boundary from the mean activity coeff. of the electrolyte is described. H. J. E.

Cell using the oxidation energy of alcohol. V. Karpen (Compt. rend., 1934, **199**, 708—710).—In the cell graphite|33% aq. HNO_3|NaOH+MeOH (50 g. NaOH+50 c.c. MeOH)|platinised Pt with a porous diaphragm separating the two solutions, the anode polarises owing to oxidation, but recovers on breaking circuit for a few min., after which the e.m.f. is 1·83 volt. The reaction at the cathode is $2HNO_3+8H=5H_2O+N_2O$, and at the anode $MeOH+2O+NaOH=HCO_2Na+2H_2O$. The e.m.f. is close to the val. calc. from the energy changes. Analogous results are obtained when MeOH is replaced by other reducing agents. R. S. B.

Electrochemistry of gallium. H. C. Fogg (Trans. Electrochem. Soc., 1934, **66**, 221—229).—The amphoteric character of Ga is compared with that of Al, and observations on the electrodeposition of the metal and its electrode potential are reviewed. H. J. T. E.

Anodic behaviour of thallium in the hydrogen halide acids. O. Pip (Z. Physik, 1934, **91**, 329—335).—Electrolytic valve action is shown by Cl′ and Br′. A. B. D. C.

" Dead space " correction in gas reaction rate measurements. A. O. Allen (J. Amer. Chem. Soc., 1934, **56**, 2053—2054).—A formula is derived for the effect on the measured pressure of the " dead space," or part of the reaction system external to the controlled-temp. bath. E. S. H.

Cause of changes in rate of some gas reactions. M. W. Travers, R. V. Seddon, and P. F. Gay (Nature, 1934, **134**, 662).—A discussion. L. S. T.

Emission wave theory of periodic reactions. III. F. M. Schemjakin (J. Gen. Chem. Russ., 1934, **4**, 444—451).—A mathematical derivation of the formula $\lambda v=$const. (this vol., 363) is given. R. T.

" After-burning " in gas explosions. B. Lewis and G. von Elbe (J. Chem. Physics, 1934, **2**, 659—664; cf. A., 1933, 368).—Conclusions reached by other workers (A., 1927, 317; 1933, 30; this vol., 368) are criticised, and experiments are recorded which show that with properly designed explosion vessels the ratio max. pressure : initial pressure in H_2–O_2 mixtures is independent of the radius of the vessel. " After-burning " is fictitious and cannot invalidate the determination of heat capacities of gases by the explosion method. F. L. U.

Effect of unequal temperature distribution on the maximum pressure developed in explosions

in a closed vessel. B. LEWIS and G. VON ELBE (J. Chem. Physics, 1934, 2, 665—668; cf. preceding abstract).—A method of calculating the difference in max. pressure due to the existence of a temp. gradient is given. For O_3 explosions the difference amounts to $<0{\cdot}2$—0·5%, and for H_2+O_2+inert gas to 0·2—0·8%. F. L. U.

Activation energies of reactions involving oxygen. I. Reaction $O+H_2=H_2O$. R. S. BEAR and H. EYRING (J. Amer. Chem. Soc., 1934, **56**, 2020—2025).—Theoretical. The activation energies of excited and normal O atoms with H_2 mols. are deduced. E. S. H.

Non-explosive thermal decomposition of azoimide. R. MEYER and H. J. SCHUMACHER (Z. physikal. Chem., 1934, **170**, 33—40).—The decomp. at 306—330° under 30—200 mm. in quartz or hard glass vessels is largely heterogeneous and follows the unimol. law. Traces of impurities have a powerful catalytic action, and easily cause explosion. At least 94% of the product of reaction consists of NH_3 and N_2; only 6% of the HN_3 decomposes into N_2 and H_2. The primary (wall) reaction is possibly $HN_3=NH+N_2$ (exothermic). After preservation of HN_3 in glass at room temp. for some months it undergoes thermal decomp. more slowly, but has a greater tendency to explode. R. C.

Kinetics of the oxidation of gaseous hydrocarbons. II. Oxidation of ethane. E. W. R. STEACIE and A. C. PLEWES (Proc. Roy. Soc., 1934, **A**, **146**, 583—597).—In the oxidation of C_2H_6 and its mixtures with MeCHO and C_2H_4 there is a long period of inhibition, which decreases as the total pressure is raised. Heating to a high temp. or long pumping intensifies the inhibition period, whilst packing diminishes it. Aldehydes, H_2, and the products of the reaction reduce or eliminate it; N_2 increases it. Chains started by C_2H_4 can be continued by C_2H_6. Analysis shows that H_2 and C_2H_4 are present at the end of the inhibitory period and throughout the reaction. It is concluded that the inhibition period is a surface effect leading to the formation of C_2H_4, and that the primary process in the oxidation of C_2H_6 is dehydrogenation, followed by a chain oxidation of the C_2H_4 thus produced. Further cracking of the paraffin occurs during the oxidation of the olefine. L. L. B.

Mechanism of thermal decomposition of hydrocarbons. Kinetics of decomposition of ethane and propane. A. I. DINTZES and A. V. FROST (Compt. rend. Acad. Sci. U.R.S.S., 1934, **3**, 510—515).—The decomp. of C_2H_6 (at 678°/1·7—22·3 mm.) and of C_3H_8 (at 616—666°/1·05—78 mm.) in a quartz bulb does not follow a unimol. law. A chain mechanism for the hydrocarbon cracking reaction is suggested. H. J. E.

Kinetics and mechanism of decomposition of hydrocarbons. II. Thermal decomposition of octane and of βε-dimethylhexane under atmospheric pressure. A. I. DINTZES and A. V. FROST (J. Gen. Chem. Russ., 1934, **4**, 610—615).—80—90% of *n*-octane (I) decomp. at 500—570° is accounted for by the reactions $CH_4+C_7H_{14}\longleftarrow(I)\longrightarrow C_2H_6+C_6H_{12}$, proceeding with equal velocity; variations in temp. influence only the velocity of these reactions, according to the equation $\log K=14{\cdot}70-14{,}100/T\pm 0{\cdot}09$. Of the olefines formed, 60—70% undergo intensive decomp. to yield a mixture of H_2, CH_4, C_2H_6, C_3H_8, C_3H_6, and C_4H_8. Under analogous conditions, 75—85% of decomposed βε-dimethylhexane (II) yields CH_4 and C_7H_{14}, 40% of which is further decomposed as in the case of (I). Cu does not catalyse the decomp. of (II). R. T.

Thermal reaction between chlorine and gaseous formaldehyde. I. R. SPENCE and W. WILD (J.C.S., 1934, 1588—1593; cf. A., 1933, 1036).—Explosions, accompanied by the emission of light, terminated the slow reaction at 150°, and also occurred in vessels activated by a long series of slow reactions. In the explosion, any excess of CH_2O is decomposed ($CH_2O=CO+H_2$), whilst during the slow reaction, CH_2O is polymerised in addition to the main reaction, $CH_2O+Cl_2=CO+2HCl$. The reaction velocity is greatly affected by the state of the surface, and the process is probably of the homogeneous chain type. J. G. A. G.

Induced decomposition of acetaldehyde. A. O. ALLEN and D. V. SICKMAN (J. Amer. Chem. Soc., 1934, **56**, 2031—2034).—The decomp. of MeCHO is induced by the decomp. of azomethane (I) occurring when their mixture is heated at about 300°. A kinetic examination of the reaction suggests that the Me radicals from the (I) start a chain-type decomp. of MeCHO. E. S. H.

Thermal decomposition of formaldehyde. C. J. M. FLETCHER (Proc. Roy. Soc., 1934, **A**, **146**, 357—362).—The thermal decomp., $CH_2O\longrightarrow CO+H_2$, is a homogeneous bimol. reaction over the pressure range 30—400 mm. Simultaneous condensation reactions occur. The energy of activation over a temp. range 510—607° is 44,500 g.-cal. The rate of reaction is approx. equal to the rate of formation of activated mols., according to the usual expression $Z\times e^{-E/RT}$. L. L. B.

Modes of activation of aldehyde molecules in decomposition reactions. C. N. HINSHELWOOD, C. J. M. FLETCHER, F. H. VERHOEK, and C. A. WINKLER (Proc. Roy. Soc., 1934, **A**, **146**, 327—333).—The curves representing the variation with pressure of the time of half-decomp. of MeCHO and of N_2O show that the reactions are kinetically composite. This can be explained on the assumption of a no. of different modes of activation of the mols., which are characterised by a study of the behaviour of CH_2O, MeCHO, EtCHO, and $CCl_3{\cdot}CHO$. L. L. B.

Thermal decomposition of propaldehyde. C. A. WINKLER, C. J. M. FLETCHER, and C. N. HINSHELWOOD (Proc. Roy. Soc., 1934, **A**, **146**, 345—356).—The thermal decomp. of EtCHO has been reinvestigated over the pressure range 400—0·5 mm. The reaction is kinetically complex and is interpreted as the resultant of several homogeneous quasi-unimol. reactions. The chemical nature of the reaction products varies a little with the pressure. The influence of H_2 on the reaction has been studied. The energy of activation shows a well-defined variation with pressure. L. L. B.

Thermal decompositions of aldehydes. W. A. Bone (Chem. and Ind., 1934, **53**, 813—814).—Polemical. In explaining the thermal decomp. of MeCHO (cf. preceding abstracts) the authors have overlooked the possibility that at the temp. employed MeCHO may be in equilibrium with $(CH_2)_2O$ and $CH_2\colon CH\cdot OH$. H. A. P.

Thermal decomposition of acetaldehyde. M. W. Travers (Nature, 1934, **134**, 569).—The view that the thermal decomp. of MeCHO is a homogeneous reaction unaffected by the character of the containing vessel (see above) is further criticised. L. S. T.

Homogeneous unimolecular decomposition of gaseous methyl nitrite. E. W. R. Steacie and G. T. Shaw (Proc. Roy. Soc., 1934, A, **146**, 388—395).—The thermal decomp. of gaseous MeO·NO ($\longrightarrow NO+0\cdot5CH_2O+0\cdot5MeOH$) is a homogeneous first-order reaction, and proceeds at a measurable rate between 190° and 240°. The rate of reaction is given by $K=1\cdot84\times10^{13}e^{-36400/RT}$ sec.$^{-1}$ L. L. B.

Influence of fluid velocity on heterogeneous reactions. III. Extension of the fundamental equation and some of its applications. S. Uchida (J. Soc. Chem. Ind. Japan, 1934, **37**, 456—457B).—Mathematical analogies with heat transfer processes are developed (cf. A., 1933, 911; this vol., 36). A. J. H.

Keten. II. Rate of polymerisation.—See this vol., 1336.

Velocity of decomposition of nitric esters at relatively low temperatures. M. Lambrey (Compt. rend., 1934, **199**, 725—726).—Guncotton (I), containing (*a*) 13·34% N, stabilised by boiling with H_2O, and (*b*) 13·80% N, stabilised by Muraour's method, when heated at 30° gives off NO with decreasing velocity, the total evolution being 0·5 mg. per kg. of (I). On raising the temp. a further quantity is evolved. It is inferred that an impurity is present. After evacuating (I) at 50° decomp. is uniform when residual impurity has been removed, and is such that 0·001 of (I) decomposes in 1100 years at 43°; the rate is 0·1 of this at 36·5°. Method (*a*) also favours removal of impurity. Similar results have been obtained with pentaerythrityl tetranitrate, and with (I)+glyceryl trinitrate. R. S. B.

Chemical kinetics of ion reactions. V. Neutral salt action in concentrated salt solutions. A. von Kiss (Magyar chem. Fol., 1933, **39**, 162—168; Chem. Zentr., 1934, i, 3435).—In six ion reactions of zero order (*e.g.*, for $CH_2Br\cdot CO_2'+S_2O_3''=S_2O_3\cdot CH_2\cdot CO_2''+Br'$) the log. of the velocity coeff. $\propto$ the concn. of the added salt (for certain salts and concn. ranges). H. J. E.

Determination of velocity of hydrolysis of acid anhydrides by the aniline–water method. II. S. E. Vles (Rec. trav. chim., 1934, **53**, 961—966; cf. A., 1933, 1250).—Velocities of hydrolysis of AcCl, BzCl, $COCl_2$, $ClCO_2Me$, and $ClCO_2Et$ have been compared. F. L. U.

Factors affecting -onium salt formation. W. C. Davies and W. P. G. Lewis (J.C.S., 1934, 1599—1604).—The rates of addition (I) at 35° of alkyl halides, RX, to substituted dimethyl- (II) and diethyl-anilines (III), phenyldiethylphosphines, and $AsPhEt_2$ have been determined in $COMe_2$, aq. $COMe_2$, and aq. EtOH, and the following products are described: p-*chlorophenyltrimethylammonium iodide*, m.p. 200—202° (decomp.), *phenyltriethylphosphonium bromide*, m.p. 187—188°, and p-*phenoxyphenyltriethylphosphonium iodide*, m.p. 181—182°. The (I) of $RBr<RI$, and $MeX>EtX>Bu^{\alpha}X$. The reactivity of the $PhEt_2$ bases is phosphine>arsine>amine, parallel with the order of dipole moments, and that of (II) is >(III) owing to steric factors. Substituents in the Ph group of (II) afford the following order of reactivity: $OEt>OMe>p\text{-}Me>H>p\text{-}Cl>p\text{-}Br>p\text{-}I>m\text{-}NO_2>p\text{-}NO_2$. The reaction involves (*a*) anionisation of the halogen in RX and (*b*) the co-ordination of the base, by its lone electron pair, to the $\colon CH_2$ in RX. Step (*b*) determines the velocity, which is accelerated by electron-releasing groups (*e.g.*, *p*-Me) and retarded by electron-attracting substituents (*e.g.*, $p\text{-}NO_2$) in the bases. J. G. A. G.

Beckmann change. II. Kinetics of the spontaneous rearrangement and solvent effects. A. W. Chapman (J.C.S., 1934, 1550—1555; cf. A., 1933, 952).—The velocity of the Beckmann rearrangement of benzophenoneoxime picryl ether (I) has been determined at 70—100° in polar and non-polar solvents. Consistent with the view that the transformation involves the development of electric charges at the ends of the linkings concerned in the migration of the picryloxy- and hydrocarbon groups, the velocity is markedly increased by substances containing polar groups, including (I) and its change product. The catalytic activities of compounds with one principal dipole are in the same order as the dipole moments, and non-polar compounds with equal and opposite dipoles in each mol. are catalysts when the dipoles are sufficiently separated. In CCl_4 at infinite dilution, mols. of (I) can be activated only by collision with solvent mols., and the activation energy, *E*, is 30,250 g.-cal., but when activation occurs by collisions between solute mols., *E* falls to approx. 23,000. J. G. A. G.

Hydration of unsaturated compounds. III. Rate of hydration of trimethylethylene in aqueous solutions of acids. H. J. Lucas and Y. P. Liu (J. Amer. Chem. Soc., 1934, **56**, 2138—2140; cf. this vol., 369).—The rate of hydration of $CHMe\colon CMe_2$ (I) (to $CMe_2Et\cdot OH$) by dil. HNO_3 (II) at 25° and 35° and const. ionic strength is unimol. with respect to both [(I)] and [(II)]. The ratio $k_{35^\circ}/k_{25^\circ}$ is 2·83 [for two concns. of (II)]; the heat of activation is 18·92 kg.-cal. For a fixed concn. of (II), the rate is increased by addition of KNO_3. (I) is hydrated at a much slower rate than *iso*butene (*loc. cit.*). The rate of hydration of (I) by the following acids (concn. approx. $0\cdot1M$) at 25° decreases in the order quoted: $H_2S_2O_6$, H_2SO_4, HCl, $HClO_4$, HBr, (II), $p\text{-}C_6H_4Me\cdot SO_3H$, picric acid, $H_2C_2O_4$, AcOH. H. B.

Mutarotation of arabinose. C. N. Riiber and N. A. Sorensen (Kong. Norske Vidensk. Selsk. Skr., 1933, No. 7, 1—49; Chem. Zentr., 1934, i, 2737—2738).—Pure arabinose, m.p. 160°, has $[\alpha]_D^{20}$ +105·46° in H_2O. The concn. and *n* of an aq. solution can be calc. from the *d* by Berner's equations, and from them the mol. solution vol. (I) and refraction (II). The vol. change on dissolution is calc. by following the process of evaporation dilatometrically. Mutarotation of arabinose takes place according to the equation $[\alpha]_{D,t}^{20} = +105{\cdot}46° + 76{\cdot}49 \times 10^{-0{\cdot}029t} + 9{\cdot}55 \times 10^{-0{\cdot}108t}$, and therefore is not a unimol. reaction. The calc. initial [α] (+191·5°) agrees better than the hitherto accepted val. (+174°) with that derived from the Hudson rule (+203°). In differences of mol. [α], (I), and (II) between glucosides and sugar, β-arabinose resembles α-*d*-galactose. The name "anomerism" is proposed for such cases. From a comparison with the corresponding α-galactose derivative the vals. $[\alpha]_D^{20}$ +84°, (I) 92·24 ml., and (II) 30·9 are calc. for non-cryst. β-arabinose. Saturation experiments at 0° show that for the modifications present besides α-arabinose, [α] = +46° approx., so that a third form must exist. This third form contains no CHO group, since the Schiff and Angeli reactions are negative, and the CHO absorption band is absent from the spectrum. R. N. C.

Kinetics of the bromination of nitroethane in hydrogen halides. R. JUNELL (Arkiv Kemi, Min., Geol., 1934, **11**, **B**, No. 27, 6 pp.).—The two phases of the bromination of $EtNO_2$ in *N*-HBr at 69·85 ±0·05° to $C_2H_4Br{\cdot}NO_2$ and $C_2H_3Br_2{\cdot}NO_2$ have unimol. velocity coeffs. ($\times 10^{-4}$) of 2·5 and 27·7 and in *N*-HCl of 2·8 and 32·0, respectively. The vals. are independent of [Br] (cf. A., 1929, 516). F. O. H.

Kinetics of the bromination of α-carboxydiethyl- and methyl-α-carboxyethyl-sulphone in aqueous solutions. L. RAMBERG and A. MELLANDER (Arkiv Kemi, Min., Geol., 1934, **11**, **B**, No. 31, 6 pp.).—With initial concns. of $> 0{\cdot}1M$ per litre of the reactants, the unimol. velocity coeffs. at 35° in *N*-HBr are dependent on [sulphone], but independent of [Br], and have vals. ($\times 10^{-3}$) of 0·379 and 0·68—0·69 for the Me and Et compounds, respectively. With lower concns. the reaction deviates from a unimol. one. The racemisation coeff. of *l*- and bromination coeff. of *dl*-$CHMe(SO_2Et){\cdot}CO_2H$ at 25·15° and under identical conditions of concn. etc. have vals. ($\times 10^{-3}$) of 0·273 and 0·249, respectively. F. O. H.

Velocity of bromination of bromosulphoacetic and α-sulphopropionic acids in hydrobromic acid. L. RAMBERG and E. SAMÉN (Arkiv Kemi, Min., Geol., 1934, **11**, **B**, No. 35, 6 pp.).—The unimol. velocity coeff. (I) ($\times 10^{-5}$) for the bromination of $SO_3H{\cdot}CHBr{\cdot}CO_2H$ (II) is 72·4—72·5 (in *N*-HBr at 60°), whilst those for $SO_3H{\cdot}CHMe{\cdot}CO_2H$ (III) are 1·04—1·22 (in *N*-HBr at 60°), 0·79 (in 0·5*N*-HBr at 60°), and 8·7 (in *N*-HBr at 80°). As with α-carboxyalkylethylsulphones (cf. preceding abstract), the reaction with (II) is unimol. with excess of Br; with equivs. of the reactants, the reaction becomes "sesquimol." as it approaches completion. With (III) such deviations are slight. Other variations of (I) with temp. are discussed. $CH_2(SO_3H)_2$ is extremely slowly brominated at 60° (cf. A., 1929, 909). F. O. H.

Kinetics of the bromination of aliphatic αα-disulphones in aqueous solution. L. RAMBERG and E. SAMÉN (Arkiv Kemi, Min., Geol., 1934, **11**, **B**, No. 40, 6 pp.).—The bromination of $CHMe(SO_2Me)_2$ (I) or $CHMe(SO_2Et)_2$ (II) in 0·5*N*- or *N*-HBr is a bimol. reaction even with large excess of Br. (I) has velocity coeffs. ($\times 10^{-3}$) of 4·67—4·84 (at 80° in *N*-HBr) and (II) of 1·91—1·92 (at 60° in *N*-HBr), 5·31—5·69 (at 60° in 0·5*N*-HBr), and 7·40—7·42 (at 80° in *N*-HBr). Br does not react with $MeSO_2Et$ (III) at 80°. Aq. (I) and (II), but not (III), develop absorption bands in the ultra-violet region on treatment with alkali. F. O. H.

Velocity of bromination and racemisation of α-phenylsulphinopropionic acid. L. RAMBERG and I. HEDLUND (Arkiv Kemi, Min., Geol., 1934, **11**, **B**, No. 41, 4 pp.).—The velocity coeff. of racemisation of *d*-$CHMe(SO_2Ph){\cdot}CO_2H$ at 25·11° in *N*-HBr is $34{\cdot}8 \times 10^{-5}$, whilst that of bromination under parallel conditions is $52{\cdot}3$—$53{\cdot}9 \times 10^{-5}$ at 30° and $31{\cdot}8 \times 10^{-5}$ at 25° (equiv. to $32{\cdot}2 \times 10^{-5}$ at 25·11°). The data are compared with those for $CHMe(SO_2Et){\cdot}CO_2H$ (cf. preceding abstract). F. O. H.

Kinetics of salt formation of nitroethane. R. JUNELL (Arkiv Kemi, Min., Geol., 1934, **11**, **B**, No. 34, 5 pp.).—The reaction $EtNO_2 + NaOH \longrightarrow CHMe{:}NO_2Na$ was followed by Br titrations. It is bimol. (k=36 at 0·05°), and is slightly retarded by NaCl or by replacing NaOH by $Ba(OH)_2$. A. G.

Rearrangement of nitroethane in acid solution. R. JUNELL (Arkiv Kemi, Min., Geol., 1934, **11**, **B**, No. 30, 6 pp.).—Acethydroxamic acid (I) is determined in the presence of $EtNO_2$ and AcOH by oxidation with $KBrO_3$ and HCl and determination of excess of oxidising agent. The formation of (I) from $EtNO_2$ in *N*-HCl is a unimol. reaction, and the coeff. ($0{\cdot}25 \times 10^{-3}$ at 69·85°) is nearly the same as that ($0{\cdot}28 \times 10^{-3}$) of the bromination of $EtNO_2$. Probably in both cases the slow stage is the formation of *aci*-$EtNO_2$, which then yields rapidly either (I) or $C_2H_4Br{\cdot}NO_2$. A. G.

Velocity of decomposition of diazo-compounds in water. XV. E. YAMAMOTO, R. GOSHIMA, and J. HASHIMA (J. Soc. Chem. Ind. Japan, 1934, **37**, 512—515B).—Decomp. velocity coeffs. for temp. of 0—60° are recorded for the diazo-compounds from β-naphthylamine-5 : 7- and -6 : 8-disulphonic acids and 8-amino-α-naphthol-3 : 6-disulphonic acid. A. G.

Kinetics of alkaline hydrolysis of betaine-amides.—See this vol., 1340.

Influence of the gaseous medium on the luminosity accompanying detonation of explosives. A. MICHEL-LÉVY and H. MURAOUR (Chim. et Ind., 1934, **32**, 783—786).—From detonation experiments with (*a*) crystals of PbN_6 placed at intervals in the form of an isosceles triangle and detonated at the apex, and (*b*) a mixture of $C(NO_2)_4$ and PhMe placed in a circular groove in a brass plate, it is concluded that the luminous effects (I) accompanying detonation are due to the shock wave propagated in the surrounding medium (II). (I) vary with the nature of (II), luminosity decreasing in the order A, N_2, CO_2 C_4H_{10}, *i.e.*, as the sp. heat increases. Results are recorded photographically. C. C.

Kinetics of benzoylation of cellulose. A. L. Bernoulli, M. Schenk, and F. Rohner (Helv. Chim. Acta, 1934, 17, 897—918).—Benzoylation of natural cellulose (I) by Bz_2O is very slow and incomplete except after pretreatment of (I) with NaOH, or in presence of a mixture (II) of C_5H_5N and CH_2PhCl (2 : 1) which disperses it. In measuring the velocity of the reaction at 94° BzCl diluted with C_5H_5N and a hydrocarbon was used for (I), viscose, and mercerised cotton, and Bz_2O for viscose dispersed in (II). The reaction in every case is topochemical and heterogeneous. In dispersed cellulose the solution units are not single mols., but crystallites. F. L. U.

Kinetics of evaporation of mercury in the presence of thin layers of capillary-active substances. S. L. Pupko and M. A. Proskurnin (J. Phys. Chem. U.S.S.R., 1933, 4, 523—528).—Using an ionisation manometer, the speed of evaporation (I) of Hg was found to decrease rapidly under a unimol. layer of oleic acid, or with a triolein layer < unimol. If the Hg is covered with a film of oleic acid (4 mols.) (I) increases gradually, probably because of evaporation of the film itself. Ch. Abs. (*e*)

Oxidation reactions initiated by hydrogen atoms. K. H. Geib and P. Harteck (Z. physikal. Chem., 1934, 170, 1—19).—In H_2–O_2 mixtures at −190° to 100° H atoms cause formation of amounts of H_2O which are of the same order at all the temp. Below −80° H_2O_2 is also formed. H atoms bring about formation of CO_2 from CO and O_2 and oxidation of CH_4 and other hydrocarbons, although under the experimental conditions they react with neither CO nor CH_4. The exact mechanism is undecided; a considerable no. of reactions are apparently involved, their relative importance varying with temp. and concn. The energies of activation of $H+O_2+H_2=H_2O+OH$ and $H+O_2+CO=CO_2+OH$ are too small to be measured. H atoms may form HO_2 with O_2, a reaction which renders impossible long reaction chains, since the further reaction of HO_2 involves a finite heat of activation. Attempts to detect the presence of OH radicals in the reaction mixtures by means of their optical absorption failed. R. C.

Behaviour of carbon suboxide, and the reaction $C_3O_2 \rightleftharpoons CO_2+C_2$ in the homogeneous gas phase. A. Klemenc, R. Wechsberg, and G. Wagner (Z. physikal. Chem., 1934, 170, 97—111; cf. this vol., 969).—The polymerisation of C_3O_2 is an irreversible reaction catalysed by the walls of the vessel, and apart from a period of induction follows the unimol. law. When C_3O_2 is heated at 200° or above, CO_2 and CO are formed both from the gas and from the solid polymerisation product. The rate of formation of CO_2 in the former reaction is reduced by addition of CO_2, which, however, does not alter the rate of formation of CO. These observations are explained if the decomp. of C_3O_2 occurs by way of $C_3O_2 \rightleftharpoons CO_2+C_2$, the equilibrium const. of which is calc. from the observed reaction velocity at 200° to be $\sim 10^{-7}$. The C_2 formed polymerises to graphite, preventing the establishment of a permanent equilibrium. The presence of C_2 in the decomp. system at 200° is proved by the appearance in the absorption spectrum of the head of the Swan band, 4737 Å. Addition of O_2 to the reacting system increases the formation of CO_2 and CO. R. C.

Oxidation of carbon monoxide catalysed by nitrogen dioxide. R. H. Crist and O. C. Roehling (Science, 1934, 80, 338).—The rates of reaction at 500° have been investigated. The effect of NO_2 increases to a max. The catalysed reaction is sensitive to small amounts of H_2 or H_2O vapour, the rate increasing with an increase in concn. The appearance in the system of at. H chains, which increase the total rate of oxidation, is probable. L. S. T.

Kinetics of the decomposition of chloral and its catalysis by iodine. F. H. Verhoek and C. N. Hinshelwood (Proc. Roy. Soc., 1934, A, 146, 334—344).—The thermal decomp. of $CCl_3{\cdot}CHO$ is predominantly homogeneous, and the principal primary change is $CCl_3{\cdot}CHO=CHCl_3+CO$. Subsequent decomps. and condensation reactions also occur. The relation between reaction rate and initial pressure corresponds with that characteristic of a quasi-unimol. reaction. The rate is > that of MeCHO or EtCHO, but the energy of activation is 49,000 g.-cal., as great as for MeCHO. The reaction is accelerated by I, the catalytic reaction being of the first order with respect to the $CCl_3{\cdot}CHO$, and its rate increases in < direct proportion to [I]. The catalysis is relatively less effective than with MeCHO. L. L. B.

Hydrolysis of phenylalanine. E. Baur and H. Schindler (Biochem. Z., 1934, 273, 381—388; cf. A., 1933, 940).—Aq. extracts (I) (containing $Ca^{\cdot\cdot}$, $Mg^{\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, $NH_4^{\cdot}$, Cl', SO_4'', PO_4''', but no org. matter) of animal C accelerate the hydrolytic deamination of phenylalanine and shift the position of the "unilateral" equilibrium, (I) acting like an enzyme which combines with or is adsorbed on the reaction product $CH_2Ph{\cdot}CH_2{\cdot}OH$. The other product is NH_4HCO_3. W. McC.

Glutathione as an inductor in the oxidation of glucose. C. C. Palit and N. R. Dhar (J. Indian Chem. Soc., 1934, 11, 661—669).—Glucose is oxidised by air at room temp. in presence of glutathione, especially when phosphates are added. Addition of $Ce(OH)_3$, $Fe(OH)_2$, $Mn(OH)_2$, or $Cu(OH)_2$ increases the rate of oxidation. The induced reaction is further accelerated by light and by photosensitisers. E. S. H.

Addition of gaseous hydrogen chloride and hydrogen bromide to propene under the influence of catalysts. Equilibrium α-bromopropane ⇌ β-bromopropane. L. G. Brouwer and J. P. Wibaut (Rec. trav. chim., 1934, 53, 1001—1010).—At room temp. HCl combines with $CH_2{:}CHMe$ slowly in presence of SiO_2 gel, more quickly if the latter is impregnated with a suitable metal chloride such as $BiCl_3$. The product is mainly $Pr^{\beta}Cl$ (I) with no $Pr^{\alpha}Cl$ (II). The reaction with HBr occurs smoothly in presence of purified SiO_2 gel at room temp., giving (I) as the main product, with 1—2% of (II). Neither reaction is affected by the presence of O_2. The "peroxide effect" observed with HBr does not occur with HCl. At 250° and 275° the equilibrium proportions of (I) and (II) are about 2 : 1. The rate of transformation is very slow. F. L. U.

Catalysts for elimination of carbon monoxide from nitrogen–hydrogen mixtures.—See B., 1934, 959.

Hydrogenation of sulphur-containing compounds. I. Mechanism of decomposition of thiophen in presence of sulphides of metals and hydrogen. II. Decomposition of various sulphur-containing compounds in presence of MoS_2 and hydrogen. B. L. Moldavski and Z. I. Kumari (J. Gen. Chem. Russ., 1934, 4, 298—306, 307—309).—I. The catalytic action of sulphides on hydrogenation of thiophen to tetrahydrothiophen, BuSH, and C_4H_{10} and H_2S at 210—270°/30 atm. diminishes in the order $MoS_2>CoS>NiS=MnS>CdS$. CuS is a negative catalyst at $> 250°$, and a positive one at $< 250°$.

II. The velocity of elimination of S from R_2S heated at 230°/30 atm. H_2 diminishes in the order $R=CH_2Ph>CH_2{:}CH{\cdot}CH>Et>Pr>$*iso*-$C_5H_{11}$, and from RSH in the order $R=Ph>Et>$*iso*-C_5H_{11}.

R. T.

Mechanism of heterogeneous catalysis. E. Audibert (Ann. Mines, 1933, [13], 4, 138—162; Chem. Zentr., 1934, i, 815).—Taylor's theory of active centres is criticised. The anomalies in the strength of the adsorption fields are assumed to depend on the local irregularities of crystal structure of the adsorbing atom. Promoters are substances which can form mixed crystals with the catalyst. L. S. T.

Activity and structure of copper–zinc catalysts for the decomposition of methyl alcohol. N. N. Zolotov and M. I. Schapiro (J. Gen. Chem. Russ., 1934, 4, 679—682).—ZnO–CuO catalyst used for the decomp. of MeOH undergoes reduction at $\nless$ 220°, the CuO being reduced completely, and the ZnO partly. In consequence, α-brass is formed, the Zn content of which increases with duration of contact.

R. T.

Influence of certain physical and chemical factors on the activity of charcoal. V. Effect of treating charcoal with aqueous nitrates and oxidising salts on its adsorptive and catalytic activity. E. V. Alexeevski and A. P. Musakin (J. Gen. Chem. Russ., 1934, 4, 669—678).—Highly active C is obtained by soaking ordinary wood C in aq. nitrates, $ZnCl_2$, or $KMnO_4$, and then washing with aq. HNO_3. The adsorptive capacity (I) falls in the series $KMnO_4>ZnCl_2>AgNO_3>$Schweitzer's reagent $> Cu(NO_3)_2 > Al(NO_3)_3 > Fe(NO_3)_3 > Pb(NO_3)_2 > NH_4VO_3>KNO_3>KClO_3>$untreated C. The catalytic activity of the C in the reaction of decomp. of H_2O_2 varies inversely with the (I). R. T.

Rapid catalytic preparation of sodamide in liquid ammonia.—See this vol., 1330.

Catalytic oxidation of trioses and related compounds.—See this vol., 1335.

Chlorination of naphthalene with chlorine.—See this vol., 1342.

Synthesis of acetone in presence of catalysts.—See this vol., 1336.

Heavy hydrogen. III. Electrolytic separation of the hydrogen isotopes. A. Farkas and L. Farkas. **IV. Hydrogenation and exchange reaction of ethylene with heavy hydrogen.** A. Farkas, L. Farkas, and E. K. Rideal (Proc. Roy. Soc., 1934, **A**, **146**, 623—629, 630—639).—III. In the electrolysis of a mixture of light and heavy H_2O a preferential liberation of H^1_2 takes place. The gas evolved may reach equilibrium with the H_2O, corresponding with the reaction $H_2O+H^1H^2 \rightleftharpoons H^1H^2O+H^1_2$, the equilibrium const. being about 3·8 at room temp.

IV. Two reactions are involved in the interaction of C_2H_4 with H^1_2 and H^2_2 at a catalytically active Ni surface; an exchange reaction $C_2H^1_4+H^1H^2 \rightleftharpoons C_2H^1_3H^2+H^1_2$, and the usual reaction $C_2H^1_4+H^1H^2 \rightleftharpoons C_2H^1_5H^2$. The steric factors and the temp. coeffs. of these reactions are dissimilar. L. L. B.

Electrolysis of salt solutions by means of electrodes immersed in distilled water. P. Jolibois (Compt. rend., 1934, **199**, 706—708).—Salt solution at the bottom of two beakers is covered with distilled H_2O without mixing; the two salt layers are joined by an inverted U. On electrolysis at 300 volts of Cu, Ni, Ag, Zn, Mg, U, and Th salt solutions with Pt electrodes in the distilled H_2O, colloidal hydrated oxide (I) of the metal is produced at the surface of separation salt solution–H_2O in the cathodic vessel. (I) then migrates to the cathode, and is deposited as such, or may be retained by a filter. Pb hydrated oxide passes through the latter, and gives some Pb on the Pt. With metals forming sol. oxides the anodic and cathodic H_2O contain after electrolysis acid and base, respectively. The basic and acidic portions of a salt may thus be separated without the formation of metal. R. S. B.

Electrodeposition of chromium from aqueous chromic acid solutions containing hydrofluoric acid.—See B., 1934, 1015.

Europium, a rare member of the rare-earth group. B. S. Hopkins (Trans. Electrochem. Soc., 1934, **66**, 167—174).—The separation of Eu from Sm and Gd, and the properties of the metal and its compounds, are reviewed. H. J. T. E.

Production of metals of the cerium group. F Trombe (Trans. Electrochem. Soc., 1934, **66**, 231—235).—Recent work by the author and others on the electrolytic extraction of pure La and Nd from their fused chlorides and of pure Ce from a bath containing fused $CeCl_3$, KCl, and CaF_2 is reviewed, and some properties of these metals are summarised.

H. J. T. E.

Formation of oxides of nitrogen in a high-current electric discharge. N. G. Zalogin and G. M. Egorova (J. Phys. Chem. U.S.S.R., 1934, 5, 20—31).—A max. yield of N oxides was obtained with 87—90% O_2 (6 mg. HNO_3 per litre of gas passed). Change of discharge strength at const. frequency changes the abs. yield, but not the mixture giving the max. yield. The yield increases with $[O_3]$ in the discharge, but the products are the same as those in absence of O_3. Ch. Abs. (e)

Photolysis of water and the action of light on electrodes. R. Audubert (J. Phys. Radium, 1934, [vii], 5, 486—496).—In order to investigate the action of light on electrodes, photo-potentials were measured using electrodes of Cu_2O, CuO, CuI, Ag_2S, and Hg_2I_2

in various org. solutions rendered conducting by the addition of NaI or KI. Data on the influence of electrode surface layers, activity of the metallic ions, [H˙], and light intensity are tabulated. Theories of the mechanism are discussed. N. M. B.

Case of photochemical retardation of reaction. M. Trautz and H. E. Haas (Z. wiss. Phot., 1934, **33**, 129—144; cf. this vol., 1079).—The early experiments of Chastaing (Ann. Chim. Phys., 1877, **11**, 145), and of Thomas on the photochemical oxidation of $FeSO_4$, Na_2SO_3, Cu_2Cl_2, MeCHO, alkaline pyrogallol, and PhCHO, by light of different colours, have been repeated, using similar apparatus and procedure. The results are detailed. Some of the work of Trautz has also been tested. The case of PhCHO has been established; blue light accelerates, and infra-red light retards, the oxidation. Some positive and some negative results were obtained with Na_2S solutions. Other cases showed no retardations. J. L.

Formation of carbonyl chloride from chloroform and oxygen sensitised by irradiated chlorine. H. J. Schumacher and K. Wolff (Z. physikal. Chem., 1934, **B**, **26**, 453—462).—The formation of CCl_4 from $CHCl_3$ and Cl_2 in light (this vol., 740) is suppressed in presence of O_2 and the above reaction occurs. The velocity is given by $d[COCl_2]/dt=kI_{abs}[CHCl_3]^{\frac{1}{2}}$, the temp. coeff. is 1·23±0·05, and the quantum yield at 65° and a $CHCl_3$ pressure of ~100 mm. is 260±15%. R. C.

Dependence of the gradation of photographic layers on the wave-length of light. F. Bürki and W. Brückner (Helv. Chim. Acta, 1934, **17**, 1239—1262; cf. B., 1930, 486).—The blackening of five varieties of plates and cut films by light of λ 400—700 mμ has been measured. If the gradation G is plotted against time of exposure (t) and intensity (I), the I curves are steeper than the t curves, the Schwarzschild coeff. p being consequently $\ngtr 1$. With emulsions of average sensitivity the difference between G vals. on the t and I scales is smaller for extreme than for intermediate wave-lengths. With the most sensitive panchromatic emulsions the differences between G_t and G_I are marked, but less variable, p being 0·66—0·86 compared with 0·51—0·97 for ordinary emulsions. With the most sensitive emulsions the limiting val. of G is attained much earlier with long than with short wave-length. In most cases the p–λ curve is a fairly exact mirror-image of the sensitivity curve. F. L. U.

Nature of colour-sensitising. Y. I. Bokinik (Kino-Photo Ind., 1933, **3**, 84—89).—The mechanism of the energy transfer from the adsorbed dye to the AgBr is discussed. Ch. Abs. (*e*)

Photo-decomposition of formic acid vapour. E. Gorin and H. S. Taylor (J. Amer. Chem. Soc., 1934, **56**, 2042—2047).—The products of decomp. of single HCO_2H mols. (I) are (*a*) $CO+H_2O$, (*b*) CO_2+H_2; the ratio is displaced in the direction of (*b*) by increase of light frequency or rise of temp. Double HCO_2H mols. (II) give (*b*) exclusively in the region 1900—2540 Å. Decomp. of the two mol. species is independent; the quantum yield is 1, independently of temp. and pressure over considerable ranges. The ultra-violet absorption spectrum of (II) is continuous, whilst that of (I) is banded. E. S. H.

Photolysis of amides and amines in sunlight. G. G. Rao and K. M. Pandalai (J. Indian Chem. Soc., 1934, **11**, 623—627).—The hydrolysis of aliphatic and aromatic amides is photo-sensitised by TiO_2. The NH_3 formed is oxidised to NO_2' in the presence of $CaCO_3$. Aliphatic amines are more easily oxidised photosensitively with ZnO to NO_2' than are aromatic amino-derivatives. J. G. A. G.

Photolysis of amino-acids in sunlight. G. G. Rao and N. R. Dhar (J. Indian Chem. Soc., 1934, **11**, 617—622).—The rate of formation of NH_3 in the oxidation, photo-sensitised with TiO_2, ZnO, and Al_2O_3, of glycine and alanine is > of aspartic and glutamic acids. It is inferred that the reaction proceeds $R{\cdot}CH{\cdot}NH_2{\cdot}CO_2H+(O) \longrightarrow RCHO+NH_3+CO_2$. *o*-$NH_2{\cdot}C_6H_4{\cdot}CO_2H$ probably first forms NH_2Ph and CO_2, but hippuric acid does not react. The significance of these results in soil chemistry is considered. J. G. A. G.

Mutual influences of dyes and of fatty acids in photo-reactions. M. Horio and S. Monden (J. Soc. Chem. Ind. Japan, 1934, **37**, 488—490b).—The photochemical formation of peroxide from linoleic acid is accelerated by the fluorescent dyes eosin (I) and erythrosin, but not by the non-fluorescent dye Victoria-blue (II), and the bleaching of (I) and (II) is accelerated by linoleic acid. Replacement of air by O_2 hinders the bleaching. A. G.

Photo-reactions of liquid and dissolved ketones. I. [Acetone and benzophenone.] E. J. Bowen and E. L. A. E. de la Praudière. **II. [Diacetyl.]** E. J. Bowen and A. T. Horton (J.C.S., 1934, 1503—1504, 1505—1506).—The m.p. of COPhMe and $COPh_2$ (I) were not changed by exposing the molten substances to the full light of the Hg arc, but (I) afforded benzpinacol in C_6H_6 and hexane (quantum efficiency, γ, 0·04), but not in CCl_4. The rate of reaction of pure $COMe_2$ (γ 0·05) was $\ll$ in hexane or with added MeOH; diacetone alcohol was probably formed. Unlike the photo-reactions of the vapours, gases were not evolved either from these liquids or from liquid MeCHO. The results are consistent with the ketone having a primary non-reactive excited level, capable of deactivation on collision, which can pass into a second reactive level (which does not dissociate instantly) after approx. 10^{-12} sec.

II. Gas was not evolved from solutions of $[CHO]_2$ and Ac_2 irradiated with $\lambda\lambda$ 4360—3660 Å. In hexane and Et_2O, Ac_2 polymerises and γ (0·9—0·1) decreases as the concn. is increased. The results are interpreted by the above hypothesis of two excited levels. J. G. A. G.

Heterogeneous and topochemical reactions. H. W. Kohlschütter (Angew. Chem., 1934, **47**, 753—756).—A lecture.

Separation of hydrogen isotopes by fractional desorption. H. S. Taylor, A. J. Gould, and W. Bleakney (Physical Rev., 1933, [ii], **43**, 496—497).—Desorption of electrolytic H_2 from adsorbent C at liquid air temp. gave a 3- to 5-fold enrichment of H^1H^2 over that initially present in the H_2. L. S. T.

Effect of fractional crystallisation on the isotopic composition of water. E. S. Gilfillan, jun. (J. Amer. Chem. Soc., 1934, 56, 2201).—Evidence is adduced to show that one crystallisation should change the *d* of ordinary H_2O by $0{\cdot}22 \pm 0{\cdot}01$ p.p.m. E. S. H.

Preparation of water of minimum conductivity. K. Gostkovski (Z. physikal. Chem., 1934, **170**, 149—152).—Triply distilled H_2O is cooled so that about half freezes, and the ice is then separated, melted, and distilled in vac. in an apparatus lined with paraffin wax. H_2O of conductivity almost as low as that of Kohlrausch and Heydweiller is obtained. R. C.

Preparation of protium oxide and determination of the proportion of deuterium in the hydrogen of normal water. E. H. Ingold, C. K. Ingold, H. Whitaker, and R. Whytlaw-Gray (Nature, 1934, **134**, 661).—The *d* of purified H_2O practically free from H^2 has been compared by a float method with that of purified ordinary H_2O. The *d* of the nearly pure "light H_2O" ("protium oxide") is < that of purified London and Leeds tap-H_2O by 12 p.p.m. at 20°. The *d* of these two tap-waters is identical and is taken as standard. The calc. mol. proportion of H^2_2O in the standard is approx. 1 in 9000, a proportion < is usually assumed. The calc. at. wt. of H^1 is 1·00789 on the scale $O^{16}=16$ and corr. to the chemical scale by Mecke and Childs' factor this becomes 1·00767, or by Babcock and Naudé's factor, 1·00777. L. S. T.

Reaction between sodium nitritopentacyanide and alkali sulphides. IV. G. Scagliarini and F. Monforte (Atti R. Accad. Lincei, 1934, [vi], 20, 41—43; cf. A., 1931, 1013).—The coloured reaction product of $Na_2[Fe^{III}(CN)_5NO]$ with Na_2S is due to the formation by hydrolysis of $Na_4[Fe^{II}(CN)_5NO_2]$, which then reacts with the Na_2S to give $Na_4[Fe(CN)_5NOS]$. O. J. W.

Copper carbonates. A. S. Cocosinschi (Bull. Soc. chim., 1934, [v], 1, 1065—1067; cf. A., 1930, 307).—Reply to a criticism by Poulenc-Ferrand (A., 1932, 1098). F. L. U.

Copper carbonates. (Mme.) Poulenc-Ferrand (Bull. Soc. chim., 1934, [v], 1, 1067—1069).—A rejoinder to Cocosinschi (preceding abstract). F. L. U.

Principles of the genetic development of material. VIII. V. Kohlschütter. **Chemical reactions in crystals. III. Thermal decomposition of cupric formate.** M. Christen [with (Frl.) L. Jacubovicz] (Helv. Chim. Acta, 1934, **17**, 1094—1119; cf. A., 1933, 38).—The decomp. of different forms of $(HCO_2)_2Cu$ at 200° was studied by chemical analysis and microscopically in order to determine the influence of cryst. form on the course of the change. The compounds examined were $(HCO_2)_2Cu$ anhyd., and with 2 and $4H_2O$, $(HCO_2)_2Cu,2(HCO_2)_2Ba$ anhyd., and with $4H_2O$, and $(HCO_2)_2Cu,3Cu(OH)_2$. In no case did the reaction conform to either of the usual equations. The main gaseous product was CO_2, with H_2, CO, and CH_4 in proportions which varied with the nature of the solid. The residue was Cu in every case. No simple relation between cryst. structure and the solid reaction was observed. F. L. U.

Amphoteric behaviour of metal hydroxides. VII. Halogen hydroxo- and pyrocatechol hydroxo-salts of bivalent heavy metals. R. Scholder (Z. anorg. Chem., 1934, **220**, 209—218).—The following *compounds* have been prepared: $Na_5[CuX(OH)_6(H_2O)],6H_2O$ (X is Cl, Br, or I); $Na_3[ZnI(OH)_4(H_2O)_2],8H_2O$; $Na_3[SnI(OH)_4(H_2O)]$; $Ba_{1{\cdot}5}[Sn_2(OH)_6I(H_2O)]$ (the corresponding Sr compound loses 1 mol. H_2O when dried over H_2SO_4); $Na_2[Pb(C_6H_4O_2)(OH)_2],4H_2O$; $Na_3[Zn(C_6H_4O_2)_2(OH)],9H_2O$. $Ni(OH)_2$ dissolves in conc. NaOH in presence of at least 0·5 mol. of pyrocatechol to 1 Ni to form a complex *pyrocatechol-hydroxo-anion*. M. S. B.

Complex salts of 2 : 2′-dipyridyl with bivalent copper. F. M. Jaeger and J. A. van Dijk (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 395—400).—Aq. Cu malonate with 1, 2, and 3 equivs. of alcoholic dipyridyl (dipy) yields after heating, in each case, dark blue crystals of $[Cu,dipy,C_3H_2O_4,(H_2O)_2]$, sol. in EtOH, gives off H_2O at 95°, gradually changes in contact with aq. solution into $[Cu,dipy,(H_2O)_2],C_3H_2O_4$. Aq. $CuSO_4$ yields with 1 and 2 equivs. of cold alcoholic dipy pale blue crystals of $[Cu,dipy,SO_4],2H_2O$, sparingly sol., gives off H_2O at 100°; with 3 equivs., dark blue crystals of $[Cu,dipy_3]SO_4,7H_2O$. Cold aq. $CuCl_2$ yields with 1 equiv. of alcoholic dipy green crystals of $[Cu,dipy,Cl_2]$, sparingly sol.; with 2 equivs. blue crystals of $[Cu,dipy_2,(H_2O)_2]Cl_2,4H_2O$ or $[Cu,dipy_2]Cl_2,6H_2O$, decomp. at 100° to give the mono-dipy salt; with 3 equivs., violet crystals of $[Cu,dipy_3]Cl_2,7H_2O$. Crystal data are recorded in most cases. R. S. B.

Energy of formation of magnesium oxide and its reduction by carbon. W. D. Treadwell and J. Hartnagel (Helv. Chim. Acta, 1934, **17**, 1372—1384).—The free energy of formation of MgO and of its reduction by C are calc. Experiments in which an equimol. mixture of MgO and C were heated by an arc in an atm. of A showed that reduction occurred readily, but about 75% of the Mg formed was reoxidised by the CO in spite of rapid cooling. F. L. U.

Preparation of phosphorescent substances. VI. Zinc sulphide. N. F. Shirov (J. Appl. Chem. Russ., 1934, 7, 343—358).—Of 61 mixtures examined, the most intense phosphorescence was given by the product of heating a mixture of Zn 2, S 1, H_3BO_3 0·3, and $ZnSiO_3$ 0·8 g. In general, the effect of adding ZnO, ZnF_2, $ZnSiO_3$, $ZnHBO_3$, $ZnHPO_4$, $ZnHAsO_4$, $ZnMoO_4$, $ZnWO_4$, ZnSe, or ZnTe, or the corresponding Cd salts, is to increase the wave-length of the phosphorescence. The above method is not suitable for factory practice, owing to the violence of the reaction; activation of ZnS by ignition is recommended. R. T.

Conditions of formation and certain properties of zinc nitride. V. A. Suchodski and K. M. Gorbunova (J. Gen. Chem. Russ., 1934, 4, 587—593).—The products of condensation of Zn vapour in N_2, or of passing NH_3 through molten Zn at 600°, contain only traces of Zn_3N_2, 5—40% yields of which are obtained from Zn dust and NH_3 at 550°. The heat of formation of Zn_3N_2 is 24,060 g.-cal.$\pm$28%. The dissociation const. of Zn_3N_2 has been calc. from Nernst's equation for the range 37—537°. R. T.

Sputtering applied to purification of mercury by electric arc still. R. K. Cowsik (Indian J. Physics, 1934, 9, 21—33).—An arc still fails to eliminate traces of Ag, Cu, and Sn, which are removed from Hg by a gas-heated still. These metals show marked sputtering in a discharge tube, and investigations with these metals and one such as Mg, which shows negligible sputtering, indicate that the impurity in the distillate from an arc must be due to sputtering at the cathode. Detailed purification of Hg and an automatic apparatus for circulating a fine spray of Hg through $HgNO_3$ solution are described. N. M. B.

Action of mercuric oxide on cadmium chloride and of cadmium oxide on mercuric chloride. E. Montignie (Bull. Soc. chim., 1934, [v], 1, 1099—1101).—The reaction is represented by $CdCl_2+HgO+H_2O \rightleftharpoons HgCl_2+Cd(OH)_2$. With excess of $CdCl_2$, $CdCl_2,Cd(OH)_2,6H_2O$ is formed. F. L. U.

Action of mercuric oxide on chlorides of silver, thallium, and lead. E. Montignie (Bull. Soc. chim., 1934, [v], 1, 1085—1087).—HgO does not react in presence of H_2O with AgCl or TlCl. With $PbCl_2$ the reaction $PbCl_2+HgO+H_2O=Pb(OH)_2+HgCl_2$ occurs, $PbCl_2,2PbO$ being formed as an intermediate product. F. L. U.

Action of mercuric oxide on cobalt chloride. E. Montignie (Bull. Soc. chim., 1934, [v], 1, 943—944).—The reaction $HgO+CoCl_2 \rightleftharpoons HgCl_2+Co(OH)_2$ is reversible. With small quantities of HgO, $CoCl_2,3CoO,3H_2O$ is formed, whilst with large quantities $HgCl_2$ separates. J. G. A. G.

Mercuric oxycyanide. F. C. J. Bird (Quart. J. Pharm., 1934, 7, 581—583).—$HgO,Hg(CN)_2$ is apparently decomposed in cold H_2O, since an insol. residue is obtained, but it is sol. in hot H_2O and remains in solution on cooling to 15·5°. Below 15·5° crystals separate. C. G. A.

Composition and stability of Donovan's solution. C. Morton and F. R. C. Bateson (Quart. J. Pharm., 1934, 7, 447—452).—Cryoscopic, conductometric, and potentiometric measurements show that the addition of HgI_2 to aq. solutions of AsI_5 gives rise to the complex electrolyte $HgI_2,2HI$ together with one containing more HI. C. G. A.

Reduction of aluminium oxide by carbon in the arc. W. D. Treadwell and J. Hartnagel (Helv. Chim. Acta, 1934, 17, 1384—1389).—Experiments similar to those with MgO (this vol., 1317) were made with mixtures of Al_2O_3 and C. The sublimate contained Al and Al_4C_3 in approx. equal proportions. Use of a high vac. did not appreciably increase the yield of Al. F. L. U.

Reactions of aqueous solutions of aluminium and chromium salts when rendered basic and on gelatin and hide substance. A. Küntzel (Collegium, 1934, 518—533).—On addition of NaOH, a cryst. ppt., which disappears after some time, is obtained from aq. $Al(NO_3)_3$, but a definite pptn. point is given by $Cr(NO_3)_3$. Al salts exert a strong buffering effect on NaOH whilst Cr salts exert much less. When rendered basic, Cr salts form monohydroxo-salts, and the conductivity titration curve shows a point of inflexion corresponding with this. Al salts do not form such basic salts, and their conductivity titration curve shows no inflexion. The hydrolysis of Cr salts finishes with the formation of basic salts and their condensation products. Al carbonato-complexes are very unstable, in contradistinction to those of Cr. The m.p. of gelatin can be raised to 100° by treatment with aq. Cr salts, but not with aq. Al salts. The so-called alum tannage is essentially a pickling effect. Technical alum leather is a combination tannage. Al salts combine with the surface only of the hide fibres and fibrils, whilst Cr salts, owing to their property of forming complexes, unite the principal valency chains in the collagen mols. D. W.

Systematic degradation of ultramarine-blue. K. Leschewski and H. Möller (Ber., 1934, 67, [*B*], 1684—1690).—Finely-divided ultramarine-blue (I) is boiled with successive quantities of NH_2Ph,HCl in H_2O containing an excess of NH_2Ph. The alkali (II) and S components of (I) are thereby independently degraded, nearly all the (II) and only about 0·25 of the S being removed. The final product (III) is grey and does not exhibit cryst. structure. It has distinctly acidic properties and becomes yellow when boiled with aq. NH_3. (III) absorbs alkali from molten $NaNO_3$, becoming green and bluish-green when washed and heated at 700°. Loss of (II) proceeds similarly to a washing-out process, and for this reason the blue colour of (I) disappears continuously without sharply-defined break. S and the SiO_2 skeleton appear closely allied. Disappearance of the lattice coincides with disappearance of the blue colour, which can persist or be developed only when S and (II) are present in a cryst. arrangement the structure of which is governed by the ultramarine lattice.

[With E. Podschus.] Treatment of (I) with successive portions of boiling 5*N*-NaOH causes most removal of S in the initial stage, the filtrate from which is yellow and contains S'' and S_n''. The filtrates from the succeeding stages are colourless and contain mainly SO_3'', finally only in traces. Otherwise only loss of SiO_2 takes place, so that the ratio $SiO_2 : Al_2O_3$ is reduced from 1·2 to 1·0. The action of conc. NaOH on (I) therefore leads to a colourless *compound*, $Na_7Al_6Si_6O_{30}S$. Maintenance of the blue colour depends essentially on the existence of the ultramarine lattice. Both are completely stable in boiling 2·5*N*-NaOH, whereas in 5*N*-NaOH the colour is slowly discharged in consequence of a transformation of the lattice, but not of a decomp. H. W.

Measurements on bi- and quadri-valent compounds of the rare earths. V. Cerium tetrafluoride. W. Klemm and P. Henkel (Z. anorg. Chem., 1934, **220**, 180—182).—*CeF_2* is obtained as a white powder by the action of F_2 on $CeCl_4$ without the application of external heat, or of F_2 on Ce_2S_3 or Ce_2S_4. It is not very sol. in H_2O, is stable at 400°

in a vac. and in H_2 at 200°, but is reduced at 300° to CeF_3. It is practically non-magnetic. *d* varies considerably (3·1—4·7) according to the method of prep. Pr and Nd form the trifluorides only.
M. S. B.

Crystallisation of carbon under high pressures. J. Basset (J. Phys. Radium, 1934, [vii], **5**, 471—474).—Attempts have been made to crystallise C as diamond over wide ranges of pressure, temp., and time by the liberation of C by the reduction of metallic oxides in presence of C leading to the decomp. of carbide during cooling, by the decomp. of carbonates, org. and inorg. solid and liquid C compounds, metallic carbides, and gaseous compounds. In all cases there was no definite evidence of the formation of any modification other than graphite. N. M. B.

Oxidation of silicon at low temperatures. A. Sanfourche (Compt. rend., 1934, **199**, 726—729).—Finely-divided Si readily oxidises at room temp. Samples of fused Si (I) and Si extracted from Si–Ag (II) and Si–Al (III) alloys were decomposed by heating in Cl_2 free from O_2. The $SiCl_4$ formed was collected in H_2O and determined; the residue from the Si was SiO_2. Fe formed $FeCl_3$ which condensed on the tube. (I), (II), and (III) contained, respectively, 0·46, 3·01, and 8·60% of SiO_2 [HNO_3 was used in preparing (III)]. This accounts for the supposed partial solubility of Si in HF. R. S. B.

Volatile transport of silica. (Frl.) R. D. Terzagli (Amer. J. Sci., 1934, [v], **28**, 391; cf. A., 1926, 36; 1929, 38, 1251). C. W. G.

Modifications of lead oxide. K. Scheringa (Pharm. Weekblad, 1934, **71**, 1197—1198).—Some samples of yellow PbO (I) turn red on keeping in subdued light due to the formation of Pb_3O_4 (II). The yellow form of (I) is obtained pure by crystallisation from hot 30% NaOH solution, in which the red form (III) is insol. (III) is obtained by boiling the pharmaceutical product with 50% NaOH. (III) reacts with acid benzidine solution alone; (II) reacts in presence of H_2O_2 and (I) fails to react. S. C.

[Constitution of azoimide and the azides.] A. Hantzsch (Ber., 1934, **67**, [*B*], 1674—1675; cf. A., 1933, 1129).—Polemical against Franklin (this vol., 477). H. W.

Amphoteric oxide hydrates, solutions of their hydrolysing salts, and their high-molecular compounds. XXVI. Polyvanadates crystallising from aqueous solutions of potassium vanadate of different [H˙]. K. F. Jahr and G. Jander (Z. anorg. Chem., 1934, **220**, 201—208).—From feebly acid K vanadate solutions, the *salts* $K_3H_4V_5O_{16}$,aq. and $K_2H_5V_5O_{16}$,aq. crystallise. In strongly acid solutions, which contain excess of V, the *compound* $2K_2O,6V_2O_5$ forms crystals similar in form and colour to the other two salts, and there are grounds for supposing that it, also, is a salt of pentavanadic acid. The formation of this anhyd. salt from an aq. solution appears to indicate that H_2O is not necessarily essential for the formation of *iso*polyacids.
M. S. B.

Isolation of 0·1 gram of the oxide of element 91 (protoactinium). A. V. Grosse and M. S. Agruss (J. Amer. Chem. Soc., 1934, **56**, 2200).—The working-up of Ra residues is described. E. S. H.

Metallic element 91. A. V. Grosse (J. Amer. Chem. Soc., 1934, **56**, 2200—2201).—Pa has been prepared by two methods from Pa_2O_5 (cf. preceding abstract). The metal does not oxidise in the air.
E. S. H.

Chromic anhydride. G. A. Kirkhgof, O. I. Korzina, and K. Y. Astrova (Khim. Farm. Prom., 1934, **1**, 38—40).—Technical $Na_2Cr_2O_7$ (1 mol. in 440 c.c.) is aged for 2 days at −5° with 1 mol. of H_2SO_4, Na_2SO_4 is sucked off, and the filtrate treated with H_2SO_4. Cr_2O_3 is centrifuged off. Alternatively $CaCrO_4$ is pptd. from a neutral solution by $CaCl_2$, converted into $CaCrO_4,0{\cdot}5H_2O$ by boiling, washed, and decomposed by H_2SO_4. $CaSO_4$ is separated and the filtrate treated with H_2SO_4 as above.
Ch. Abs. (*e*)

Sodium paratungstate. R. H. Vallance and E. G. K. Pritchett (J.C.S., 1934, 1586—1588).—Electrometric and refractivity experiments establish that the cryst. products of the titration of hot aq. Na_2WO_4 with HCO_2H and 1 : 1 aq. HCl are identical. The product, $Na_{10}(W_{12}O_{41}),28H_2O$ (I), does not contain acidic or nuclear H. The max. increase in the rotatory power of tartaric acid does not coincide with the addition of a simple mol. proportion of (I), and micelle formation probably accompanies chemical combination between the reactants. J. G. A. G.

Preparation of fluorine. A. Tian (Bull. Soc. chim., 1934, [v], **1**, 1010—1014).—Earlier methods (A., 1926, 139; 1931, 1248; B., 1927, 297) are reviewed and modified. F_2 is determined by reaction with dry KI. J. G. A. G.

Damp mixtures of chlorates and sulphur and other reactions of damp chlorates. J. Amiel (Compt. rend., 1934, **199**, 787—789).—A reply to Taradoire (this vol., 1186). H. J. E.

Direct oxidation of iodine and iodides at high pressures. J. Basset and M. Dodé (Compt. rend., 1934, **199**, 668—670).—On heating I in O_2 or O_2+N_2 at 250—400° for 1—4 hr. at pressures of $O_2 \not> 2000$ kg. per sq. cm., 0·2—2% of I_2O_5 is formed. Under similar conditions KI forms KIO_3, a 90% yield of almost colourless KIO_3 being formed in 5—6 hr. at 410°. H. J. E.

IF_5, IOF_3, and the possibility of the production of lower iodine fluorides. O. Ruff and A. Braida (Z. anorg. Chem., 1934, **220**, 43—48).—IF_5 has d^0 3·75 approx., d^{-193} 4·07; m.p. 9·6°; b.p. 98±1·5°. If *p* is the v.p., $\log p = 11{\cdot}764 - 3035/T$ and $8{\cdot}3 - 2205/T$ for solid and liquid IF_5, respectively. IOF_3 has been obtained as fine white crystals by the action of IF_5 on I_2 and F_2 containing O_2, at the temp. of liquid air. It is decomposed at 400° and by numerous reagents. It behaves differently from the previously known $IOF_3,5H_2O$. No proof of the existence of lower fluorides has been obtained. M. S. B.

Structure of oxides of manganese, and the rational analysis of manganese ores. A. M. Zanko and V. F. Stefanovitsch (J. Gen. Chem. Russ., 1934, **4**, 404—407).—Potentiometric data indicate that Mn_3O_4 reacts in hot $2N$-H_2SO_4 as follows : $Mn_3O_4+4H_2SO_4 \longrightarrow MnSO_4+Mn_2(SO_4)_3$ (I) $+4H_2O$; (I)$+3H_2O \longrightarrow MnSO_4+H_2MnO_3+2H_2SO_4$. Potentiometric titration of Mn^{III} in Mn ores is recommended. R. T.

Chemistry and electrochemistry of rhenium. IV. Action of reducing agents on sulphuric acid solutions of potassium perrhenate. H. Hölemann (Z. anorg. Chem., 1934, **220**, 33—42).—$KReO_4$ can be titrated potentiometrically in H_2SO_4 solution to Re^{VI}, Re^{V}, or Re^{IV}, depending on the reducing agent employed. The acid concn. must always be higher than for reduction in HCl solution. $FeSO_4$, $SnSO_4$, and $Ti_2(SO_4)_3$ reduce to the Re^{V} stage, and the course of the titration can be followed by the colour changes only, and not by any sudden change of potential. $CrSO_4$ reduces Re^{VII} to Re^{IV}, but the intermediate Re^{VI} and Re^{V} stages can be recognised in conc. acid solution only. $CrSO_4$ is, on the whole, less suitable for potentiometric reduction than $CrCl_2$. The valency stages and the related colour changes can also be observed in the reverse direction by oxidation with $KMnO_4$. M. S. B.

Quinquevalent rhenium. W. F. Jakób and B. Jeżowska (Z. anorg. Chem., 1934, **220**, 16—30).—The production of Re^{V} as the first stage in the reduction of Re^{VII} by 2 equivs. of HI (cf. A., 1933, 1254) is confirmed. The next stage is the reduction by a third equiv. of HI to Re^{IV}, which may also be obtained by the decomp. of Re^{V} compounds as follows : $3Re^{V} \rightleftharpoons 2Re^{IV}+Re^{VII}$. The equilibrium moves to the left in strongly acid solution at room temp. The valency of Re in its compounds can be determined by both iodometric and oxidation methods. By the action of conc. HCl and KI on $HReO_4$, *K_2ReOCl_5* is obtained as yellowish-green crystals stable in dry air. The morphological characteristics of the crystals are given. In HCl solution the colour changes from yellow to bluish-green as the concn. of acid diminishes. Conc. H_2SO_4 gives a reddish-brown solution. A strongly acid solution is stable in air, but gives $HReO_4$ with oxidising agents. Acid solutions, on dilution, ppt. a black hydroxide ReO_2,xH_2O, and with H_2S a black sulphide. The compound previously described as $K_2[Re(OH)_2Cl_5]$ (*loc. cit.*), is probably K_2ReOCl_5,H_2O. *$(NH_4)_2ReOCl_5$* has also been obtained as greenish-yellow crystals isomorphous with the K salt. The relation between the salts X_2ReOCl_5 and the $ReCl_5$ prepared by Geilmann *et al.* (A., 1933, 1259) is indicated. M. S. B.

Preparation of perrhenic acid. J. T. Dobbins and J. K. Colehour (J. Amer. Chem. Soc., 1934, **56**, 2054).—$HReO_4$ is prepared by oxidation of ReO_2 with H_2O_2. E. S. H.

Preparation of a stable form of ferrous chloride. F. E. Carter (Quart. J. Pharm., 1934, **7**, 389—391).—Solutions of $FeCl_2$ can be stabilised against oxidation by addition of 1% (wt./vol.) of citric acid. C. G. A.

Ferromagnetic variety of iron sesquioxide. H. Forestier and G. Guiot-Guillain (Compt. rend., 1934, **199**, 720—723).—A new ferromagnetic variety of Fe_2O_3 has been prepared by decomp. of $Fe_2O_3,4BeO$ (I). The ppt. obtained by adding aq. $Fe(NO_3)_3+$ aq. $Be(NO_3)_2$ to aq. NH_3 is dried and becomes magnetic when heated at 720° for 6 min., with a Curie point at 220°, but long heating above 700° destroys the magnetism. There is a second Curie point at 675°, when stable Fe_2O_3 is formed. *X*-Ray analysis suggests that the magnetic material consists of BeO, and rhombohedral Fe_2O_3 corresponding with slightly deformed oligist (II). (II) can be isolated by dissolving the BeO in dil. HCl, and has the same magnetic properties as decomposed (I). R. S. B.

Behaviour of ferrous salt solutions on oxidation with bromine. Rodt and Charisius (Mitt. Materialprüf., 1934, 271).—When aq. $FeBr_3$ is boiled Br is slowly evolved, and if the solution is evaporated to dryness the residue consists almost entirely of $FeBr_2$ and not of Fe_3Br_8 as stated in the lit. These facts should be borne in mind in the iodometric determination of $Fe^{\cdot\cdot\cdot}$ after oxidation of $Fe^{\cdot\cdot}$ with Br. A. R. P.

Separation of metallic sulphates by selective dissociation. L. Wöhler and K. Flick (Ber., 1934, **67**, [*B*], 1679—1683).—The total tensions of $NiSO_4$ and $CoSO_4$ have been measured by the air-buffer method ; the production of basic sulphates is not observed. The following quant. separations of metallic sulphate have been effected by selective dissociation of sulphate mixtures in a current of SO_3 at temp. $\not>$ 800° and in SO_2–O_2 mixtures at higher temp. : Co and Ni ; Fe and Zn ; Fe and Ti ; Fe and Al ; Fe and Mn ; Zn and Mn ; Cr^{III} and Al ; Cr^{III} and Fe^{III}. Al, Fe, and Ti are quantitatively isolated from bauxite and total Ti from the red residue of the Bayer process for the prep. of Al_2O_3. H. W.

Complex periodides. II. G. Spacu and P. Spacu (Bul. Soc. Ştiinţe Cluj, 1934, **7**, 367—373 ; Chem. Zentr., 1934, ii, 582 ; cf. this vol., 41).—The following *compounds* have been prepared :

$[Co\ en_2(NO_2)_2]I,I_3(\tfrac{1}{6})$, $[Co\ en_2(NO_2)_2]I,I_3(\tfrac{1}{2})$,
$[Co\ en_2(CNS)_2]I,I_2(\tfrac{1}{6})$, $[Co\ en_2(CNS)_2]I,I_2(\tfrac{1}{2})$,
$[Co\ en_2(Cl)_2]I,I_2(\tfrac{1}{6})$, $[Co\ en_2I_2]I,I_2(\tfrac{1}{2})$,
$\{Co[Co(OH)_2en_2]_3\}I_6,I_3$, and $[Cr\ en_3]I_3,2I_2$.

H. J. E.

Substituted cyanocobaltiates. Diaquotetracyanocobaltic acid. Cobaltic cyanide. P. R. Rây and T. Guptachaudhuri (Z. anorg. Chem., 1934, **220**, 154—162).—By oxidation of $2SO_3$ in $Na_5[(SO_3]_2Co(CN)_4]$ (A., 1933, 476) and subsequent removal and replacement by $2H_2O$, the *salt* $Na[(H_2O)_2Co(CN)_4],H_2O$ is obtained. The Ag, $K(0{\cdot}75H_2O)$, NH_4, $Li(3{\cdot}5H_2O)$, $Ba(3{\cdot}5H_2O)$, $Sr(1{\cdot}5H_2O)$, and $Ca(3{\cdot}5H_2O)$ *salts* have been obtained and also the *compound* $(PbO_2){\cdot}Pb[(H_2O)_2Co(CN)_4]_2$ and the free *acid*. The acid and its salts cannot be cryst. from solution, but on evaporation they give a red glass suggesting the probability of polymerisation. This view is supported by electrical conductivity data, which indicate a basicity of approx. 3, and by determinations of *d* which show that the mol. vol. of the anion is small. By heating $H[(H_2O)_2Co(CN)_4]$, deep blue *$Co(CN)_3$* is formed. It is insol. in H_2O, but is gradually transformed into red *$Co(CN)_3,2H_2O$*. The transition temp. to anhyd. $Co(CN)_3$ is 118°. The magnetic susceptibility of the hydrate, 14·61, is only slightly > that of the anhyd. salt, 13·58. M. S. B.

Complex cobaltioxalates. G. Spacu, J. G. Murgulescu, and M. Vancea (Z. anorg. Chem., 1934, **220**, 1—15).—Measurements of the electrical conductivity and extinction coeff. of solutions of Durrant's salt show its constitution to be $[(C_2O_4)_2Co(OH)(OH_2)]K_2$ (I). The action of acids results in the following decomp. : (I)+HCl= $[(C_2O_4)Co(OH_2)_2]K$ (II)+KCl and 2(II)=$2CoC_2O_4+K_2C_2O_4+2CO_2+4H_2O$. The decomp. of (II) is shown by the spectro-photometric method to be unimol. The results have been confirmed by a comparison of the absorption spectra of chromioxalates and cobaltioxalates. No salts of the ion $[(C_2O_4)_2Co(OH_2)_2]'$ could be pptd. M. S. B.

Stability of $[Co(NH^1_3)_6](NO_3)_3$ in water containing H^2_2O. H. Erlenmeyer and H. Gärtner (Helv. Chim. Acta, 1934, **17**, 1008—1010; cf. preceding abstract).—Dissolution of $[Co(NH^1_3)_6)(NO_3)_3$ in H_2O containing H^2_2O, followed by recovery of the H_2O, shows that complete exchange occurs between the H of the H_2O and of the NH_3. Similar exchangeability of H atoms in the NH_3 of the solid crystals could not be detected. F. L. U.

Isolation of precipitates in quantitative analysis by centrifuging. A. I. Amiantov (J. Appl. Chem. Russ., 1934, 7, 630—631).—Centrifuging is in many cases preferable to filtration. R. T.

Rational concentration of solutions for titration. S. K. Tschirkov (J. Appl. Chem. Russ., 1934, 7, 646—655).—The optimum concn. of standard solutions is, for acids, $N=(K[HR]-[R']\sqrt{k_\omega})Va/[R']$, and for alkalis, $N=(k_\omega[R']-K[HR]\sqrt{k_\omega})Va/K[HR]$, where K is the dissociation const. of the indicator HR, k_w that of H_2O, V is the final vol. of the solution, and a the no. of drops delivered per ml. of standard solution. R. T.

Magneto-optic method of chemical analysis. F. G. Slack (J. Franklin Inst., 1934, **218**, 445—462).—Work on time lags in the Faraday effect and the magneto-optic method of chemical analysis is reviewed. Min. were observed, but no positive conclusions could be reached. Observed phenomena are described as a type of N-ray phenomena and are subject to the same physiological and psychological effects. W. R. A.

Comparison of the colorimetric, electrometric, and catalytic methods for determining hydrogen-ion concentration. M. Kilpatrick, E. F. Chase, and L. C. Riesch (J. Amer. Chem. Soc., 1934, **56**, 2051—2053).—Tests on AcOH–NaOAc solutions by the three methods give concordant results. The classical dissociation const. of AcOH increases slightly between 25° and 35°. E. S. H.

Determination of acidity in non-aqueous solutions. O. Tomíček and J. Feldmann (Coll. Czech. Chem. Comm., 1934, 6, 408—421).—Acid–alkali titrations in simple alcohols, C_6H_6, $COMe_2$, and similar org. solvents and their mixtures have been studied by the indicator and potentiometric methods. Besides the H_2 and quinhydrone electrodes the Sb and Te electrodes are suitable. The Te electrode is serviceable in non-aq. solutions over the range p_H 5·3—11·5. E. S. H.

Photometric micro-analysis of water. XII. Iron.—See B., 1934, 1038.

Micro-titration of bromides and iodides in presence of chlorides. I. Bellucci (Gazzetta, 1934, **64**, 688—695).—The aq. solution of the three halides is acidified slightly with H_2SO_4 and a few cg. of $NaNO_2$ are added. The liberated I is separated by means of CCl_4 and titrated with 0·002N-$Na_2S_2O_3$. The aq. layer is made slightly alkaline with NaOH, evaporated to dryness on the H_2O-bath, and the bromide dissolved out with $COMe_2$ and titrated by Volhard's method using 0·01N-$AgNO_3$. O. J. W.

Microchemical detection of elementary sulphur. A. Schönberg (Nature, 1934, **134**, 628).—A well-ground mixture of the specimen and $CH_2Ph\cdot N:C(C_6H_4\cdot OMe\text{-}p)_2$ (from $CH_2Ph\cdot NH_2$ and dianisyl ketone chloride, or from the ketone and $CH_2Ph\cdot N_3$) is heated in a m.-p. tube to 210° for 5 min. and then extracted with C_6H_6. If the unknown contains elementary S ($\nless$ 0·04 mg.) the extract is coloured blue owing to the formation of pp'-dianisyl thioketone (I). When a crystal of $HgCl_2$ is added, the blue colour decreases in intensity within a few hr., and its surface is coloured an intense red owing to the formation of an additive compound of (I) and $HgCl_2$. L. S. T.

Detection of sulphurous acid and its salts and of tin. H. Freytag (Ber., 1934, **67**, [*B*], 1477—1480).—The green photo-product of 2-benzylpyridine (A., 1933, 1256) becomes red in presence of traces of SO_2. The moist reagent paper is adapted for the detection of S in org. compounds and natural sulphides which are burnt in air, and for the detection of sulphites from which SO_2 is best liberated by acids and detected in the gas phase. Sn^{II} as $SnCl_2$ in HCl causes similar change from green to red. H. W.

Colour reaction for sulphites. Z. Rudnitski (J. Appl. Chem. Russ., 1934, 7, 402—405; cf. A., 1933, 687).—The reaction serves for the detection of $\nless 5\times10^{-5}$ g. of SO_3'' in 100 ml. of solution. Heavy metals and CN', but not other ions, interfere. R. T.

Determination of substances in low concentration. V. Sulphates, sulphites, and sulphides. M. V. Alexeeva (J. Appl. Chem. Russ., 1934, 7, 616—622).—Köszegi's method (A., 1929, 782) serves for determination of 0·01—0·1 mg. of SO_4''. 0·002—0·01 mg. of H_2S in 10 ml. of solution can be determined by Mecklenburg and Rosenkränzer's method (A., 1914, ii, 380). Gurevitsch's method (A., 1930, 879) for the simultaneous determination of S'' and SO_3'' gives good results when the SO_4'' produced is determined nephelometrically. R. T.

Determination of sulphate in water-soluble sulphates. L. Sümegi (Magyar chem. Fol., 1933, **39**, 180; Chem. Zentr., 1934, i, 3088).—Excess of aq. $BaCl_2$ of known concn. is added. Excess of $BaCl_2$ is pptd. as $BaCO_3$ with $(NH_4)_2CO_3$, the ppt. being added to a known vol. of N-HCl and the excess of HCl determined with N-NaOH. H. J. E.

Potentiometric determination of selenocyanate in the presence of iodide. G. Spacu and P. Spacu (Z. anal. Chem., 1934, **98**, 179—183).—The titration

is made in a neutral solution containing $MgSO_4$ using $0·1N$-$AgNO_3$ and a Ag wire indicator electrode. Mechanical agitation is necessary to overcome adsorption of iodide by the AgI ppt. The potential of pptn. of AgI is −0·16 volt and that of AgCNSe +0·06 volt against the N-Hg_2Cl_2 electrode.
A. R. P.

Gravimetric determination of tellurium as dioxide by means of pyridine. A. Jílek and J. Kota (Coll. Czech. Chem. Comm., 1934, 6, 398—407).—$TeCl_4$ is dissolved in HCl containing NH_4Cl, the solution is almost neutralised with aq. NH_3, Me-orange is added, and C_5H_5N run in dropwise until the colour change is complete. The cryst. ppt. of TeO_2 is collected in a Gooch crucible, dried rapidly at 120°, and weighed.
E. S. H.

Determination of nitrate-nitrogen by the Devarda process.—See this vol., 1422.

Colour reactions of solutions of some organic substances in concentrated sulphuric acid with nitrates and other oxidising agents. M. Eitel (Z. anal. Chem., 1934, 98, 227—234).—H_2SO_4 solutions of phenols and quinones not substituted in the nucleus give colour reactions with NO_3' (I), to a smaller extent with other oxidising agents, but not with NO_2'. p-Benzoquinone (about 0·01% solution) gives a reddish-brown colour; the blackish-green (0·02%) solution of phenanthraquinone shows a reddish colour with traces of (I) in solid substances. Diphenyleneglycine [colourless 0·1% H_2SO_4 solution (II)] gives a sensitive green coloration with aq. solutions of (I). 10 mg. of (I) per litre of solution may be detected by adding 1 c.c. to 5 c.c. of H_2SO_4+10 drops of (II). Benzidine similarly detects 0·1 mg. of (I) per litre, and 2 : 7-diaminofluorene (III) 0·001 mg. per litre. NO_2' and $K_2S_2O_8$ give reddish-yellow colorations with (III).
J. S. A.

Detection of nitrates and iron in water.—See B., 1934, 990.

Determination of cyanide-nitrogen by the Kjeldahl method. A. Tettamanzi (Atti R. Accad. Sci. Torino (Cl. Sci. fisich.), 1932—1933, 68, 153—160; Chem. Zentr., 1934, i, 2166).—N in both simple and complex cyanides may be determined by the Kjeldahl method. NaCN and KCN must be examined as solids. HCN is evolved from their solutions. $K_2Pt(CN)_4$ is exceptional. After long heating with conc. H_2SO_4, $Pt(CN)_2$ is pptd. on dilution.
H. J. E.

Colorimetric micro-determination of arsenic.—See this vol., 1422.

Determination of arsenic in sulphur.—See B., 1934, 960.

Determination of arsenic, antimony, tin, and bismuth in lead glances and similar minerals. H. Biltz and K. Hoehne (Z. anal. Chem., 1934, 99, 1—12).—The application of the procedure of A., 1930, 1144 to the determination of As, Sb, and Sn in various Pb glances is described. For the determination of Bi, the mineral is dissolved in HCl and evaporated with HNO_3. The solution is neutralised with Na_2CO_3 and just re-acidified (Me-orange). Bi is then pptd. by a suspension of HgO, redissolved in HNO_3, and evaporated down with H_2SO_4. Any $PbSO_4$ is removed and Bi in the solution determined colorimetrically.
J. S. A.

Chemical and microscopical determination of arsenic, antimony, tin, and bismuth in the chief Silesian lead sulphides. K. Hoehne (Chem. Erde, 1934, 9, 219—268).—The results of microscopical examination and chemical analysis of 111 different specimens of mineral PbS, 14 samples of ZnS, and other minerals are described. Methods of determining As, Sb, Sn, and Bi, present as impurities, are recommended from among those published; the accuracy attainable is As 0·01, Sb 0·03, Sn 0·005, Bi 0·002—0·005%. The geological significance of these impurities is discussed.
E. S. H.

Complex mercury–arsenic compounds and their identification. H. Kühl and B. Czyżewsky (Pharm. Zentr., 1934, 75, 660—666).—Satisfactory As mirrors are unobtainable in the Marsh test when Hg is present. This is due to the formation of a stable, black amalgam. Microscopic evidence is given of the formation of Hg–As double salts. Hg As sulphate when heated gives Hg_3AsO_4 and a sublimate consisting of characteristic octahedral crystals of $As_2(SO_4)_3$ surrounded by haloes of yellow HgO.
S. C.

Colorimetric determination of silica in boiler water.—See B., 1934, 991.

Use of boron trioxide in determination of minerals. H. Versluys (Proc. K. Akad. Wetensch. Amsterdam, 1934, 37, 407—408).—A review and extension of the use of B_2O_3 as a flux for examining minerals by bead tests.
R. S. B.

Volumetric determination of potassium with methylene-blue following its precipitation as potassium picrate. A. Bolliger (J. Biol. Chem., 1934, 107, 229—234).—K is pptd. as picrate by an EtOH solution of Ca picrate and the ppt. titrated with a standard methylene-blue solution (this vol., 47, 1017). The method is applicable to solutions containing twice as much Na as K (0·04—10 mg. K).
C. G. A.

Standard carbonate-free sodium hydroxide solutions. W. W. Kay and H. L. Sheehan (Biochem. J., 1934, 28, 1795—1797).—CO_2-free NaOH is prepared by pptn. of Na_2SO_4 with $Ba(OH)_2$.
H. G. R.

Standardisation of sodium thiosulphate solution by means of $Cu(NH_4)_2Cl_4,2H_2O$. A. V. Filosofov (J. Appl. Chem. Russ., 1934, 7, 628—629).—Aq. $Na_2S_2O_3$ is conveniently standardised by means of $Cu(NH_4)_2Cl_4,2H_2O$.
R. T.

Optimum conditions of precipitation of sodium silicofluoride. V. J. Anosov and S. K. Tschirkov (J. Appl. Chem. Russ., 1934, 7, 503—508).—Na_2SiF_6 is obtained in 90% yield by adding a 50% excess of 20% aq. NaCl to 5—6% aq. H_2SiF_6, pptn. being complete after 5 min.
R. T.

Determination of calcium and magnesium. A. M. Vasiliev and R. G. Hendel (Zavod. Lab., 1933, No. 5, 12—14).—Ca is pptd. as CaC_2O_4, and, without filtering, Mg as $MgNH_4PO_4$; the washed ppt. is dissolved in H_2SO_4, the phosphate titrated with NaOH (Me-orange), and the $H_2C_2O_4$ with $KMnO_4$. CH. ABS.

Volumetric determination of cadmium. G. SPACU and M. KURAŠ (Z. anal. Chem., 1934, 99, 26—28).—To the $Cd^{\cdot\cdot}$ solution is added excess of 0·1*N*-NH_4CNS and C_5H_5N, pptg. $Cd(CNS)_2,2C_5H_5N$. The liquid is filtered, C_5H_5N neutralised with HNO_3 (using α-dinitrosophenol), and the excess of CNS′ titrated back with $AgNO_3$ using diphenylcarbazone as indicator. J. S. A.

Volumetric determination of lead. I. TANANAEV (Z. anal. Chem., 1934, 99, 18—22).—Pb is pptd. as PbFCl from neutral (Me-orange) solution by addition of NaF+NaCl, each 0·2*N*. Excess of Cl′ or F′ is titrated back with $AgNO_3$ or $AlCl_3$, respectively. Cu or Zn does not interfere. J. S. A.

Potentiometric titration of thallic salts by sodium thiosulphate. F. ČŮTA (Coll. Czech. Chem. Comm., 1934, 6, 383—397).—$Tl^{\cdot\cdot\cdot}$ is reduced by S_2O_3'' at 90° in presence of HgI_2 as catalyst according to the equation $4Tl^{\cdot\cdot\cdot}+S_2O_3''+5H_2O=4Tl^{\cdot}+2SO_4''+10H^{\cdot}$. The reaction can be used for determining $Tl^{\cdot\cdot\cdot}$ by electrometric titration with $Na_2S_2O_3$, using a Pt electrode. The mean error is about ±0·66%. The titration can be carried out in presence of Br, Cl_2, Cl′, Br′, $Hg^{\cdot\cdot}$, $Cd^{\cdot\cdot}$, SO_4'', PO_4''', and ClO_4', but $Cu^{\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, and As^{V} interfere. E. S. H.

Application of electrolytic reduction methods in analytical chemistry. III. Direct determination of copper and iron by electrolytic precipitation and reduction. G. GALFAJAN (Z. anal. Chem., 1934, 99, 32—34; cf. A., 1933, 138).—Cu may be deposited and $Fe^{\cdot\cdot\cdot}$ simultaneously reduced in 10—20% H_2SO_4 solution, using a Pt cathode. J. S. A.

Quantitative precipitation of copper with gallotannic acid. M. B. DARBINIAN and A. G. KANKANIAN (Z. anal. Chem., 1934, 99, 29—32).—Gallotannic acid ppts. Cu quantitatively in presence of NH_4OAc, but not in ammoniacal solution. $Cu^{\cdot\cdot}$ is thereby reduced to $Cu^{\cdot}$. J. S. A.

Coloured precipitate for colorimetric determinations. V. CUVELIER (Z. anal. Chem., 1934, 99, 15—18).—Co-pptn. of Cu or Co with Zn as $ZnHg(CNS)_4$ gives mixed crystal ppts. of colour ∝ the Cu (Co) content. Incomplete pptn. with insufficient $(NH_4)_2Hg(CNS)_4$ leads to increased sensitivity by concentrating the Cu in the ppt. relative to the Zn. The sensitivity for Cu is > in colorimetry with aq. NH_3. J. S. A.

Spectrographic detection and determination of minute quantities of impurities in copper.—See B., 1934, 965.

Determination of copper in red lead.—See B., 1934, 971.

Electrolytic determination of copper in aluminium alloys.—See B., 1934, 1015.

Alkalimetric determination of mercury as amido-compounds. S. ŠKRAMOVSKÝ and R. UZEL (Časopis. czechoslov. Lék., 1934, 14, 33—45).—The amido-compound (I) is pptd. from $HgCl_2$ solution by treatment with NH_3 in the presence of alkali chloride and hydroxide. After brief heating excess of NH_3 is neutralised (cold) with HCl. Addition of S_2O_3'' or I′ produces the complex $Hg(S_2O_3)_2''$ or HgI_4'' with the liberation of 2(OH′) for each $Hg^{\cdot\cdot}$ present. The liquid is then titrated with HCl or H_2SO_4 (Me-red). In the analysis of $HgCl_2$ tablets eosin must be destroyed by $KClO_3$ or alternatively bromocresol-green or Congo-red may be used as indicator. Any Hg or Hg_2Cl_2 present in the sample is converted into $HgCl_2$ by HCl–HNO_3 prior to pptn. of (I). A. G. P.

Detection of mercury in presence of all the cations. M. SCHTSCHIGOL (Khim. Farm. Prom., 1934, No. 1, 44—45).—The sample is treated with excess of 10% KI and 30% NaOH, heated, and filtered. The filtrate containing K_2HgI_4 is treated with 1 c.c. of glycerol and 2—3 c.c. of aq. NaOH, and boiled for several min. Darkening of the solution or a black ppt. indicates Hg. CH. ABS. (*e*)

Pyroelectric concentration for the spectral determination of Y, La, and other rare earths in lead minerals. S. PIÑA DE RUBIES and J. DOETSCH (Z. anorg. Chem., 1934, 220, 199—200).—About 1 g. of the mineral is volatilised in the arc and two or three spectrum photographs are taken during the process. The rare earths begin to emit when a considerable portion of the mineral has been volatilised and they have become more conc. Y, La, Yb, Gd, and Er only have, so far, been definitely shown to be present by this method. M. S. B.

Determination of aluminium in aluminium and its alloys.—See B., 1934, 890.

Detection of small quantities of indium, gallium, and thallium. E. PIETSCH and W. ROMAN (Z. anorg. Chem., 1934, 220, 219—224).—A pptn. method for the detection of In, Ga, or Tl by the use of quinalizarin in presence of aq. NH_3 and NH_4Cl is described. It is very much less sensitive for Tl than for In or Ga. The last two elements can also be detected by this method in presence of comparatively large quantities of Al and Zn, if NH_2Et in place of NH_4Cl is added to the Al, and C_5H_5N together with the NH_4Cl to the Zn. M. S. B.

Potentiometric determination of iron in ores.—See B., 1934, 1013.

Drop reaction for cobalt. L. M. KUHLBERG (J. Appl. Chem. Russ., 1934, 7, 406—408).—1 ml. of solution is made acid with HCl, Al is added, and the solution is filtered after 2·5 min. The filtrate is boiled for 2 min. with 2—3 drops of HNO_3, made neutral with aq. NH_3, and acid with AcOH, and 0·1 ml. of reagent (I) [saturated aq. $(NH_4)_2Hg(CNS)_4$] is added. $Fe(CNS)_3$, if present, is decolorised with saturated aq. NaF, and 0·5 g. of $ZnSO_4$ and 1 ml. of (I) are added, when a blue ppt. indicates $\not< 2\cdot5\times10^{-10}$ g. of Co. R. T.

Volumetric determination of cobalt. G. SPACU and M. KURAŠ (Bul. Soc. Ştiinţe Cluj, 1934, 7, 377—383; Chem. Zentr., 1934, i, 2797).—Co is pptd. with 0·1*N*-NH_4CNS and C_5H_5N as the complex $[Co(C_5H_5N)_4(CNS)_2]$, and excess of NH_4CNS determined with 0·1*N*-$AgNO_3$, using HNO_3+aq. $Fe(NH_4)_2(SO_4)_2$ as indicator. The method is applicable in presence of all elements not pptd. under these conditions. H. J. E.

1-Nitro-β-naphthol as precipitant for cobalt and palladium. C. Mayr (Z. anal. Chem., 1934, **98**, 402—408).—$Co^{\cdot\cdot}$ is oxidised to $Co^{\cdot\cdot\cdot}$ by adding 30% H_2O_2 to the slightly acid solution. $Co(OH)_3$ is pptd. by NaOH and redissolved in AcOH. Excess of 1-nitro-β-naphthol (I), as 1% solution in 50% aq. AcOH, then ppts. $Co(C_{10}H_6{\cdot}O{\cdot}NO_2)_3$ of stoicheiometric composition (cf. A., 1933, 1025); this is dried at 130°. Using AcOH concns. $\nless$ 25—35%, Co may be quantatively separated from Ni, Zn, Cr, and Al. Small amounts of Fe may first be pptd. with cupferron; larger amounts (*e.g.*, in analysis of Co steels) should first be quantitatively removed by pptn. with ZnO (cf. A., 1914, ii, 494). With Pd in $\ngtr$ 5% AcOH solution, (I) ppts. $Pd(C_{10}H_6{\cdot}O{\cdot}NO_2)_2$, dried at 130—140°. J. S. A.

Determination of chromium in steels containing vanadium and molybdenum.—See B., 1934, 1014.

Spectral analysis by sensitive lines within the range of the glass spectrograph: measurements in the spark spectrum of a high-% molybdenum-iron alloy. W. Kraemer (Z. anal. Chem., 1934, **98**, 240—245).—Results are given for an 80 : 18% Mo–Fe alloy (see A., 1933, 1110). J. S. A.

Colorimetric determination of bismuth. Y. Yamamoto (Bull. Inst. Phys. Chem. Res. Japan, 1934, **13**, 1265—1266).—To the Bi solution 1 g. of Na K tartrate and 5—10 c.c. of 1% aq. gum arabic are added, and then sufficient aq. NH_3 to make the solution alkaline ($p_H > 8$). A few drops of 10% aq. Na_2S are added, and the solution is diluted to 100 c.c. The reddish-brown colloidal Bi_2S_3 produced is matched against a standard. 1·5 mg. per litre can be determined with an error $\ngtr$ 2%. The Bi_2S_3 sol can be boiled without coagulation, and its colour intensity does not vary on keeping over-night. R. S. B.

Colour reaction of bismuth. J. V. Dubský and A. Okáč (Chem. Obzor, 1934, **9**, 3—4; Chem. Zentr., 1934, i, 3498).—Dimercaptothiodiazole (0·7 g. $C_2H_2N_2S_3$ in 35 c.c. 0·1*N*-KOH) gives with a Bi salt in dil. HCl a red ppt. (limiting concn. 1 : 28,000, 0·0012 mg. Bi). H. J. E.

"VIKP" thermoelectric relay. S. A. Pavlov and N. K. Baramboim (J. Appl. Chem. Russ., 1934, **7**, 437—438).—A simple and inexpensive electric thermo-regulator is described. R. T.

High-frequency calorimeter for investigating the dielectric loss of liquids. L. Pungs and H. Rieche (Z. tech. Physik, 1933, **14**, 483; Chem. Zentr., 1934, i, 1676). L. S. T.

Thermal leakage rates of Dewar bottles. W. P. White (Rev. Sci. Instr., 1934, **5**, 379).—The heat flow depends on how the throat of the bottle is filled. C. W. G.

Attainment of temperatures below 1° abs. by demagnetisation of $Gd_2(SO_4)_3,8H_2O$. W. F. Giauque and D. F. MacDougall (Physical Rev., 1933, [ii], **43**, 768).—Temp. of 0·53°, 0·34°, and 0·25° abs. have been reached. L. S. T.

Chemical intensification of *X*-ray spectrograms. E. Wainer (Physical Rev., 1933, [ii], **43**, 303).—The use of U baths improves the contrast and detail of *X*-ray spectrograms used for qual. chemical analysis. L. S. T.

Application of the photo-cell in spectrography. W. Kroll (Metall u. Erz, 1934, **31**, 105—107; Chem. Zentr., 1934, i, 3496).—A crit. discussion. H. J. E.

Spark apparatus for spectral analysis. O. Feussner (Zeiss Nachr., 1933, **4**, 6—13; Chem. Zentr., 1934, i, 576).—For reproducibility in quant. spectrum analysis the discharge should be extinguished after a min. no. of high-frequency oscillations. A suitable apparatus is described. H. J. E.

Direct-reading, two-crystal *X*-ray spectrometer. F. K. Richtmyer and S. W. Barnes (Rev. Sci. Instr., 1934, **5**, 351—355).—Wave-lengths are read directly to 10^{-5} Å. C. W. G.

Portable vacuum spectrograph. T. H. Osgood (Rev. Sci. Instr., 1934, [ii], **5**, 368—369).—The camera and *X*-ray tube may be detached from the pumping system for removal to a dark-room. C. W. G.

Grating microspectrograph and its application to microchemistry. E. E. Jelley (Phot. J., 1934, **74**, 514—521).—A description of the instrument and its use in determining the optic axial angles of biaxial crystals is given. A new technique of micro-identification of org. substances depends on the production of characteristic birefringence spectrograms of wedge-shaped crystals obtained by fusion of the unknown, and of known substances having approx. the same m.p. Illustrations are given for $PhSO_2{\cdot}NHPh$, NHAcPh, antipyrine, *m*-nitroaniline, *p*- and 2 : 4-di-nitrophenol. N. M. B.

Application of Henner cylinders to Hahn and Klockmann's colorimetric procedure. N. P. Komar (J. Appl. Chem. Russ., 1934, **7**, 420—423).—A colorimeter serving for determinations by Hahn and Klockmann's method (A., 1931, 54) is described. R. T.

Foundations and applications of absolute colorimetry. XI. Highly stable grey solution. A. Thiel (Chem. Fabr., 1934, **7**, 383—384; cf. this vol., 912).—Extinction measurements show the solution to be practically ideal as a light-weakening medium. E. S. H.

Physical methods in the chemical laboratory. XXII. Light absorption and chemical composition. A. Smakula (Angew. Chem., 1934, **47**, 657—665).—The val. of absorption spectra in determining, *e.g.*, the no. and positions of ethylenic linkings is described and discussed, many typical curves being reproduced. The relation between absorption bands and mol. refraction and m.p. is discussed. H. F. G.

Derivation of photometric standards for tungsten filament lamps. H. T. Wensel, W. F. Roeser, L. E. Barbrow, and F. R. Caldwell (J. Res. Nat. Bur. Stand., 1934, **13**, 161—168).—The C-filament standard lamps are compared with a black body immersed in Pt at the m.p., and the gas-filled W-filament lamps with a black body in Ir at the m.p. The relative brightnesses of the black bodies is calc.

from the observed brightnesses at one wave-length. Test lamp results agreed to within 1% with those made with vac. W standards. H. F. G.

Application of photo-cells as actinometers. H. Lux (Fotograf. Ind., 1934, **32**, 168—172; Chem. Zentr., 1934, i, 2948).—Since the spectral sensitivity of photo-cells (I) varies with wave-length and the sensitivity max. of plates varies, the uncontrolled use of (I) in actinometry leads to errors unless corrections are applied. H. J. E.

Use of the prism for the determination of the principal indices of refraction in crystals. II. A. Cavinato (Atti R. Accad. Lincei, 1934, [vi], **19**, 812—816; cf. this vol., 984).—A further discussion of the previous theoretical paper. O. J. W.

Identification of crystalline substances by means of the petrographic microscope. T. N. McVay (Bull. Amer. Ceram. Soc., 1934, **13**, 255—260).—A scheme of examination is outlined and the technique of thin-section and immersed grain petrography described with special reference to determination of *n*. Canada balsam is being replaced by "Kollolith," which is particularly suitable for mounting friable materials. "Arochlor 4465 and 5460" are media having a high *n* (1·65). An extensive bibliography is given. J. A. S.

Densitometry and photographic printing. Illumination of the negative and its effect on density. C. Tuttle (J. Opt. Soc. Amer., 1934, **24**, 272—278).—Practical optical systems which yield density vals. intermediate between the specular (projection) and diffuse (contact) vals. are discussed. J. W. S.

Dose measurement of super-hard *X*-rays. R. Jaeger (Physikal. Z., 1934, **35**, 841—844).—A comparison of various chambers is made. A. J. M.

Method of measuring electrolytic conductivities without metallic electrodes. E. Denina and F. S. De Paolini (Gazzetta, 1934, **64**, 675—687).—The method (*a*) previously described (A., 1933, 1265) has been improved, and abs. conductivities can be measured with a high degree of accuracy. O. J. W.

Laboratory arrangement for electrolytic fractionation of hydrogen isotopes. II. H. Erlenmeyer and H. Gärtner (Helv. Chim. Acta, 1934, **17**, 1226—1231; cf. this vol., 262).—Details of procedure are described. F. L. U.

Apparatus for electrodialysis. P. D. Watson and P. N. Peter (Rev. Sci. Instr., 1934, [ii], **5**, 362—365).—The dialysis chamber consists of permanent diaphragms of alundum or porcelain. The p_H of the solution therein is regulated by a siphon device. C. W. G.

High-pressure Wilson expansion chamber. L. M. Mott-Smith (Rev. Sci. Instr., 1934, [ii], **5**, 346—350).—Spectroscopic photographs at pressures up to 20 atm. show tracks not markedly different from those obtained at 1 atm. C. W. G.

Meaning and calibration of the p_H scale. D. A. MacInnes (Cold Spring Harbor Sympos. Quant. Biol., 1933, **1**, 190—194).—The p_H of solutions is related to the potentials of galvanic cells containing the solution, but cannot be interpreted as a measure of $[H^{\cdot}]$. $H^{\cdot}$ activity cannot be defined thermodynamically. Ch. Abs.

Absolute measurement of coefficients of magnetisation and magnetic susceptibilities of liquids. G. Dupouy and C. Haenny (Compt. rend., 1934, **199**, 781—783).—A narrow quartz bar (I) 18 cm. long is suspended in the liquid (II) (20 c.c.) between the poles of a magnet, the susceptibility of (II) being deduced from the apparent susceptibility of (I), as measured by the Gouy method. The method is adaptable for liquefied gases or gases, and the temp. may be varied. H. J. E.

Microburette for the determination of quantities of the order of $0{\cdot}2\times10^{-6}$ g. W. Düsing [with H. Fürst] (Chem. Fabr., 1934, **7**, 313—317).—The burette consists of a capillary tube, inclined at about 30° to the horizontal, in which operates a steel plunger moved by a micrometer screw at the lower end. A drop of Hg separates the steel from the reagent. The upper end of the tube is bent down at 90°. The total vol. contained may be 50—100 cu. mm., and readings may be taken to within 0·005 cu. mm. Typical titrations and results are described. 2—4×10^{-6} g. of H_2SO_4 or HCl may be determined with an error generally $< 1\%$, and similar results are obtained for $H_2C_2O_4$–$KMnO_4$, I–$Na_2S_2O_3$, and $BaCl_2$–K_2CrO_4 titrations. H. F. G.

Apparatus for constant delivery of equal weights of two or more liquids. R. H. Lambert (Science, 1934, **80**, 361—362). L. S. T.

Simple immersion filter for the volumetric determination of precipitates, especially in Bertrand's sugar determination. J. Blom (Z. anal. Chem., 1934, **98**, 178).—The filter consists of a thick-walled glass tube expanded into a small funnel (I) at the lower end. (I) is fitted with a Pt gauze cone which is filled with asbestos for use, suction being applied at the upper end of the tube. Asbestos and ppt. are stirred up with the solution for the titration. A. R. P.

Gas stopcocks lubricated with metaphosphoric acid. A. Pinkus (Bull. Soc. chim. Belg., 1934, **43**, 462—466).—The portion lubricated with HPO_3 is separated by a groove in the plug from the upper end, which is lubricated with an org. grease. Such stopcocks can be used for long periods without renewing the HPO_3. R. S.

Hot-wire indicator vacuum gauge. H. Murmann (Z. tech. Physik, 1933, **14**, 538—540; Chem. Zentr., 1934, i, 896).—A vac. gauge in which the temp. of a wire carrying a const. current (45 m.-amp.) is used to indicate pressure is described. L. S. T.

Check valve for vacuum pumps. G. Narasimhamurthy (J. Indian Chem. Soc., 1934, **11**, 659—660). A device for overcoming back suction is described. E. S. H.

Automatic recording micro-osmometer for colloidal osmotic pressures. F. Urban (Rev. Sci. Instr., 1934, [ii], **5**, 375—377).—The vol. of solution required is small, the Cellophane membrane is rigidly supported, no gaskets or washers are used, and the osmotic pressure is continuously and automatically balanced. C. W. G.

Purification of inert gas by mischmetal. C. C. Van Voorhis, A. G. Shenstone, and E. W. Pike (Rev. Sci. Instr., 1934, [ii], 5, 367—368).—Mischmetal heated as cathode in a d.c. discharge is effective in cleaning Ne. C. W. G.

Quantitative addition tube. J. Greenspan (J. Amer. Chem. Soc., 1934, 56, 2053—2054).—A device to assist adding a weighed amount of solid through a narrow opening. E. S. H.

Automatic gas-holder using concentrated sulphuric acid. A. Pinkus (Bull. Soc. chim. Belg., 1934, 43, 467—470; cf. this vol., 750).—An all-glass apparatus is described for the storage and supply at const. pressure of Cl_2 etc. Movement of the aspiratory liquid is controlled by glass valves. R. S.

Determination of dielectric constant of conducting liquids. A. N. Tschilaev (J. Gen. Chem. Russ., 1934, 4, 273—289).—A resonance method for determining the dielectric const., D, of conducting and non-conducting liquids and solids is described; the mean error is $\pm 0{\cdot}5\%$. The D of dil. aq. NaCl, KCl, and $CuSO_4$ rises continuously with increasing concn. R. T.

Extraction apparatus for solids and liquids. E. L. Mays and F. L. Warren (J.C.S., 1934, 1652).—The boiling solvent (I) and the material (II) to be extracted are in separate flasks, and interposed between the reflux condenser and (II) is a device for returning the extract to (I) when the vol. with (II) reaches a predetermined level. J. G. A. G.

Laboratory apparatus. B. Kisch (Biochem. Z., 1934, 273, 349).—(*a*) To the neck of a reagent bottle (I) (for solids) with ground hollow stopper (II) a side tube (with or without stopcock) is sealed and a hole is bored at the appropriate level in the wall of (II). (I) may be evacuated and used for storing hygroscopic or oxidisable substances. (*b*) Observation of the evolution of minute amounts of gas in eudiometers is facilitated by introducing an additional wide-bored stopcock into the lower part of the measuring tube. W. McC.

Stirring apparatus for flasks. Berg (Chem.-Ztg., 1934, 58, 842).—A vertical screw rests in a guide lying on the neck of the flask and carries at the lower end two hinged vanes. When inserting these lie longitudinally, but rapid rotation of the screw causes them to take up a lateral position, and the whole works up and down the flask by manual operation. C. I.

Electromagnetic torsion viscosimeter. G. Berraz (An. Inst. Invest. cient. tecn., 1931, 2, 79—84; Chem. Zentr., 1934, i, 2455).—A closed glass tube loaded with Hg is caused to rotate in the liquid. The viscosity of the liquid is deduced from the current required in an electromagnetic control system to restore equilibrium. H. J. E.

Determination of density and viscosity of gases with the Schilling–Bunsen apparatus. W. Schiller (Forsch. Ingenieurwes. Ausg. *A*., 1933, 4, 225—229; Chem. Zentr., 1934, i, 2455).—Results with this method (flow through a nozzle) depend on both the d and viscosity of the gas. Experiments with air and H_2 are described. H. J. E.

Constant-rate dropping device for liquids. H. F. Pierce (Science, 1934, 80, 339). L. S. T.

Apparatus for determining specific gravity of solutions. J. Ciochina (Z. anal. Chem., 1934, 98, 416—417).—The heights of balanced columns of liquid are compared. J. S. A.

Automatic device for maintaining constant pressure. C. Chandrasekhariah (Current Sci., 1934, 3, 112—113).—An automatic, electrically-controlled arrangement for maintaining pressure to within $\pm 0{\cdot}5$ cm. Hg is described. L. S. T.

Technique of ultrafiltration. J. J. Quigley (Amer. J. Hyg., 1934, 20, 218—224).—An ultra-filter for large quantities, and the prep. of cellulose nitrate-impregnated alundum thimbles are described. Ch. Abs. (*e*)

Drop weight as a function of the drop velocity and diameter of the drop surface. A. Adler (Physikal. Z., 1934, 35, 864—867).—The drop velocities for best results in the drop wt. method of determining surface tension are given for H_2O, C_6H_6, MeOH, and Et_2O. A. J. M.

Evaporation technique for aluminium. J. Strong (Physical Rev., 1933, [ii], 43, 498).—The technique of the evaporation of Al from a W helix is described. Al mirrors thus made are superior to those of Ag. Reflectivity for ultra-violet light is greater, the mirrors do not tarnish, and they are inert to corrosive agents. They can be washed with soap and H_2O without damage or scratching. L. S. T.

Aluminium–magnesium mirrors. H. W. Edwards (Physical Rev., 1933, [ii], 43, 205).—Metals evaporated in a vac. and deposited on glass show high reflexion in the visible spectrum. Al–Mg mirrors reflect 94%. L. S. T.

Geochemistry.

Atmospheric ozone investigations conducted at Scoresby Sound during the polar year. A. Dauvillier (J. Phys. Radium, 1934, [vii], 5, 455—462).—Chemical, spectrographic, and photo-electric measurements of the daily atm. $[O_3]$ were obtained and plotted for a year. A large increase after nightfall, reaching a max. of 57 mg. per 100 cu. m. of air, and returning to normal val. after sunrise, was observed. Theories of formation and variation with time and locality are reviewed. Results can be interpreted only on the auroral theory. N. M. B.

Origin of helium in beryllium minerals. O. Hahn (Naturwiss., 1934, 22, 744).—He could be formed by the effect of γ-rays on Be, which emits a neutron, becoming Be^8, which then breaks down to $2He^4$. A. J. M.

Examination of the gases of boric acid soffioni, with special reference to their content of helium and other noble gases. U. Sborgi (Mem. R. Accad. Italia, 1934, **5**, 667—713).—The following data are given for various Tuscan soffioni : wt. of vapour expelled per hr., ratio of gas to condensible vapour, temp., yields of NH_3 and H_3BO_3, and composition and radioactivity of the gas. In most cases the gas contains about 0·002% He and 0·001% A by vol. and has in some cases a radioactivity of the order of 10^{-5} millicurie per litre. D. R. D.

Mineral waters of the upper Adige and the Trentino. Chemical and physico-chemical investigations. I. M. Betti and G. B. Bonino (Mem. R. Accad. Italia, 1933, **5**, 1—56).—Physical properties, physico-chemical consts., and chemical analyses are recorded. D. R. D.

Changes in the composition of natural waters. A. Massink and L. G. M. B. Becking (Rec. trav. chim., 1934, **53**, 1047—1060).—The composition of a natural H_2O may be conveniently represented on triangular diagrams, each relating to three selected components (*e.g.*, Na, Ca, Mg). Lines on such diagrams can indicate any continuous change in composition with geographical position or with time. Examples of the application of the method are given. The freshening of the Zuiderzee is discussed. In certain special cases the composition may be determined graphically on the basis of a single measurement of electrical conductivity. F. L. U.

Mineral waters of Venice. Ferruginous water of Romano d'Ezzelino. G. Bragagnolo (Annali Chim. Appl., 1934, **24**, 483—486).—Composition and physico-chemical consts. are given. T. H. P.

Mud and salt water of eight mud lakes. P. Kaschinski, E. Gubareva, N. Vesselovski, and K. Lasarev (Hydrochem. Mater., 1931, **7**, 3—123; Chem. Zentr., 1934, i, 524—525).—Analytical data are recorded. The absorption of H_2O by the mud and the adsorption of methylene-blue by the washed mud were studied. H. J. E.

Condition of silicic acid in mineral waters. L. Fresenius (Arch. Med. Hydrology, 1932, **10**, 81—82).—Rather $<$ 1% of the SiO_2 content of waters is mol. dispersed chiefly as dissolved disilicic acid. The latter is more active therapeutically than is colloidal SiO_2. Ch. Abs. (*p*)

Physico-chemical variables in a Minnesota lake. H. J. Oosting (Ecolog. Monogr., 1933, **3**, 493—533).—Data for Ham Lake (N. of Minneapolis) are recorded. Ch. Abs.

Proportion of heavy water in the water of crystallisation of minerals. E. H. Riesenfeld and H. E. Riesenfeld (Ber., 1934, **67**, [*B*], 1659—1660).—Examination of the H_2O of crystallisation (I) from gypsum and polyhalite shows that no such enrichment in H_2^2O has occurred as to enable (I) to be used technically for further enrichment. The pyknometer is insufficiently sensitive to establish a difference in the ratio $H_2^2O : H_2O$ in (I) and ordinary H_2O. H. W.

Occurrence of heavy water from the geochemical viewpoint. V. Vernadsky (Compt. rend., 1934, **199**, 694—696).—It is suggested that the following should be examined for their content of H_2^2O : the remains of Quaternary glaciers, isolated salt lakes, salt hydrates formed by the evaporation of ancient lakes, volcanic vapours, chlorites, and micas. The concn. of H_2^2O by gravitation is discussed. R. S. B.

Agency of algæ in the deposition of travertine and silica from thermal waters. E. T. Allen (Amer. J. Sci., 1934, [v], **28**, 373—389).—Geologically the influence of algæ is unimportant, and inorg. causes involving loss of CO_2 account satisfactorily for the deposits. C. W. G.

Relation between colour and composition of autunite from Lurisia. L. Francesconi and R. Bruna (Gazzetta, 1934, **64**, 650—652).—The range of colour of various samples of autunite from sulphur-yellow to yellowish-green runs parallel to the increasing arsenate content of the sample. O. J. W.

Pleochroism of minerals in the ultra-violet. N. Melancholin (Compt. rend. Acad. Sci. U.R.S.S., 1934, **3**, 505—506).—Results of the examination of a series of minerals are recorded. H. J. E.

Interglacial kieselguhr from Ober-Ohe and its chemical and geological relation to recent saproliths. W. Benade and R. Potonié (Mitt. Lab. preuss. geol. Landesanst., 1933, 59—71; Chem. Zentr., 1934, i, 2914).—The dry material contains 20—30% of org. matter. The material sol. in org. liquids and the non-hydrolysable material are $>$ in recent saproliths. H. J. E.

Specific gravity of lapis lazuli. B. W. Anderson and C. J. Payne (Nature, 1934, **134**, 627).—Of 500 specimens 95% had *d* 2·75—2·90, the extreme limits being 2·45 and 2·94, in contrast with the generally-accepted vals. between 2·38 and 2·45. L. S. T.

Nickel-bearing goslarite, epsomite, and melanterite from County Durham. J. A. Smythe (The Vasculum, 1933, **19**, 12—17; Mineralog. Abs., **5**, 283).—The sol. salts from a barite–witherite vein are homogeneous isomorphous mixtures with up to 12·79% $(Fe,Mn)SO_4,7H_2O$ in the goslarite and epsomite, and 11—55% $(Mg,Zn,Ni)SO_4,7H_2O$ in melanterite. Ch. Abs. (*e*)

Effect of heating on physical and chemical properties of fused basic rocks. K. Kani (J. Japan. Assoc. Min. Pet., 1931, **5**, 124—130, 166—176).—Several rocks were fused at 1350° and held at 1050°, the thermal expansion, heat loss and absorption, and changes in microscopic properties and in the solubility in HCl being recorded. Ch. Abs. (*e*)

Corundum in the region of Sludyanski (Ural) phlogopite deposits. A. Suloev and A. Ponomorev (Min. Suir., 1934, **9**, No. 3, 31—33). Ch. Abs.

Weathering of silicate minerals. O. Tamm (Arkiv Kemi, Min., Geol., 1934, **11**, A, No. 14, 27 pp.).—By rotation in H_2O or C_6H_6 hard minerals are reduced to particles of dimensions $< 1\ \mu$: K felspar particles obtained by grinding in C_6H_6 absorb 5—6% H_2O not lost at 105°, have a considerable buffer action at p_H 6—10, and are considerably decomposed by H_2O with dissolution of K silicate. When ground in H_2O the particles reversibly exchange $K^{\cdot}$ for $H^{\cdot}$ at p_H 6—10. In this and other respects they behave like muscovite particles ground in C_6H_6, and it is probable that the felspar lattice is converted by H_2O into the muscovite lattice. Particles of desmin, a typical zeolite, react reversibly with H_2O at p_H 6→9. Wollastonite particles buffer strongly at p_H 8 owing to their considerable solubility (0·245 g. per litre). A. G.

Crystal morphology of vesuvianite. G. Kalb (Z. Krist., 1934, **89**, 18—23).—External morphology only. B. W. R.

Lilac ortho-pyroxenes from Koratagere, Mysore State. B. R. Rao and M. B. R. Rau (Current Sci., 1934, **3**, 114—115).—A few of the outcrops of the cordierite-hypersthene rocks near Bidaloti show a violet or lilac orthopyroxene which has the usual characteristics of hypersthene (I). It is closely associated with the normal pink to green pleochroic (I), cordierite (II), and biotite (III), and is probably a derived species from the reconstruction of the altered products of (II) and (III). L. S. T.

Petrology of the alkaline stock at Pleasant Mountain, Maine. W. F. Jenks (Amer. J. Sci., 1934, [v], **28**, 321—340).—Chemical and Rosiwal analyses are given. C. W. G.

Occurrence of pyrites deposits at Lam in the Bavarian forest. F. Hegemann and A. Maucher (Chem. Erde, 1934, **9**, 173—199).—The nature of the deposits is described and their mode of origin discussed. E. S. H.

Biological origin of deposits of iron and sulphur. G. Bargagli-Petrucci (C.R. Intern. Geol. Congr., 1930, **2**, 309—314).—Bacteria of the type of *Bacillus ferrigenus* deposit Fe and S from bog-H_2O, producing ore deposits. Ch. Abs. (*e*)

Separation in the system Cu–Fe–S and its significance as a "geological thermometer." H. Borchert (Chem. Erde, 1934, **9**, 145—172).—A study of Cu pyrites, cubanite, and other minerals belonging to the system Cu–Fe–S has been made, particularly with regard to the temp. of separation of the various phases and the behaviour on oxidation. The geological bearing of the results is discussed. E. S. H.

"Terra Roxa" in São Paulo, Brazil. F. W. Freise (Econ. Geol., 1934, **29**, 280—293).—The rock disintegration is discussed. Ch. Abs. (*e*)

Radioactive phlogopite from the Kira-Kira region in Eastern Transbaikalia. J. Shafranovski (Trans. Geol. Prosp. Serv. U.S.S.R., 1931, **50**, 765—769).—Analytical data are recorded. The radioactivity is due to the presence of a small quantity of zircon. Ch. Abs. (*e*)

Calcite marble. G. W. Bain (Econ. Geol., 1934, **29**, 121—139).—In the Vermont marble deposits, the development of cryst. marbles was due to thermal metamorphism of bituminous limestone by hot solutions flowing along bedding planes, the flow channels being marked by bands of chlorite, actinolite, and mica. Ch. Abs. (*e*)

Iron ores of Minas Del Rif, Spanish Morocco. A. Heim (Econ. Geol., 1934, **29**, 294—300).—The ore at Uixan is a massive, bluish hæmatite (Fe 60—64, SiO_2 6, S 1—3%). That at Setolazar is of sedimentary origin with magmatic intrusions of hæmatite and magnetite. Ch. Abs. (*e*)

Ore base of Pribalkhashstroy (Russian Mid-Asia). M. P. Rusakov (Tzvet. Met., 1933, No. 2—3, 27—40).—Porphyritic Cu ores discovered near Lake Balkhash, Kasakstan, are described. Ch. Abs.

Paragenesis of the oxidised ores of copper. G. M. Schwartz (Econ. Geol., 1934, **29**, 55—75).—The paragenesis is discussed. Two oxidation sequences are observed: (1) sulphides are oxidised to cuprite, then to black oxide, which is hydrated and carbonated to malachite (I); (2) sulphides are replaced directly by (I). Ch. Abs. (*e*)

Rich ores of Goldfield, Nevada. C. F. Tolman and J. W. Ambrose (Econ. Geol., 1934, **29**, 255—279).—The development of the ores is traced. The approx. formula of goldfieldite is $Cu_6Sb_2(S,Te)_9$. Ch. Abs. (*e*)

Weathering of felspars in relation to soil formation. P. Zemyatchenski (Trans. Dokuchaev Inst. Soil Sci., 1933, **8**, No. 1, 1—42).—Atm. action on felspars in N.W. U.S.S.R. and the Murman coast produces a material resembling muscovite in optical properties, but much higher in H_2O. Ch. Abs. (*e*)

Felspars of the Chibina massif. B. Kupletski (Mem. Soc. Russe Min., 1931, [ii], **60**, 51—64).—The felspars contain BaO. Anorthoclase from the Kukiswumtschor Mts. contains 2·44% of Fe orthoclase. Ch. Abs. (*e*)

Grünerite from Mt. Humbolt, Michigan. N. Sundius (Geol. Fören. Stockholm, 1934, **56**, 98—100; Chem. Zentr., 1934, i, 2730).—The % composition was SiO_2 50·08, TiO_2 0·01, Al_2O_3 0·25, Fe_2O_3 0·58, FeO 38·55, MnO 1·58, MgO 6·24, CaO 0·45, Na_2O and K_2O trace, H_2O 2·05%. H. J. E.

Specific gravity of Japanese acid clay. K. Yamamoto and H. Ishikawa (Mem. Fac. Sci. Eng. Waseda Univ., 1934, **11**, 11).—Japanese acid clay has *d* 2·4—2·5, after treatment with alkaline solutions 2·5—2·6, and with acid solutions 2·2—2·4. The *d* after heating depends on the temp., and is max. (2·5—2·6) after heating at 200—400°. A. G.

Lignites of the Moscow Basin. R. A. Waehner (Brennstoff-Chem., 1934, **15**, 365—368).—These lignites appear to have originated in the remains of plants allied to the conifers and belonging to a more recent geologic age than the bituminous coal flora. The lignites contain no cellulose, 5—6% of humic acids, and 1·3—2·5% of bitumen. The fossil lignin, which constitutes about 90% of the lignites, is a partly esterified hydroxycarboxylic acid similar in constitution to the lignin of present-day plants. The results are discussed briefly in relation to the mechanism of the formation of lignites. A. B. M.

Mineral formations in the Sredni coal seam in the Karaganda coal basin. N. A. Volkov, V. I. Luchitzki, and S. D. Chetverikov (Min. Suir., 1934, **9**, No. 2, 48—50).—The minerals are quartzine, kaolinite, and celestine. Ch. Abs.

Evolution of mineral coals. I, II. J. V. Lewis (Econ. Geol., 1934, **29**, 1—38, 157—202).—A discussion. Ch. Abs. (*e*)

Soil profiles and the accompanying forest vegetation in the neighbourhood of Montpellier. E. Blanck, J. Braun-Blanquet, and W. Heukeshoven (Chem. Erde, 1934, **9**, 200—220).—The chemical and mineralogical nature of the soil is compared with the type of vegetation. E. S. H.

Geography of the podsol stage of soil formation. V. A. Kovda (Trans. Dokuchaiev Soil Inst., 1934, **10**, No. 2, 1—30).—The conception of a unique podsol zone in the cold region must be replaced by a more exact conception of podsolised soils in different thermic zones: subpolar-cold (dwarf podsols), cool temperate (podsols of the forest zone), warm temperate (podsolised soils of Precaucasia, "zheltozems") subtropical (podsols of Abkhasia, Mediterranean, America), and tropical (podsols of Java, Brazil). A. M.

Organic Chemistry.

Slow oxidation of propane. R. N. Pease and W. P. Munro (J. Amer. Chem. Soc., 1934, **56**, 2034—2038).—Org. peroxides, aldehydes (mainly CH_2O), and alcohols (mainly MeOH) are formed as secondary products, but the primary reaction is unknown. When the interior of the reaction bulb is coated with KCl, peroxides are almost completely eliminated, whilst the reaction rate is not materially altered. E. S. H.

Action of oxides of nitrogen on hydrocarbons. I. Action of nitric oxide on saturated hydrocarbons in presence of catalysts. M. S. Platonov and S. P. Schaikind (J. Gen. Chem. Russ., 1934, **4**, 434—437).—The products of reaction of NO with *n*-C_5H_{12}, -C_6H_{14}, and -C_7H_{16} in presence of Al_2O_3–CeO_2–ThO_2–kaolin at 450—500° were NH_3 15—20, NO 30, CO 1—10%, and unsaturated hydrocarbons, CH_4, and N_2, and in presence of V_2O_5 at 290—310°, or of Pt-black at 250—300° H_2O, CO, N_2, and unchanged hydrocarbons. Carboxylic acids and nitriles were not detected. R. T.

Thermal decomposition of octane and of βε-dimethylhexane.—See this vol., 1311.

Syntheses by means of unsaturated compounds. B. A. Kazanski (Uspekhi Khim., 1934, **3**, 116—162).—A comprehensive review. Ch. Abs. (*e*)

Addition of gaseous hydrogen chloride and bromide to propene.—See this vol., 1314.

Rate of hydration of trimethylethylene.—See this vol., 1313.

Conjugated oxidation of unsaturated hydrocarbons and aldehydes. Oxidation of octene with acetaldehyde or benzaldehyde. V. V. Pigulevski (J. Gen. Chem. Russ., 1934, **4**, 616—621).—The oxidation of MeCHO (I) and of PhCHO (II) by atm. O_2 is inhibited by octene (III), and diminishes with increasing O_2 concn. The oxidation of (III) is activated by (I) or (II); in particular, AcO_2H (IV) and BzO_2H formed as intermediates convert (III) into octene oxide. The velocity of oxidation of (III) by (IV) is > that of (I) by (IV). R. T.

Decenes produced from methyl*iso*propylcarbinol by sulphuric acid. N. L. Drake, G. M. Kline, and W. G. Rose (J. Amer. Chem. Soc., 1934, **56**, 2076—2079).—$CHMePr^{\beta}\cdot OH$ and 75% H_2SO_4 at 80° give a mixture (*A*) of approx. equal amounts of γεε-trimethyl-Δ^{β}-heptene (I) and γδεε-tetramethyl-Δ^{β}-hexene (II), since ozonolysis of (*A*) affords MeCHO, δδ-dimethylhexan-β-one (III) [from (I)], b.p. 154·4°/768 mm. [*semicarbazone*, m.p. 169·5°; 2 : 4-*dinitrophenylhydrazone*, m.p. 146·5—147°; *oxime* (IV), b.p. 101°/13 mm.], and γδδ-trimethylpentan-β-one (V) [from (II)], b.p. 147·2°/766 mm. [*semicarbazone*, m.p. 148°; p-*nitrophenylhydrazone*, m.p. 73°; 2 : 4-*dinitrophenylhydrazone*, m.p. 109·5°; *oxime* (VI), b.p. 113°/27 mm.]. (III) is oxidised (NaOBr) to ββ-*dimethylvaleric acid* (VII), b.p. 103—104°/13 mm., 213°/778 mm. (*amide*, m.p. 76·5°; *anilide*, m.p. 105·5—106°; *Me*, b.p. 49—50°/17 mm., and p-*phenylphenacyl*, m.p. 74°, esters); (V) similarly gives αββ-*trimethylbutyric acid*, b.p. 76°/5 mm., 103—104°/20 mm., m.p. 24·5° (*amide*, m.p. 106°; *anilide*, m.p. 104·5°; *Me*, b.p. 46°/18 mm., and p-*phenylphenacyl* ester, m.p. 68·5°). (IV) and PCl_5 in Et_2O afford the N-*Ac* derivative, b.p. 125°/13 mm., of ββ-dimethylbutylamine [N-2 : 4 : 6-*trinitrophenyl*, m.p. 88—88·5°, prepared by the action of *s*-$(NO_2)_3C_6H_2Cl$ in EtOH, and *benzenesulphonyl*, m.p. 59—59·5°, derivatives]; the amine is also prepared by reduction (Na, EtOH) of $CMe_2Et\cdot CN$. (VI) is similarly rearranged to the N-*Ac* derivative, b.p. 130—131°/20 mm., m.p. 68—68·5°, of αββ-trimethylpropylamine (N-2 : 4 : 6-*trinitrophenyl*, m.p. 107°, and *benzenesulphonyl*, m.p. 96°, derivatives; *aurichloride*), also prepared by reduction (Na, EtOH) of $CMeBu^{\gamma}{:}N\cdot OH$. The above amines are obtained from their Ac derivatives by hydrolysis with aq. H_3PO_4 at 230—240° (sealed tube). γ-Methyl-γ-ethylpentan-β-one (2 : 4-dinitrophenylhydrazone, m.p. 92—92·5°) is prepared (method: Nyberg, A., 1922, i, 802) for comparison with (III). α-Methyl-α-ethylpropionic acid (amide, m.p. 78·5°; anilide, m.p. 88·5°; *p*-phenylphenacyl ester, m.p. 76°) is synthesised (from $CMeEt_2\cdot MgCl$ and CO_2) for comparison with (VII). (I) and (II) are also present in the "diamylene" obtained as a by-product during chlorination of mixed pentanes. Whitmore's theory of the polymerisation of olefines by acid catalysts explains the formation of (I) but not of (II). H. B.

Sodium in liquid ammonia as a dehydrohalogenation agent and its use in the synthesis

of acetylenes. T. H. VAUGHN (J. Amer. Chem. Soc., 1934, **56**, 2064—2065).—Na (2 mols.) in liquid NH_3 is added with vigorous stirring to CHPh:CHBr in Et_2O–liquid NH_3, the mixture is then partly evaporated, and treated with H_2O (and a little HCl); CPh:CH (I) is thus obtained in 96% yield. $CClPh:CH_2$ similarly gives 15% of PhEt; α-chloro-*p*-methylstyrene affords 63% of *p*-tolylacetylene; β-bromo-Δ^α-decene yields 56% of Δ^α-decene; $(\cdot CHBrPh)_2$ furnishes (with 15 mols. of Na) 73% of dibenzyl; $CHBrPh\cdot CH_2Br$ gives (with 3 mols. of Na) 66% of (I). The acetylenes are contaminated with hydrogenation products.
H. B.

Rapid catalytic preparation of sodamide in liquid ammonia and its uses in preparation of acetylenic materials. T. H. VAUGHN, R. R. VOGT, and J. A. NIEUWLAND (J. Amer. Chem. Soc., 1934, **56**, 2120—2122).—$NaNH_2$ (I) is readily prepared from Na and liquid NH_3 in presence of Na oxides and NH_3-sol. Fe, Ni, or Co salts. The method adopted is: Na (1 g.) is added to a mixture of liquid NH_3 (500 c.c.) and $Fe(NO_3)_2,6H_2O$ (?) (0·3 g.), air is then bubbled through the solution until the blue colour disappears, and Na (25 g.) is added in small pieces. (I) thus prepared is more sol. and more reactive than commercial $NaNH_2$. Cl:CBu is converted by (I) in liquid NH_3 into CH:CBu; αβ-*dibromo*-Δ^α-*heptene*, b.p. 93—96°/11 mm. [from amylacetylene (II) and Br in CCl_4 at −34°], similarly gives (II); $(\cdot CHBrPh)_2$ affords stilbene; CHBr:CHPh, CH_2:CClPh, and $CH_2Br\cdot CHBrPh$ all yield CH:CPh; β-bromo-Δ^α-octene furnishes hexylacetylene; p-$C_6H_4Me\cdot CCl:CH_2$ gives p-$C_6H_4Me\cdot C:CH$; αβ-dibromodecane affords octylacetylene. α-Ethyl-β-amylacetylene is not rearranged by (I).
H. B.

Preparation of derivatives for identification of alkyl chlorides. H. W. UNDERWOOD, jun., and J. C. GALE (J. Amer. Chem. Soc., 1934, **56**, 2117—2120; cf. Schwartz and Johnson, A., 1931, 597).—The AlkCl (I) (18 studied) is converted into MgAlkCl and thence by ArNCO into Alk·CO·NHAr (Ar=Ph, p-C_6H_4Me, and α-$C_{10}H_7$); the *p*-toluidides are useful for distinguishing between (I) of similar b.p. The following are new: α-*methylbutyr*-p-*toluidide*, m.p. 92·5—93°, and -α-*naphthylamide*, m.p. 128—129°; αα-*dimethylpropion*-p-*toluidide*, m.p. 119—120°, and -α-*naphthylamide*, m.p. 146—147°; iso*hexo*-p-*toluidide*, m.p. 61·5—62·5°, and -α-*naphthylamide*, m.p. 110—111°; αα-*dimethylbutyr*-p-*toluidide*, m.p. 83—83·5°, and -α-*naphthylamide*, m.p. 137—138°; α-*methylvaler*-p-*toluidide*, m.p. 90—91°, and -α-*naphthylamide*, m.p. 102·5—103·5°; α-*ethylbutyr*-p-*toluidide*, m.p. 107·5—108·5°, and -α-*naphthylamide*, m.p. 117—118°; α-*methylhexoanilide*, m.p. 91—92°.
H. B.

Kinetics of salt formation and of bromination of nitroethane. Rearrangement of nitroethane.—See this vol., 1313.

Hydrogenation of acetic and trifluoroacetic anhydrides. Trifluoroethyl alcohol. F. SWARTS (Bull. Soc. chim. Belg., 1934, **43**, 471—481).—Mainly a detailed account of work already reported (this vol., 170). The formation of $CMeF_3$ from $(CF_3\cdot CO)_2O$ is not due to secondary reduction of $CF_3\cdot CH_2\cdot OH$ (I), as this is not hydrogenated under the experimental conditions. (I) with HNO_3 and H_2SO_4 gives βββ-*trifluoroethyl nitrate*, b.p. 66·15°, and with AcCl, the *acetate*, b.p. 77·8°. $CF_3\cdot CO\cdot NH_2$ is slowly hydrogenated (Pt-black–Et_2O) to (I). With H_2 at 21°/30—45 atm. and Pt-black, Ac_2O yields C_2H_6, EtOAc, and AcOH.
H. N. R.

Non-saponifiable matter of shea-nut fat. I. I. M. HEILBRON, G. L. MOFFET, and F. S. SPRING (J.C.S., 1934, 1583—1585).—Acetylation of the unsaponifiable resin (I), m.p. 65—85°, (5%) obtained (in addition to illipene; Hopkins *et al.*, B., 1932, 30) from shea-nut fat affords β-amyrin acetate, and an *acetate*, m.p. 141°, $[\alpha]_D$ +22·4° in $CHCl_3$ (2 double linkings by BzO_2H), hydrolysed by 3% KOH–EtOH to an *alcohol*, $C_{30(29)}H_{(50)48}O$, m.p. 109·5°, $[\alpha]_D$ −11·9° in $CHCl_3$ (*Bz* derivative, m.p 130°). From the product of benzoylation of (I) are isolated lupeol and β-amyrin benzoates.
J. W. B.

Action of sodium hypobromite on dimethylpinacols. J. PALMÉN (J. pr. Chem., 1934, [ii], **141**, 113—122).—*s*-Dimethylpinacols, OH·CMeR·CMeR·OH, are converted by shaking with an excess of cold alkaline NaOBr into CBr_4 (66—95% of 2 mols.) and RCO_2H [31—90% of 2 mols. (or 1 mol. of dibasic acid)]. Thus, $(\cdot CMe_2\cdot OH)_2$ gives AcOH; $(\cdot CMeEt\cdot OH)_2$ affords $EtCO_2H$; $(\cdot CPhMe\cdot OH)_2$ yields BzOH; 9 : 10-dihydroxy-9 : 10-dimethyl-9 : 10-dihydrophenanthrene furnishes diphenic acid; santene glycol gives *cis*-*cyclo*pentane-1 : 3-dicarboxylic acid; 1 : 2-dihydroxy-1 : 2-dimethylcamphane affords camphoric acid.
H. B.

Condensation of polyhydric alcohols, sugars, and hydroxy-acids with aldehydes under the influence of phosphorus pentoxide. J. W. PETTE (Rec. trav. chim., 1934, **53**, 967—987).—Condensation of polyhydric alcohols with aldehydes in presence of P_2O_5, HCl, and H_2SO_4 gives (the product being dependent on the conditions): *tri-benzylidene-*, m.p. 223—224°, $[\alpha]_D^{17}$ −16·5°, -(4-*methoxy*-, m.p. 235°, $[\alpha]_D^{21}$ −21°, -(4-*methyl*-, m.p. 255°, $[\alpha]_D^{20}$ −6·5°, -(2-*nitro*-, m.p. 222°, $[\alpha]_D^{22\cdot5}$ −62°, -(3-*nitro*-, m.p. 268°, $[\alpha]_D^{17}$ −36°, and isomeric forms of -(4-*nitro*-, m.p. 296°, $[\alpha]_D^{21}$ −54°, and m.p. 152°, $[\alpha]_D^{24}$ −7°; *di*-(4-*nitro*-, m.p. 315—320°, $[\alpha]_D^{20}$ +106·5° in C_5H_5N; *tri*-(2-, m.p. 260°, $[\alpha]_D^{20}$ +36°, -(3-, m.p. 212°, $[\alpha]_D^{18}$ −23°, and -(4-*chloro*-, m.p. 187°, $[\alpha]_D^{20}$ +7°, and -(4-*chloro*-3-*nitro*-*benzylidene*)-*mannitol*, m.p. 300—302°; *di-benzylidene-*, -(4-*methoxy*-, m.p. 219—220°, -(4-*methyl*-, m.p. 235°, -(2-, m.p. 241°, -(3-, m.p. 269°, and -(4-*nitro*-, m.p. 286°, -(2-, m.p. 222°, -(3-, m.p. 193°, and -(4-*chloro*-, m.p. 235°, and -(4-*chloro*-3-*nitro*-*benzylidene*)-*erythritol*, m.p. 253°. Condensation of sugars with aldehydes appears to be facilitated by low temp. *d*-Tartaric, citric, and *dl*-mandelic acids condense with aldehydes to give *di*-(4-*methoxy*-, m.p. 155°, $[\alpha]_D^{16}$ +112°, -(3-, m.p. 165°, $[\alpha]_D^{19}$ +72°, and -(4-*nitro*-, m.p. 163°, $[\alpha]_D^{19}$ +39°, -(2-, m.p. 171°, $[\alpha]^{16}$ −34°, -(3-, m.p. 172°, and -(4-*chloro*-*benzylidene*)-d-*tartaric acid*, m.p. 187°, $[\alpha]_D^{20}$ +95°; 3-, m.p. 163°, and 4-*nitrobenzylidenecitric acid*, m.p. 180°; *benzylidene-*, m.p. 103°, 2-, m.p. 95°, 3-, m.p. 104°, and 4-*nitro*-, m.p. 106°, and 2-, m.p. 74°, 3-, m.p. 63°, and 4-*chloro*-*benzylidene*-*mandelic acid*, m.p. 77°. All rotations are in $CHCl_3$, unless otherwise stated.
F. R. S.

Migration of the phosphoric radical during the hydrolysis of sodium methyl β-glycerophosphate. Transition from β- into α-glycerophosphates. O. Bailly and J. Gaumé (Compt. rend., 1934, **199**, 793—795).—Successive treatment of Na β-glycerophosphate with Me_2SO_4 and $CaCl_2$ affords *Ca Me β-glycerophosphate*, m.p. 255° (block; decomp.). Hydrolysis of Na Me β-glycerophosphate with NaOH at 100° gives about 33% of Na_2 α-glycerophosphate (corresponding Ba salt also isolated), whilst 66% transition is observed when hydrolysis is effected by acid. H. W.

Xylosephosphoric acids. II. P. A. Levene and A. L. Raymond (J. Biol. Chem., 1934, **107**, 75—83; cf. A., 1933, 1141, 1144).—The homogeneity of the *iso*propylidenexylose 5-benzoate previously used has been confirmed by conversion into *iso*propylidenexylose 5-benzoate 3-*p*-toluenesulphonate (I) unaccompanied by any by-product. 5-Carbobenzyloxy*iso*propylidenexylose (II) and *p*-$C_6H_4Me{\cdot}SO_2Cl$ give *5-carbobenzyloxy*iso*propylidenexylose 3-*p*-toluenesulphonate* (III), m.p. 128·5—129·5°, $[\alpha]_D^{20}$ −25° in $CHCl_3$, which on hydrogenation (Ni) and benzoylation yields (I), identical with that prepared above. Hydrolysis of (III) with $Ba(OMe)_2$ yields *xylose 3-*p*-toluenesulphonate*, m.p. 123—124°, $[\alpha]_D^{20}$ +40·2° in EtOH (rate of glucoside formation similar to 3-methylxylose). (II) on successive phosphorylation, acid hydrolysis, and hydrogenation (Ni) yields a *xylosephosphoric acid* (*Ba* salt). The rates of hydrolysis of a no. of xylosephosphoric acids are given, the rate being much higher with a 3-derivative. It is concluded that the migration previously observed (*loc. cit.*) is real, and a mechanism, involving an intermediate *ortho*-bridge, is proposed. H. N. R.

Mannose monophosphate. III. Phosphomannonic acid and its lactones. V. N. Patwardhan (Biochem. J., 1934, **28**, 1854—1862).—Mannose monophosphate (I) oxidised by Br in presence of aq. $Ba(OH)_2$ yields *phosphomannonic acid* (II), isolated as the amorphous neutral *Ba* salt, $(C_6H_{10}O_{10}PBa)_2Ba$. (II) heated in aq. solution (III) in a sealed tube for 1 hr. yields the *γ-lactone*, m.p. 125—125·5°, $[\alpha]_{5461}$ +54·1°, but when (III) is evaporated in vac. at room temp. the *δ-lactone*, m.p. 127·5—128·5°, $[\alpha]_{5461}$ +60·6°, is formed. The rate of dephosphorylation (IV) of (II) in *N*-HCl at 100° falls after 8 hr. and attains a const. val. equal to the rate of (IV) of the lactones under comparable conditions. (I) is undoubtedly mannose 6-phosphate. A. E. O.

Bromination of aliphatic αα-disulphones.—See this vol., 1313.

Addition of iodine and thiocyanogen to unsaturated compounds. B. P. Caldwell and F. A. Piontkowski (J. Amer. Chem. Soc., 1934, **56**, 2086—2089).—The nos. quoted after the following compounds are the I val. (Hanus) and $(SCN)_2$ val. [determined by Kaufmann's method (B., 1926, 447); reaction time ≮ 30 and ≯ 48 hr.], respectively: oleic 91·38, 86·18, erucic 75, 73, ricinoleic 119·87, 87·82, furoic 9·12, 5·2, maleic 0, 0, acrylic 1·77, 0·64, crotonic 7·01, 0·92, and cinnamic acid 26·26, 1·12; Et 0·22, 0·6, phenacyl 0·63, 2·7, and *p*-nitrobenzyl maleate 0, 1; Et 30·31, 0·5, phenacyl 11·82, 1·05, and *p*-nitrobenzyl cinnamate 8·98, 1·79; citronellol 162·4, 173·8; citronellol acetate 133·3, 114·1. Allyl alcohol gives indefinite vals. The results are discussed in connexion with the effect of negative groups (near to the C:C) retarding addition. H. B.

Detection and determination of volatile fatty acids. I. *n*-Butyric acid. L. Klinc (Biochem. Z., 1934, **273**, 1—23).—$PrCO_2H$ (I) can be detected by oxidation in H_2SO_4 solution with H_2O_2 using $FeNH_4(SO_4)_2$ as catalyst with subsequent pptn. as the insol. $Hg(CN)_2$ complex. Methods are described for the determination of 5—20 mg. of (I) by macro-iodometric, of 0·5—5 mg. by micro-iodometric, methods and of 0·006—0·06 mg. nephelometrically. A modification of the methods permits determination of (I) in presence also of HCO_2H, AcOH, $EtCO_2H$, and lactic acid. P. W. C.

Migration of the double linking of oleic acid on heating in presence or absence of metals. K. H. Bauer and M. Krallis (Fettchem. Umschau, 1934, **41**, 194—196; cf. A., 1931, 1034).—Ozonolysis of the "solid" acids (Twitchell separation) from the products showed that Δ^{η}-*iso*oleic acid (I) as well as the Δ^{ι} isomeride (II) was formed when oleic acid was heated with a Ni–kieselguhr catalyst (≡2%, or 5%, of Ni) at 200° or 250° for 8 hr. in a Normann beaker. In parallel experiments, but when the Ni was omitted or replaced by a Cu or Cu–Ce catalyst, (II) was formed, but (I) could not be identified. The amount of "solid" acids produced was much greater at the higher temp.; it was not much affected by the presence or absence of Ni, but was notably reduced when the Cu catalysts were used. E. L.

New eicosenoic acid from pilot-whale oil.—See this vol., 1381.

Gadoleic acid in see-whale and humpback-whale oils.—See this vol., 1381.

Highly unsaturated C_{24}-acid in herring, cod-liver, pilot-whale, and aburazame liver-oils.—See this vol., 1381.

Synthesis of higher aliphatic compounds. IV. Synthesis of *n*-triacontanoic acid from stearic acid. (Mrs.) G. M. Robinson (J.C.S., 1934, 1543—1545).—Condensation of Et κ-bromoundecoate with $CHAcNa{\cdot}CO_2Et$ affords *Et α-acetylbrassylate* (I), b.p. 202°/0·5 mm., hydrolysed by boiling AcOH–H_2SO_4–H_2O to *μ-ketomyristic acid*, m.p. 75° (reduced to myristic acid). Condensation of (I) with stearoyl chloride and Na in dry Et_2O, and subsequent hydrolysis with boiling 5% H_2SO_4, affords *μ-keto-*n*-triacontanoic acid*, m.p. 104°, reduced (Clemmensen) to *n*-triacontanoic acid (II), the *Et* ester, m.p. 70·5°, of which is reduced by Na–$Bu^{\alpha}OH$ at 150° to *n*-triacontan-α-ol (III) (*Ac* derivative, m.p. 69°; *iodide*, m.p. 68·5°). (II) and (III) are identical with specimens isolated from lucerne (Chibnall *et al.*, this vol., 391). A similar synthesis using the chloride of (II) affords *μ-keto-*n*-dotetracontanoic acid*, $Me{\cdot}[CH_2]_{28}{\cdot}CO{\cdot}[CH_2]_{11}{\cdot}CO_2H$, m.p. 110°. J. W. B.

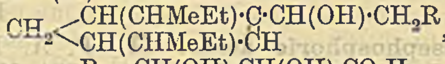
Aldol condensations. II. Synthesis of unsaturated aliphatic α-keto-acids. F. G. Fischer and O. Wiedemann (Annalen, 1934, **513**, 251—259).—

Crotonaldehyde (I), MeCHO, and a little piperidine give (cf. Kuhn and Hoffer, A., 1930, 1406) $\Delta^{\alpha\gamma}$-hexadienal (II), b.p. 64—65°/11 mm., $\Delta^{\alpha\gamma\epsilon}$-octatrienal (III), b.p. 62—64°/0·4 mm., m.p. 56°, and $\Delta^{\alpha\gamma\epsilon\eta}$-decatetraenal, b.p. 110—115°/0·5 mm., m.p. 108—109° [which, like (III), can be kept for several weeks in N_2]. Addition of 40% NaOH (3—4 c.c.) to a shaken emulsion of (I) (0·05 g.-mol.) and a saturated aq. solution of $AcCO_2Na$ (0·05 g.-mol.) at 0° gives (after 15—20 min.) a little of the Na salt (separated) of α-*keto*-$\Delta^{\beta\delta}$-*heptadienoic acid*, m.p. 89° (decomp.) [*phenylhydrazone*, m.p. 147° (decomp.); p-*nitrophenylhydrazone*, m.p. 188° (decomp.)]. (II) similarly affords α-*keto*-$\Delta^{\beta\delta\zeta}$-*nonatrienoic acid*, m.p. 116° (decomp.) [*semicarbazone*, m.p. 185°; *oxime*, m.p. 167°; *phenylhydrazone*, m.p. 152—153° (decomp.); p-*nitrophenylhydrazone*, m.p. 185° (decomp.)], whilst (III) gives α-*keto*-$\Delta^{\beta\delta\zeta\theta}$-*undecatetraenoic acid*, m.p. 135° (decomp.). These acids are coloured (cf. Kuhn and Hoffer, *loc. cit.*), are decomposed by warm aq. alkali, and undergo ready autoxidation (air) (they can be kept in N_2); they are reduced (catalytically) to the saturated α-CO-acids. H. B.

ψ-Halogens. XXVIII. Reaction of the silver salts of dibasic (polybasic) acids with iodine in presence of *cyclo*hexene. L. Birckenbach, J. Goubeau, and H. Kolb (Ber., 1934, **67**, [*B*], 1729—1734; cf. this vol., 995).—The action of I on a suspension of Ag_2S in *cyclo*hexene–Et_2O gives a mixture of 55% free S, 2% of *cyclo*hexene-1 : 2-sulphide, and 10% of di-2-iodo*cyclo*hexyl sulphide. Ag_2SO_4 gives a black tar which separates I when distilled and is completely decomposed, probably owing to oxidation by liberated SO_3. Ag_2WO_4 slowly absorbs I. Ag_2CO_3 affords *di-2-iodo*cyclo*hexyl carbonate*, whilst $Ag_2C_2O_4$ affords *di-2-iodo*cyclo*hexyl oxalate*, m.p. 118—119°, and a *substance*, $(C_4H_4O)_x$. Ag_2 succinate gives a little succinic acid and a product which could not be purified, whereas o-$C_6H_4(CO_2Ag)_2$ affords o-$C_6H_4(CO_2H)_2$ and *di-2-iodo*cyclo*hexyl* o-*phthalate*, m.p. 126°. H. W.

Complex cobaltioxalates.—See this vol., 1321.

Plant growth substances. X. Constitution of auxin-*a* and -*b*. F. Kögl and H. Erxleben (Z. physiol. Chem., 1934, **227**, 51—73; cf. this vol., 1044).—Oxidation of auxin-*a* (I), its lactone, or auxin-*b* (II) with alkaline $KMnO_4$ gives a *dicarboxylic acid* (III), $C_{13}H_{24}O_4$, m.p. 129°, $[\alpha]_D^{20}$ −11·9° in 96% EtOH, mol. surface 46—52 $Å.^2$ (*di*-p-*phenylphenacyl* ester, m.p. 169°). Oxidation of dihydroauxin-*a* with CrO_3 in AcOH affords $H_2C_2O_4$ and a *ketone* (an oil), $C_{13}H_{24}O$, $[\alpha]_D^{20}$ −9·5° in 96% EtOH (p-*nitrophenylhydrazone*, m.p. 125·5°). On heating with boiling Ac_2O and distillation in vac., (III) yields the *anhydride*, m.p. 95·5—96°. With Br and red P, (I) gives the αα′-Br_2-*acid* (IV), $C_{13}H_{22}O_4Br_2$, m.p. 90°. The Me_2 ester of (IV) (obtained by way of Ag_2 salt and MeI) by Grignard reagent and oxidation of the resulting diglycol with $Pb(OAc)_4$ affords a 1 : 3-*diketone* (an oil), $[\alpha]_D^{20}$ +9·5° in 96% EtOH, since hydrolysis with aq. KOH gives a C_5-acid (V) and a C_6-ketone (VI). (V) yields a p-*phenylphenacyl* ester, $C_{19}H_{20}O_3$, m.p. 71°, $[\alpha]_D^{20}$ +9·9° in 80% EtOH, which is identical with the corresponding derivative of (+)-α-methyl-*n*-butyric acid. (VI) gives a 2 : 4-*dinitrophenylhydrazone*, m.p. 72°, identical with the derivative from Me *sec.*-Bu ketone. Hence (III) is αα′-di-*sec.*-butylglutaric acid. The "ketone half" although racemic as isolated must possess the same configuration as the "acid half" of the 1 : 3-diketone. The $KMnO_4$ oxidation of (II)-acetal lactone yields, in addition to (III), *cis*-glutaconic acid, m.p. 134°. Oxidation of dihydroauxin-*a* with $Pb(OAc)_4$ gives glyoxylic acid (identified by colour reaction), and an aldehyde, which on oxidation with $KMnO_4$ gives an acid, $C_{16}H_{30}O_3$ (p-*phenylphenacyl* ester, m.p. 120°). This indicates 2 OH groups at α and β. (I) and (II) are therefore



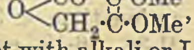
$$CH_2\begin{cases}CH(CHMeEt)\cdot C\cdot CH(OH)\cdot CH_2R\\ CH(CHMeEt)\cdot CH\end{cases},$$

(I) R=·CH(OH)·CH(OH)·CO_2H
(II) R=·CO·CH_2·CO_2H. J. H. B.

Synthesis of long-chain aliphatic ωω′-dicarboxylic acids. E. Schwenk and H. Priewe (J. Amer. Chem. Soc., 1934, **56**, 2101—2102).—*m*-Tolyl adipate, m.p. 85—87° [prepared by slow addition of $POCl_3$ (1 mol.) to the acid (1 mol.) and *m*-cresol (2 mols.) at about 120°], is rearranged by $AlCl_3$ at 165° to αδ-*di*-(2-*hydroxy*-4-*methylbenzoyl*)*butane*, m.p. 122—123°, reduced (Clemmensen) to αζ-*di*-(2-*hydroxy*-4-*methylphenyl*)*hexane*, m.p. 102—103°. This is reduced (H_2 and Ni in methyl*cyclo*hexane at 230° and 100 atm.) to αζ-di-(2-hydroxy-4-methyl*cyclo*hexyl)hexane, b.p. 205—208°/1·5 mm., which is oxidised (CrO_3, AcOH) to αζ-*di*-(2-*keto*-4-*methyl*cyclo*hexyl*)*hexane*, m.p. 60—65°, or εμ-*diketo*-βο-*dimethylhexadecane*-απ-*dicarboxylic acid* (I), m.p. 70—71°, according to the conditions used. Clemmensen reduction of (I) gives βο-*dimethylhexadecane*-απ-*dicarboxylic acid*, m.p. 64—68°. H. B.

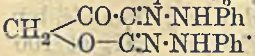
Ketolic condensations of ethyl acetoacetate with formaldehyde. H. Gault and J. Burkhard (Compt. rend., 1934, **199**, 795—797).—$CH_2Ac\cdot CO_2Et$ is added gradually to 30% CH_2O containing K_2CO_3 at $\not>$ 8°. When the mixture gives no colour with $FeCl_3$, it is saturated with $(NH_4)_2SO_4$ and extracted with Et_2O at −10°. The extract is dried successively with anhyd. $MgSO_4$ and P_2O_5 at −10° to −15° and *Et di*-αα-*hydroxymethylacetoacetate* (I) is pptd. by light petroleum. When dry, (I) is stable at room temp., it gives an Ac_2 derivative, b.p. 114°/14 mm., and is transformed by NH_3 into a *ketimine*, m.p. 185°. *Et* δ-*hydroxy*-αγ-*diacetylbutane*-αγ-*dicarboxylate* (II) (viscous acyclic and solid cyclic forms) is obtained from (I) and $CH_2Ac\cdot CO_2Et$ in presence of aq. K_2CO_3 or from $CH_2Ac\cdot CO_2Et$ and CH_2O followed by further addition of $CH_2Ac\cdot CO_2Et$. Gradual addition of 30% CH_2O to $CH_2Ac\cdot CO_2Et$ in presence of K_2CO_3–H_2O–EtOH at 28—30° gives Et_2 αε-*dihydroxy*-βδ-*diacetylpentane*-βδ-*dicarboxylate*, m.p. 100°, also obtained from (II) and CH_2O. H. W.

Hydroxytetronic acid. F. Micheel and F. Jung (Ber., 1934, **67**, [*B*], 1660—1664; cf. A., 1933, 1143).—Hydroxytetronic acid (I), m.p. 153° (prep. from Et benzoylglycollate and K described), is transformed by CH_2N_2 into the *Me_2 ether*,



$$O\begin{cases}CO-C\cdot OMe\\ CH_2\cdot C\cdot OMe\end{cases},$$

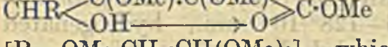
b.p. 128°/13 mm., which does not react with alkali or I and is converted by the successive action of O_3 in AcOH and MeOH–NH_3 into oxamide and $OH\cdot CH_2\cdot CO\cdot NH_2$, m.p. 116°. (I) is transformed by $NHPh\cdot NH_2$ in AcOH into αβ-*diketo*-γ-*hydroxybutyro*-

lactonediphenylhydrazone, labile form, m.p. about 180°, stable variety, m.p. 238°, also obtained from αβ-*di-keto-γ-hydroxybutyrolactone* (II), prepared by oxidising (I) with $Cu(OAc)_2$ and removal of Cu by salicylaldoxime or with *p*-$O:C_6H_4:O$; it is regarded as  $CH_2<\begin{matrix}CO\cdot C:N\cdot NHPh\\ O-C:N\cdot NHPh\end{matrix}$. The corresponding *di*-p-*nitrophenylhydrazone* has m.p. 295°. (II) is unstable, but, immediately after prep., is reduced by H_2S to (I); on keeping or, particularly, on warming in H_2O it loses CO_2 and the residue is converted by $NHPh\cdot NH_2$ into $CO_2H\cdot CMe:N\cdot NHPh$. (II) and 1 : 3 : 4-$C_6H_3Me(NH_2)_2$ give the *quinoxaline* derivative, $C_{11}H_8O_2N_2$.

H. W.

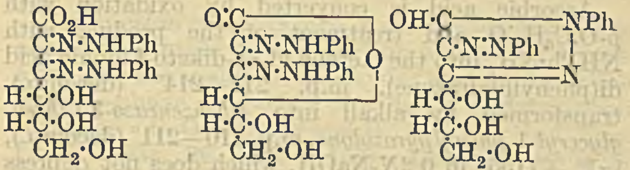
Preparation of citroanilide. F. Di Mento (Annali Chim. Appl., 1934, 24, 464—468).—Pebal's method (Annalen, 1852, 82, 87) gives poor yields. By heating citric acid with NH_2Ph, first at 60—70° and later at 120—130°, citroanilide, m.p. 199°, mixed with very little citromonoanilic acid and citrodianilide, m.p. 179°, is obtained.

T. H. P.

Methyl ethers of ascorbic acid. W. N. Haworth, E. L. Hirst, and F. Smith (J.C.S., 1934, 1556—1560).—*l*-Ascorbic acid (I) with CH_2N_2–Et_2O at −10° gives mainly (90%) its 3- (II), m.p. 121°, $[\alpha]_D^{20}$ +29° in H_2O (absorption band at 245 mμ; slow reaction with I in acid solution; intense blue with $FeCl_3$; Na salt, $[\alpha]_D$ +49·3° in H_2O), and its (?)2-*Me* derivative (III), m.p. 162°, $[\alpha]_D^{22}$ +200° in H_2O (band at 280 mμ; transient colour with $FeCl_3$; Na salt $[\alpha]_D^{22}$ +223° in H_2O). After ozonolysis of (II) the action of NH_3 gives $[\cdot CO\cdot NH_2]_2$ and l-*threonamide*, m.p. 88—90°, $[\alpha]_D^{20}$ +58° in H_2O. With excess of CH_2N_2 in MeOH at −5° (II) gives the 2 : 3-Me_2 derivative (IV) (non-reducing), identical with a specimen obtained directly from (I). With MeI–Ag_2O (IV) gives 2 : 3 : 5 : 6-tetramethyl-*l*-ascorbic acid (V) (band at 235—240 mμ), the ozonolysis product of which with MeOH–NH_3 gives only $[\cdot CO\cdot NH_2]_2$ and 3 : 4-dimethyl-*l* threonamide and no erythronamide, the presence of which in previous work (A., 1933, 1143) arose from the presence of isomeric forms of (IV). With NaOH or $Ba(OH)_2$ (IV) and (V) both yield salts of the corresponding open-chain acid, lactonisation to the original compound occurring on acidification. With Me_2SO_4–40% KOH in aq. $COMe_2$ and subsequent esterification (Ag_2O–MeI) (IV) affords a Me tetramethylketogulonate, b.p. 105°/0·03 mm., $[\alpha]_D^{20}$ −51° in MeOH, probably  $CHR<\begin{matrix}C(OMe):C(OMe)\\ OH\longrightarrow O\end{matrix}>C\cdot OMe$ $[R{=}OMe\cdot CH_2\cdot CH(OMe)\cdot]$, which resists further methylation and attack by O_3, oxidation with HNO_3 and subsequent methylation affording $Me_2C_2O_4$ and Me *d*-dimethoxysuccinate. Similar methylation of (V) gives a mixture of the open-chain acid $HO\cdot CHR\cdot C(OMe):C(OMe)\cdot CO_2H$ and some fully methylated derivative, subsequent treatment with Ag_2O–MeI affording, respectively, (V) and $MeO\cdot CHR\cdot C(OMe):C(OMe)\cdot CO_2Me$. (III) gives no $H_2C_2O_4$ on ozonolysis (? double linking between C_1 and C_2) and with CH_2N_2–Et_2O affords a *Me_2 eiher*, $[\alpha]_D^{20}$ +107° in MeOH (band at 270 mμ), which isomerises to (IV) when heated. With MeI–Ag_2O (III) affords mainly (V). These results establish the superior acidity of the 3-OH in (I), and the presence of labile derivatives indicates that (I) can react in > one structural modification.

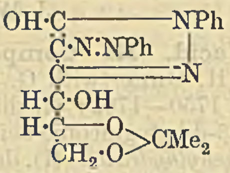
J. W. B.

***d*-Glucosaccharosonic acid. III Compounds with phenylhydrazine.** H. Ohle [with G. Böckmann] (Ber., 1934, 67, [*B*], 1750—1762; cf. this vol., 392, 634).—Treatment of αβ-diketogluconic acid with $NHPh\cdot NH_2$ leads to its *diphenylhydrazone* (I), decomp. 159—160°, $[\alpha]_D^{20}$ +241° to −92° in C_5H_5N, $[\alpha]_D^{20}$ +107·8° to +1192° in 0·2*N*-NaOH, the corresponding

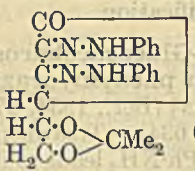


lactone (II), m.p. 202—203° (slight decomp.), $[\alpha]_D^{20}$ −93·5° in C_5H_5N, and 4-*benzeneazo*-1-*phenyl*-3-αβγ-*trihydroxypropylpyrazolone* (III), m.p. 215—216° (slight decomp.), $[\alpha]_D^{20}$ −53·1° in C_5H_5N, +1305° in 0·08*N*-NaOH. In presence of mineral acid (I) and (II) are mainly produced, whereas in presence of AcOH (I) is scarcely formed and (III) appears. Recrystallisation from $COMe_2$ or EtOAc converts (I) partly into (II); C_5H_5N behaves similarly, whilst dil. NaOH at 20° accelerates the production of (III). In contrast to (I) and (III), (II) is insol. in cold, dil. alkali, whereas boiling alkali transforms it into (III). (III) yields a *Na* salt (+$2H_2O$), m.p. 131—132°, $[\alpha]_D^{20}$ +1054°, or (+$1H_2O$), m.p. 187—191°, $[\alpha]_D^{20}$ +1125°. (III) is transformed by Ac_2O in C_5H_5N at 100° into the *Ac_3* derivative (IV), m.p. 109—110°, $[\alpha]_D^{20}$ +37·6° in $CHCl_3$, +54·4° in C_5H_5N, +74·2° in C_6H_6, whilst the fourth OH is not affected by boiling Ac_2O. (IV) and CH_2N_2 give a non-cryst. Me derivative, hydrolysed by *N*-NaOH to 4-*benzeneazo*-5-*methoxy*-1-*phenyl*-3-αβγ-*trihydroxypropylpyrazole* (V), m.p. 165—166°, $[\alpha]_D^{20}$ +672° in C_5H_5N, better obtained from (III) and CH_2N_2 in $COMe_2$. Reductive fission of (III) with $SnCl_2$ and conc. HCl gives NH_2Ph, whereas 4-amino-1-phenyl-3-αβγ-trihydroxypropylpyrazolone could not be isolated as such or as its salts. Oxidation of (V) by $KMnO_4$ in $COMe_2$ gives 4-*benzeneazo*-5-*methoxy*-1-*phenylpyrazole*-3-*carboxylic acid* (VI), m.p. 180—181°, converted by boiling alkali into 4-benzeneazo-1-phenylpyrazolone-3-carboxylic acid (VII). (VII) with a large excess of CH_2N_2 gives *Me* 4-*benzeneazo*-5-*methoxy*-1-*phenylpyrazole*-3-*carboxylate*, m.p. 133—134°, transformed by partial hydrolysis into (VI). *Me* 4-*benzeneazo*-1-*phenylpyrazolone*-3-*carboxylate*, m.p. 136·5—137·5°, is obtained in poor yield from (VII) and MeOH–HCl. (III), $COMe_2$, and conc. H_2SO_4 yield 4-*benzeneazo*-1-*phenyl*-3-α-*hydroxy*-βγ-iso*propylidenedioxypropylpyrazolone* (VIII), m.p. 181—182°, $[\alpha]_D^{17}$ −73·8° in C_5H_5N [*Na* salt, slow decomp. > 200° after softening at 170°; *Me ether*, m.p. 137—138°, $[\alpha]_D^{18}$ +475·6° in C_6H_6 (Me in pyrazole system); *Ac* derivative, m.p. 152—153°, $[\alpha]_D^{20}$ −14·22° in C_6H_6, which yields a resinous Me derivative]. (VIII) does not react with CPh_3Cl. (III) and CPh_3Cl give an amorphous product converted by $COMe_2$–conc. H_2SO_4 into (VIII). (IV) is transformed by $COMe_2$–H_2SO_4 into the *compound* (IX), alizarin-red needles, m.p.

224—225°, accompanied by a (?) desmotropic *modification*, brownish needles, m.p. 223—224°. (IX) is



(VIII.)



(IX.)

insol. in dil. alkali, sol. in NaOH–EtOH, and from the solution CO_2 ppts. (VIII).

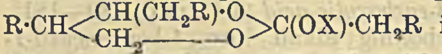
Ascorbic acid is converted by oxidation with *p*-$O{:}C_6H_4{:}O$ and treatment of the product with $NHPh{\cdot}NH_2$ into the lactone of αβ-diketo-*l*-idonic acid di(phenylhydrazone), m.p. 212—214° (decomp.), transformed by alkali into 4-*benzeneazo*-3-l-*threo-glyceryl*-1-*phenylpyrazolone*, m.p. 210—211° (decomp.), $[\alpha]_D^{20}$ +1155° in 0·2*N*-NaOH, which does not depress the m.p. of (III), but is not identical therewith, since its iso*propylidene* derivative has m.p. 170—171°, $[\alpha]_D^{25}$ −31·3° in C_5H_5N.

d-Glucosaccharosonic acid couples with PhN_2Cl, but the product does not yield the substances described above when acted on by $NHPh{\cdot}NH_2$. H. W.

Velocity of bromination of bromosulphoacetic and α-sulphopropionic acids.—See this vol., 1313.

Velocity of bromination and racemisation of α-phenylsulphinopropionic acid.—See this vol., 1313.

Kinetics of bromination of α-carboxydiethyl- and methyl-α-carboxyethyl-sulphone.—See this vol., 1313.

Reaction of aldehydes with metals and their catalytic hydrogenation under pressure. J. von Braun and G. Manz (Ber., 1934, 67, [*B*], 1696—1712).—Hydrogenation of aldehydes, $CH_2R{\cdot}CHO$ (I), in presence of Ni in a steel bomb causes partial conversion into the corresponding primary alcohol; the remainder of (I) is in part condensed to the αβ-unsaturated alcohol, in part transformed into $CH_2R{\cdot}CH(OX){\cdot}CHR{\cdot}CHO$ (X=metal) (II), both of which are hydrogenated to $CH_2R{\cdot}CH_2{\cdot}CHR{\cdot}CH_2{\cdot}OH$. A smaller portion of (II) escapes the action of H and passes through $CHO{\cdot}CHR{\cdot}CH(CH_2R){\cdot}O{\cdot}CH(OX){\cdot}CH_2R$ and  $R{\cdot}CH{<}{\begin{matrix}CH(CH_2R){\cdot}O\\CH_2\text{———}O\end{matrix}}{>}C(OX){\cdot}CH_2R$ into the glycol ester, $CH_2R{\cdot}CH(OX){\cdot}CHR{\cdot}CH_2{\cdot}O{\cdot}CO{\cdot}CH_2R$.

The phenylimido-chloride of fencholic acid, m.p. 165°, is converted by NH_2Ph in Et_2O into the *diphenylamidine*, $C_{22}H_{23}N_2$, m.p. 236°, which is reduced by Na and EtOH to the *diamine*, $C_9H_{17}{\cdot}CH(NHPh)_2$, m.p. 216°, whence fencholaldehyde (I) is obtained by means of HCl and steam. Hydrogenation (Ni in steel autoclave, 200°/50 atm.) of (I) gives exclusively the corresponding primary alcohol, b.p. 104—105°/15 mm. Similarly campholaldehyde affords campholcarbinol, b.p. 100°/18·5 mm., m.p. 60°. *n*-Decaldehyde gives *n*-decyl alcohol, b.p. 118—119°/13 mm., and β-n-*octyl*-n-*dodecyl alcohol* (II), b.p. 230°/17 mm. (II) is transformed by HBr at 120° into the corresponding *bromide* (III), b.p. 195°/4 mm., converted by the successive action of Mg and acid into β-n-*octyldodecane*, b.p. 200°/14 mm., better obtained by hydrogenation (Pd) of β-n-*octyl*-Δ$^{\alpha}$-*dodecene*, b.p. 193—195°/12 mm., derived from (III) by action of $KOH{-}EtOH{-}H_2O$. The residue from distillation of the hydrogenated product affords decoic acid when hydrolysed. Pr$^{\alpha}$CHO is hydrogenated at 200° to Bu$^{\alpha}$OH and β-*ethyl*-n-*hexyl alcohol* (IV), b.p. 84—86°/15 mm. (IV) is transformed by conc. HBr at 120° into β-*ethyl*-n-*hexyl bromide*, b.p. 73—76°/15 mm., which with NMe_3 in C_6H_6 at 100° yields the quaternary *bromide*, m.p. > 200° after softening, transformed by successive treatment with Ag_2O and distillation with alkali into *dimethyl*-β-*ethyl*-n-*hexylamine*, b.p. 177—179° (*methiodide*, m.p. 215°), and β-*ethyl*-Δ$^{\alpha}$-*hexene* (V), b.p. 116—118°. Ozonisation of (V) affords COEtBu$^{\alpha}$, b.p. 140—142° (*semicarbazone*, m.p. 103°). Hydrogenation of Pr$^{\alpha}$CHO in an autoclave without catalyst causes separation of Cu (from packing rings), giving unchanged Pr$^{\alpha}$CHO, α-ethyl-Δ$^{\alpha}$-pentenal, b.p. 172° (identified by hydrogenation and conversion into α-*ethylvaleraldoxime*, b.p. 104—106°/10 mm., which is transformed by PCl_5 in Et_2O into α-*ethylhexonitrile*, b.p. 75°/10 mm., hydrolysed by HCl at 120° to α-ethyl-*n*-hexoic acid, b.p. 122—124°/10 mm.), and *monobutyryl*-β-*ethyl*-n-*hexane*-αγ-*diol* (VI), b.p. 148—150°/10 mm., which contains 1 OH (Zerevitinov). (VI) is hydrolysed to Pr$^{\alpha}CO_2H$ and β-*ethylhexane*-αγ-*diol* (VII), b.p. 131—133°/12 mm., converted by 1 Pr$^{\alpha}$COCl into (VI) and by 2 Pr$^{\alpha}$COCl into the *dibutyryl* derivative, b.p. 154—158°/12 mm., also obtained from (VI) and Pr$^{\alpha}$COCl in C_5H_5N. Conc. HCl or HBr at 120° converts (VI) into the unstable αγ-*dichloro*-, b.p. 50°/0·2 mm., and αγ-*dibromo*-, b.p. 82°/0·2 mm., -β-*ethyl*-n-*hexane*, respectively. Oxidation of (VII) with Beckmann's mixture in a current of steam leads to β-*hydroxy*-α-*ethyl*-n-*hexaldehyde*, b.p. 100—103°/12 mm. [*oxime*, b.p. 140—145°/(?)12 mm.], and *n*-heptane-γδ-dione (VIII), b.p. 147—149° (dioxime, m.p. 172°; *phenylosazone*, m.p. 106°). (VIII) is also obtained by oxidation of (VI), which affords mainly the *keto*-ester, COPr$^{\alpha}{\cdot}CHEt{\cdot}CH_2{\cdot}O{\cdot}$COPr$^{\alpha}$, b.p. 130—134°/12 mm. Treatment of (VI) with PCl_3 in CH_2Cl_2 followed by distillation under diminished pressure and subsequent hydrolysis leads to Pr$^{\alpha}CO_2H$ and β-*ethyl*-Δ$^{\beta}$-*hexenyl alcohol* (IX), b.p. 68—71°/12 mm. (*Ac* derivative, b.p. 79—81°/? pressure). (IX) and PBr_3 in $C_2H_2Cl_2$ give β-*ethyl*-Δ$^{\beta}$-*hexenyl bromide*, b.p. 68—70°/12 mm., which with NMe_3 in C_6H_6 readily yields the quaternary *bromide*, m.p. about 175°, and is converted by NH_4CNS in EtOH into the *thiocarbimide*, $C_8H_{15}N{:}C{:}S$, b.p. 105—110°. When heated with PhCHO, Pr$^{\alpha}$CHO yields unchanged materials, (IX), and α-*ethylcinnamaldehyde*, b.p. 126—128°/10 mm., hydrogenated to β-*benzyl*-n-*butyl alcohol*, b.p. 126—128°/10 mm. Pr$^{\alpha}$CHO reacts with finely-divided metals in N_2, evolution of H_2 being most marked with Zn and, particularly, Mg. The amount of glycol ester is invariably small, whereas that of the acraldehyde derivative diminishes in the sequence Mg, Co, Ni, Fe, Cu, Cr; in absence of metal Pr$^{\alpha}$CHO remains unchanged. When heated under pressure at 200°, Pr$^{\alpha}$CHO is extensively altered, and the ratio of the products is considerably affected only by the more active metals, which themselves appear to undergo change. (Pr$^{\alpha}$CHO)$_3$ is less readily affected than is Pr$^{\alpha}$CHO.

Hydrogenation of heptaldehyde under pressure leads to heptyl alcohol and β-n-*amyl*-n-*nonyl alcohol* (X), transformed by HBr into β-n-*amyl*-n-*nonyl bromide*, b.p. 154—156°/11 mm., which with NMe_3 in C_6H_6 gives the non-cryst. quaternary bromide (XI) (corresponding *platinichloride*, decomp. 218°). Treatment of (XI) with Ag_2O and fission of the base yields *dimethyl*-β-n-*amyl*-n-*nonylamine*, b.p. 143—145°/11 mm. (non-cryst. *methiodide*, *hydrochloride*, and *picrate*), and β-n-*amyl*-Δ^{α}-*nonene*, b.p. 117—118°/11 mm., ozonised to n-*amyl* n-*heptyl ketone*, b.p. 128—129°/11 mm., m.p. 18·5° (non-cryst. *semicarbazone*). When heated in an autoclave at 200—210° in N_2 heptaldehyde gives α-heptylideneheptaldehyde (XII) [hydrogenated to (X) and oxidised by $KMnO_4$ (=4 O) to hexoic and heptoic acid], and the *heptoyl* derivative, b.p. 176—178°/0·3 mm., of β-n-*amylnonane-αγ-diol*, oxidised by Beckmann's mixture to the *diketone*, $C_6H_{13}·CO·CO·C_5H_{11}$, b.p. about 110°/12 mm. The behaviour of heptaldehyde towards metals in glass closely resembles that of $Pr^{\alpha}CHO$. The view that (XII) can arise by direct condensation is supported by the isolation of α-*n*-amylcinnamaldehyde, b.p. 155—158°/13 mm., from heptaldehyde and PhCHO.

Pressure hydrogenation of *iso*valeraldehyde (XIII) gives *iso*amyl alcohol (about 60%) and ε-*methyl*-β-iso*propyl*-n-*hexyl alcohol*, b.p. 92—95°/11 mm. ε-*Methyl*-β-iso*propyl*-n-*hexyl bromide*, b.p. 92—95°/11 mm., and NMe_3 give the quaternary *bromide*, m.p. 152°, whence *dimethyl*-ε-*methyl*-β-iso*propyl*-n-*hexylamine*, b.p. 196—198° (*methiodide*, m.p. 132°), and ε-*methyl*-β-iso*propyl*-Δ^{α}-n-*hexene*, b.p. 150°, ozonised to Pr^{β} *γ-methylbutyl ketone*, b.p. 58°/10 mm. (*semicarbazone*, m.p. 119°). Decomp. of (XIII) in an autoclave in N_2 at 200° is less extensive than that of $Pr^{\alpha}CHO$, giving unchanged material, α-*iso*valerylidene*iso*valeraldehyde, and the glycol ester (XIV), $CH_2Pr^{\beta}·CH(OH)·CHPr^{\beta}·CH_2·O·CO·CH_2Pr^{\beta}$. Treatment of (XIV) with PCl_3 in CH_2Cl_2 followed by distillation and hydrolysis leads to heptoic acid and ε-*methyl*-β-iso*propyl*-Δ^{β}-*hexenyl alcohol*, b.p. 80—85°/12 mm. The behaviour of (XIII) towards cold metals is very similar to that of $Pr^{\alpha}CHO$. MeCHO becomes blue and green after prolonged contact with Cu and Co, respectively, and yields crotonaldehyde and, possibly, γ-hydroxy-*n*-butyl acetate. H. W.

Preparation of αβ-unsaturated aldehydes by the chromous chloride method. J. von Braun and W. Rudolph (Ber., 1934, 67, [*B*], 1735—1739; cf. this vol., 393).—δθ-Dimethyl-$\Delta^{\alpha\gamma\eta}$-decatrienoic acid is converted into the corresponding phenylimido-chloride, which is reduced by $CrCl_2$ in Et_2O; the product is treated with 10% $H_2C_2O_4$ and steam, thereby giving δθ-*dimethyl*-$\Delta^{\alpha\gamma\eta}$-*decatrienal*, b.p. 81—82°/0·15 mm., in nearly 30% yield; the *semicarbazone*, p-*nitrophenylhydrazone*, and *$NaHSO_3$* compound are described. Citronellal and $CH_2(CO_2H)_2$ give a mixture of acids, b.p. 178—180°/12 mm., transformed by PCl_5 into the mixed chlorides, b.p. 110—114°/0·4 mm., from which a cryst. *anilide* (I), m.p. 49—51°, is isolated. (I) is transformed into the phenylimido-chloride, converted by $CrCl_2$ in Et_2O into δθ-*dimethyl*-$\Delta^{\alpha\eta}$-*decadienal*, b.p. 108—110°/12 mm. (*oxime*, b.p. about 140°/12 mm.; *semicarbazone*, m.p. 135° after softening at 120°; non-cryst. p-*nitrophenylhydrazone*). Citral is reduced under pressure (Ni and H_2) to γη-dimethyloctan-1-ol, which is oxidised to inactive dimethyloctanal, condensed with $CH_2(CO_2H)_2$ in C_5H_5N at 40—50° to δθ-*dimethyl*-Δ^{α}-*decenoic acid* (II), b.p. 168—170°/12 mm. (II) is transformed through the *chloride*, b.p. 97°/0·2 mm., *anilide*, b.p. 225°/0·2 mm., m.p. 70°, and phenylimido-chloride into δθ-*dimethyl*-Δ^{α}-*decenal*, b.p. 122—125°/14 mm. (*semicarbazone*, m.p. 142°). Pentenoanilide yields Δ^{α}-pentenal, b.p. 125—128° (semicarbazone, m.p. 180°; *p*-nitrophenylhydrazone, m.p. 123°). H. W.

Production of a mixture of aldehydes and acids containing eight to ten carbon atoms. Factors affecting the yields of aldehydes and acids in the vapour-phase oxidation of a liquid hydrocarbon fraction. C. Q. Sheely and W. H. King (Ind. Eng. Chem., 1934, 26, 1150—1153).—Detailed results of the effects of hydrocarbon ratio (I), reaction time (II) (3·5, 5·2, and 10·4 sec.) and temp. (III) (335°, 387°, 444°), and of the v.p. of the HNO_3 catalyst (IV) (0—150 mm.) within the limits given in parentheses, on the yields of C_8—C_{10} aldehydes (V) and acids (VI) formed by the atm.–HNO_3 vapour oxidation of liquid hydrocarbons (cleaner's naphtha, b.p. approx. 165—216°) in the vapour phase at 645 mm., are tabulated and discussed. Optimum conditions [19·73% yield of (V) and 25·39% yield of (VI), on hydrocarbon burned] are (I) 37·3, (II) 3·5, (III) 444°, and (IV) 67·5 mm. The (V) obtained compared favourably (80% purity by NH_2OH,HCl assay) with the best market samples for perfumery, the estimated cost being only about 10% of the market price. The yield of (VI) is increased by increasing (IV), lowest yields being obtained at 444°. No alcohols are formed unless HNO_3 is absent. J. W. B.

Atmospheric oxidation. III. Catalytic oxidation of trioses and related compounds. H. A. Spoehr and H. W. Milner (J. Amer. Chem. Soc., 1934, 56, 2068—2074).—*dl*-Glyceraldehyde (I) is readily oxidised (to CO_2) by air in presence of a mixture of Na ferropyrophosphate (II) and Na_2HPO_4 at 37·9°. There is no induction period and the largest amount of CO_2 is produced during the first 24 hr. The decrease in the rate of formation of CO_2 is more pronounced with very small concns. of (I), and may be due to condensation or rearrangement of (I). Much more oxidation occurs when (I) is added in, *e.g.*, 5 successive portions at intervals of 3 days, rather than at the beginning. The initial rate of oxidation of (I) is much lower in the absence of Fe. The rate of oxidation of $CO(CH_2·OH)_2$ is slightly < that of (I). $CH_2Ac·OH$ (Nef, A., 1905, i, 3) is also oxidised readily; $AcCO_2H$ (III) is also formed. Glycerol also undergoes oxidation to CO_2, but at a slow initial rate. AcCHO is oxidised more slowly than any of the above compounds, whilst (III) is unaffected (or oxidised exceedingly slowly). Lactic acid and $Pr^{\beta}OH$ are oxidised in presence of (II) (not with Na ferripyrophosphate) to (III) and $COMe_2$, respectively. Volatile aldehydic products (but no CO_2) are obtained from EtCHO, $Pr^{\alpha}OH$, $OH·CHMe·CH_2·OH$, and $(CH_2)_3(OH)_2$. Experiments with glucose (cf. A., 1924, i, 836; 1926, 385) under sterile conditions and in presence of $HgCl_2$ or $Hg(CN)_2$

indicate that micro-organisms are not responsible for the production of CO_2 (cf. Theriault *et al.*, A., 1933, 680). H. B.

Physical interpretation of the Lapworth–Robinson theory. H. A. C. McKay (Chem. and Ind., 1934, 870—871).—The Lapworth–Robinson postulation $(>\overset{\curvearrowright}{C=O})$ of the reactivity of the CO group is more satisfactorily represented by the view that the structures (i) $>C=O$ and (ii) $>C\longrightarrow O$ (co-ordinate linking) lead, by a linear combination of eigenfunctions $(a\psi_1+b\psi_2)$, to a resonance state. Reaction of the CO involves (ii) rather than (i); the condition for reaction is $b \gg a$, *i.e.*, when the internuclear distance between C and O is large. This is represented by a potential-energy diagram, which gives a probable val. for the energy of activation (I) of CO. Electromeric and inductive effects are ascribed to changes in (I). H. B.

Constitution and properties of keto-anils. M. Montagne (Compt. rend., 1934, 199, 671—673).—The anils derived from COEtPr (I) and COPhEt react with MgMeI at 80°, but not at room temp. The Grignard derivative of the anil from (I) with Ac_2O yields a mixture of two Ac derivatives, b.p. 178—185°/19 mm., one of which is hydrolysed by cold H_2SO_4 to yield NH_2Ph and COPr·CHMeAc, the other being stable to HCl but hydrolysed by boiling 48% HBr to yield NH_2Ph and (I). Direct acetylation of the anil yields almost exclusively the stable Ac derivative. The anil probably reacts in the imino-form towards MgMeI, and the formation of two Ac compounds by subsequent acetylation is due to partial addition of Ac_2O at the double linking and elimination of MgI·OAc. A. E. O.

Keten. II. Rate of polymerisation. F. O. Rice and J. Greenberg (J. Amer. Chem. Soc., 1934, 56, 2132—2134; cf. this vol., 1091).—Keten (I) does not polymerise appreciably in the gaseous phase at room temp. during several hr.; polymerisation occurs (erratically) at one or more points of the vessel. Liquid (I) is stable at −80° provided it is freed (by distillation) from C particles, traces of rubber, or resinous material; polymerisation occurs rapidly at 0° (in sealed tubes). The rate (approx. bimol.) of polymerisation of (I) in different solvents at 0° is determined. Polymerisation is independent of the presence or absence of O_2 (or peroxides) or inhibitors (quinol; anthraquinone). In general, the rate is slower in solvents of low dielectric const. The energy of activation of the polymerisation process in $COMe_2$ is 11,000 g.-cal. (from measurements at 0° and 20°). H. B.

Photo-reactions of liquid and dissolved ketones. I. [Acetone and benzophenone.]—See this vol., 1316.

Syntheses of ketones and β-diketones with the help of boron trifluoride. H. Meerwein and D. Vossen (J. pr. Chem., 1934, [ii], 141, 149—166).—Mainly a more detailed account of work previously reviewed (A., 1933, 360). The following appears to be new. C_6H_6 (1 mol.), Ac_2O (2 mols.), and BF_3 at 0° give 13·7% of COPhMe; *cyclo*hexene similarly affords 27% of 1-acetyl-Δ^1-*cyclo*hexene; 1-keto-1 : 2 : 3 : 4-tetrahydronaphthalene yields 83% of the 2-*Ac* derivative, b.p. 173—175°/12 mm., m.p. 55—56°; $COEt_2$ furnishes βδ-diketo-γ-methylhexane and some CH_2Ac_2 (from the Ac_2O); $COMe_2$ gives CH_2Ac_2; deoxybenzoin does not react with Ac_2O, but is converted into α-benzoyl-αβγ-triphenyl-Δ^α-propene. The compound BF_3,Ac_2O, m.p. 194°, of Bowlus and Nieuwland (A., 1931, 1404) is actually $(CHAc_2{\cdot}CO)_2O,3BF_3$ (cf. *loc. cit.*). $(Pr^\beta CO)_2O$ and BF_3 at 0° similarly give $BF_3,2Pr^\beta CO_2H$, b.p. 68—70°/15 mm., and the *compound*, $(Pr^\beta CO{\cdot}CMe_2{\cdot}CO)_2O,3BF_3$, m.p. 117—119°, which is decomposed by warm H_2O to CO_2 and $COPr^\beta{}_2$. The *Cu* salts of αα-dipropionylethane and αα-di-*n*-butyrylpropane have m.p. 172—174° and 171—172°, respectively. CH_2BzAc and BF_3 give a 1 : 1-*compound* (cf. Morgan and Tunstall, A., 1924, i, 1359). H. B.

Synthesis of acetone from acetylene and steam in presence of catalysts. M. S. Platonov, V. A. Plakidina, and K. K. Beltistov (J. Gen. Chem. Russ., 1934, 4, 421—433).—The highest yields of $COMe_2$ from 10 : 1 H_2O–C_2H_2 using different catalysts are: 2ZnO–V_2O_5–kaolin (I) 50—60, 2ZnO–V_2O_5 50, 2CdO–V_2O_5 (II) 50, Fe_2O_3 40, MnO–V_2O_5 1·3, ZnO–V_2O_5–$CaCO_3$ 21—25, CdO–$CaCO_3$ 15, ZnO–Fe_2O_3 16, Fe_2O_3–V_2O_5–kaolin 12, CeO_2–ThO_2–kaolin 26, ThO_2–Al_2O_3 13, ZnO–MgO–$CaCO_3$ 14, ZnO–MgO–V_2O_5–$CaCO_3$ 12·4% of theory. The optimum temp. using (I) is 425—450°, 470° for (II), and 450° for Fe_2O_3. The yields of MeCHO and AcOH, obtained as by-products, increase as the temp. falls below the optimum. The yield of $COMe_2$ increases with increasing concn. of H_2O in the vapour phase, but is independent of the velocity of flow up to 12,000 vols. per hr. per vol. of catalyst. (I) undergoes partial inactivation with time, but may be regenerated by passing air at 350—500°. (II) undergoes reduction to metallic Cd, which is volatilised into the receiver; for this reason (II) cannot be reactivated. R. T.

Iodometric determination of acetone. W. H. Hatcher and J. F. Horwood (Canad. J. Res., 1934, 11, 378—381).—The effects of the concn. of $COMe_2$ (I), NaOH (II), and I, and of the order of addition, in the determination of (I) by Messinger's method show that the two main factors are (*a*) the enolisation of (I) by (II) which is rapid, and (*b*) the reaction $I_2+OH' \longrightarrow HIO+I'$. With the correct order of addition, (I), (II), I, using a min. concn. of (II) 0·03*N* (better 0·048*N*) the rapid action (*b*) concurrently with (*a*) completes the formation of CHI_3 in approx. 10 min. With addition orders, (I), I, (II), or (II), I, (I), (*a*) and (*b*) are in conflict, (*b*) also removing OH′, and the absorption of I is incomplete even after prolonged periods. J. W. B.

Highly-polymerised compounds. CII. Polymethyl *iso*propenyl ketones. H. Staudinger and B. Ritzenthaler (Ber., 1934, 67, [*B*], 1773—1783).—Polymerisation of cold $COMe{\cdot}CMe{:}CH_2$ occurs readily at room temp., giving a very viscous, hard eucolloidal material (I) which is sol. and hence consists exclusively of thread mols. Since (I) is reduced by HI and As to a complex hydrocarbon, it must have the structure $\cdot CAcMe{\cdot}CH_2{\cdot}[CAcMe{\cdot}CH_2]_x{\cdot}CAcMe{\cdot}CH_2\cdots$. Polymerisation of $COMe{\cdot}CMe{:}CH_2$ at 100° leads to βζ-dimethyl-Δ^{α}-octene-γη-dione, which is not an intermediate in the production of (I). Polymerisation with $SnCl_4$ affords black, resinous products, whereas Florida earth is inactive. Irradiation of $COMe\cdot CMe{:}CH_2$ by the Hg-vapour lamp gives a product (II) with mean degree of polymerisation 480 which swells slightly, is much less hard than (I), and is pptd. as a powder by addition of MeOH to its solution in $COMe_2$. (I) does not react with $NHPh\cdot NH_2$, NH_2Ph, etc. In relatively very viscous solutions (II) obeys the Hagen–Poiseuille law, whilst with (I) the deviations in solutions of low viscosity are so small that they do not affect the calculation of mol. wt. In more viscous solutions the deviations are more marked and of approx. the same magnitude as those observed with polystyrenes of similar degree of polymerisation. Variation of concn. of solutions of (I) or (II) causes variations similar to those produced by the polymeric-analogous polystyrenes. η_{sp}/c of (I) appears independent of temp. The degree of polymerisation of (I) is about 1400. H. W.

Diacetylethylene. K. F. Armstrong and R. Robinson (J.C.S., 1934, 1650).—Oxidation of $(\cdot CH_2Ac)_2$ (I) with SeO_2 in boiling H_2O affords (15% yield, together with a liquid mixture of isomerides, b.p. 87—91°/15 mm.) βε-*diketo*-Δ^{γ}-n-*hexene*, m.p. 75·5—76·5° (*bis*-2 : 4-*dinitrophenylhydrazone*, m.p. 291—292°), reduced by H_2 (1 mol.)–Pt–SiO_2 in MeOH or AcOH to (I). J. W. B.

Synthesis and structure of dipropionylacetone and of di-*n*-butyrylacetone. S. S. Deshapande, Y. V. Dingankar, and D. N. Kopil (J. Indian. Chem. Soc., 1934, **11**, 595—602).—2 : 6-Diethyl-4-pyrone (I) with hot aq. $Ba(OH)_2$ gives the *Ba* salt (II) of *dipropionylacetone* (III), which with dil. HCl affords the ketone as a yellow oil, α-*form* (IV), m.p. 117°/6 mm., which changes on keeping into a red β-*form* (V), reconvertible into (IV) on distillation. Boiling with very dil. MeOH–HCl reconverts (III) into (I). (IV) with $p\text{-}NO_2\cdot C_6H_4\cdot NH\cdot NH_2$ (VI) (1 mol.) in EtOH gives 1-p-*nitrophenylimino*-2 : 6-*diethyl*-4-*pyridone*, m.p. 78° (VII) (*platinichloride*, m.p. 198°), but (V) with (VI) (2 mols.) gives the p-*nitrophenylhydrazone* (VIII), m.p. 164° (*platinichloride*, m.p. 157°), of (VII). (VIII) cannot be obtained from (VII) and (VI), but on hydrolysis (AcOH+HCl gas) it gives (VII). (II) with the hydrochloride of (VI) (2 mols.) in Et_2O, gives at room temp. the γε-(or γη-)*di*-p-*nitrophenylhydrazone*, m.p. 148°, of (III). *Di*-n-*butyrylacetone* (IX), b.p. 136°/4 mm. (one form), from 2 : 6-di-*n*-propyl-4-pyrone (X) readily reverts to (X) on distillation. Pure (IX) (from *Cu* salt) with (VI) (1 mol.) gives the ζ-p-*nitrophenylhydrazone* (XI), m.p. 71°, which in contact with conc. HCl and $PtCl_4$ changes to the *platinichloride* of 2 : 6-*di*-n-*propyl*-4-*pyrone*-p-*nitrophenylhydrazone*. Hydrolysis of (XI) gives (IX). With 2 mols. of (VI), (XI) gives 1-p-*nitrophenylimino*-2 : 6-*di*-n-*propyl*-4-*pyridone*-p-*nitrophenylhydrazone*, m.p. 140°. The reactions of (III) and (IX) are readily explained on the basis of open-chain formulæ (cf. diacetylacetone, J.C.S., 1921, **119**, 1550). Both ketones give violet colorations with $FeCl_3$. F. S. H. H.

Diacetylmonoxime. A. K. Plisov (J. Gen. Chem. Russ., 1934, **4**, 290—297).—The yields of Ac_2 obtained when $CAcMe{:}NOH$ (I) is treated with various substances are : NO 85, NO_2 44, N_2O_3 85, HNO_2 60, $HgNO_3$ 87, $Cu(NO_3)_2$ 48, and $NaNO_3$ 37% of theory. (I) when heated at 140—145° with CuO or MnO_2 yields chiefly Ac_2, NH_3, and N_2 : $3(I) \longrightarrow NH_3+N_2+3Ac_2$; at higher temp. the reaction $(I) \longrightarrow AcOH+MeCN$ predominates. R. T.

Structure of the nitrogen and oxygen chains of the organic compounds suitable for the formation of complex salts. I. Iron salts of the oximino-ketones. L. Cambi (R. Ist. lombardo Sci. Lett., Rend., 1933, [ii], **66**, 791—798; Chem. Zentr., 1934, i, 1603—1604).—Three series of salts are distinguished : green, basic salts with the ratio oximino-ketone (I) : Fe $< 2 : 1$; blue, neutral salts, and blue acid salts. Reactions with alkali cyanides and magnetic susceptibility data indicate a linking of Fe^{II} to N. The analogy between the groupings of the glyoximes and (I) is pointed out, both forming similar complex salts with metals. Such relationships also exist between 2 : 2′-dipyridyl and phenanthrolin, on the one hand, and pyridine-2- and quinoline-2-carboxylic acids on the other. Where the formation of a six-membered ring is possible, typical red complex salts of Fe^{III} in general appear, and where a stable five-membered ring can be formed, blue or violet complex salts of Fe^{II} are produced. Examples are the Fe^{III} salts of benzoylacetone and the Fe^{II} salts of benzoylacetaldehyde and of oxalylacetone. L. S. T.

Immersion filter for Bertrand's sugar determination.—See this vol., 1325.

Forms of arabinose. E. Montgomery and C. S. Hudson (J. Amer. Chem. Soc., 1934, **56**, 2074—2076).—Very slow crystallisation (from C_5H_5N at 6° or aq. $COMe_2$ at room temp.) of arabinose (I) gives the pure β-form (II), $[\alpha]_D$ (in H_2O) $+187\cdot 8°$ (1 min.) $\longrightarrow$ $+105\cdot 1°$ (const.), whence $[\alpha]_D$ (initial) $+201\cdot 5°$. Details are given for the prep. from (I) of the compounds, $\beta\text{-}C_5H_{10}O_5,CaCl_2,H_2O$, m.p. 210° (decomp.) (cf. Dale, this vol., 635) [giving $[\alpha]_D$ (initial) $+201\cdot 7°$ for (II)], and $\alpha\text{-}C_5H_{10}O_5,CaCl_2,4H_2O$, m.p. 204° (darkens at 185°) (cf. Austin and Walsh, this vol., 635) {giving $[\alpha]_D$ $+89\cdot 4°$ in H_2O, for α-*l*-arabinose (III)}. The above vals. for (II) and (III) agree with those calc. (+200° and +87°, respectively) from the rotations of α- and β-methylarabinosides by isorotation rules. All $[\alpha]_D$ are determined at $20 \pm 0\cdot 5°$. H. B.

Preparation of arabinose from gum acacia (gum kordofan). H. C. Carrington, W. N. Haworth, and E. L. Hirst (J.C.S., 1934, 1653).—An improved prep. of arabic acid (I) from gum acacia, and its hydrolysis by $0\cdot 01N\text{-}H_2SO_4$ at 95° to *l*-arabinose [18 g. from 100 g. of (I)], are described. J. W. B.

Mutarotation of arabinose.—See this vol., 1312.

Methylation of *l*-rhamnose. J. Minsaas (Kong. Norske Vidensk. Selsk. Forhandl., 1934, **6**, 177—179; Chem. Zentr., 1934, i, 2738).—α-*Methylrhamnoside* (I), m.p. 109—110°, $[\alpha]_D^{20}$ $-62\cdot 5°$, is prepared by Fischer's method. β-Methylrhamnoside is obtained from the mother-liquor from (I) by distillation in vac. Cryst., anhyd. rhamnose has $[\alpha]_D^{20}$ $+44°$. R. N. C.

Powell and Whittaker's method for the determination of pentosans. T. S. Krishnan (J.

Indian Chem. Soc., 1934, **11**, 651—657).—In the above method, the determination of furfuraldehyde (I) by Br absorption gives erratic results, but accurate vals. may be obtained, even for very small quantities (for which the phloroglucinol pptn. method fails), if the temp. be maintained at 30°. At lower temp. the absorption of Br is not ∝ the amount of (I). F. S. H. H.

Inter-relationships amongst oligosaccharides. E. F. Armstrong and K. F. Armstrong (Chem. and Ind., 1934, 912—913).—The probable modes of synthesis (in nature) of various polysaccharides are discussed. Sucrose [fructofuranose(2)-α-(1)glucose; the nos. indicate the points of attachment of the sugar units] (I) and glucose (II) under the influence of β-glucosidase give gentianose [fructofuranose(2)-α-(1)glucose(6)-β-(1)glucose], hydrolysed by invertase (III) to gentiobiose [glucose(6)-β-(1)glucose] (IV), which occurs only in glycosides. Oxidation of (IV) to the glycuronic acid and subsequent decarboxylation affords primeverose [glucose(6)-β-*d*-(1)xylose]. Galactose (V) and (I) with α-galactosidase give raffinose [fructofuranose(2)-α-(1)glucose(6)-α-(1)galactose] (VI), hydrolysed by (III) to the unknown (in nature) melibiose [glucose(6)-α-(1)galactose], convertible [as for (IV)] into vicianose [glucose(6)-β-*l*-(1)arabinose]. (V) and (VI) afford stachyose [fructofuranose(2)-α-(1)glucose(6)-α-(1)galactose(6)-?-(1)galactose], hydrolysed by (III) to manninotriose [glucose(6)-α-(1)galactose(6)-?-(1)galactose]. (I) and (II) with α-glucosidase (maltase) give melezitose [glucose(1)-α-(6)fructofuranose(2)-α-(1)glucose], hydrolysed [dil. acid, not by (III)] to turanose [glucose(1)-α-(6)fructofuranose] (cf. Pacsu, A., 1931, 1149). H. B.

Action of chloroacetic anhydride on sugars, cellulose and its acetates. K. Brass and E. Kurz (Cellulosechem., 1934, **15**, 99—102).—Glucose with $(CH_2Cl{\cdot}CO)_2O$ (I) and AcOH with or without $ZnCl_2$ or H_2SO_4 at 65° gives mixtures; a *tetra*(*chloroacetate*), $+3C_5H_5N$, m.p. 131°, $[\alpha]_D^{17}$ +44·23° in $CHCl_3$, and $+4C_5H_5N$, m.p. 116°, $[\alpha]_D^{17}$ +35·22° in $CHCl_3$, are isolated in poor yield. Fructose gives similarly a *tri*(*chloroacetate*), $[\alpha]_D^{17}$ −10·49° in $CHCl_3$, and $+2C_5H_5N$, hygroscopic. Cellulose triacetate, (I), and a little H_2SO_4 at 70° give α-glucopyranose 2 : 3 : 4-triacetate 1 : 6-di(chloroacetate). Cellulose under various conditions gives only mixed cellobiose derivatives. R. S. C.

Molecular combinations of β-methyl-*d*-glucoside, -*d*-xyloside, and -*l*-fucoside with potassium acetate. A. J. Watters, R. C. Hockett, and C. S. Hudson (J. Amer. Chem. Soc., 1934, **56**, 2199).—Compounds, $C_7H_{14}O_6$,KOAc, m.p. 181—182° (corr.), $[\alpha]_D^{20}$ −22° in H_2O, $C_7H_{14}O_5$,KOAc, m.p. 208—212° (corr.), $[\alpha]_D^{20}$ +8·9° in H_2O, and $C_6H_{12}O_5$,KOAc, m.p. 171—172° (corr.), $[\alpha]_D^{20}$ −41·3° in H_2O, are obtained by mixing conc. EtOH-solutions of anhyd. KOAc and β-methyl-*d*-glucoside, -*l*-fucoside, and -*d*-xyloside, respectively. The glucoside can be recovered by pptn. of K as K H tartrate (in 50% EtOH); acetylation (Ac_2O) gives the glycoside acetates. Similar compounds could not be prepared from α- and β-methyl-*d*-arabinosides, -*d*-galactosides, and -*d*-lyxosides, and α-methyl-*d*-glucoside, -*d*-xyloside, and -*l*-fucoside. H. B.

Further method of preparation of sugar derivatives with seven-membered rings (septanoses). F. Micheel and W. Spruck (Ber., 1934, **67**, [*B*], 1665—1667; cf. A., 1933, 596, 1278).—Galactose Et_2 mercaptal is converted by CPh_3Cl and C_5H_5N and treatment of the product with Ac_2O into 6-*triphenylmethylgalactosedi* Et_2 *mercaptal* 2 : 3 : 4 : 5-*tetra-acetate* (I) (impure), $[\alpha]_D$ −10·8° in C_5H_5N. Addition of $HgCl_2$ in $COMe_2$ to (I) and $CdCO_3$ in $COMe$–H_2O at 15—20° leads to 6-*triphenylmethylgalactose hydrate* 2 : 3 : 4 : 5-*tetra-acetate*, m.p. 152°, $[\alpha]_D^{20}$ −47° to −15° in C_5H_5N, converted by HCl–$CHCl_3$ or HBr–AcOH into *al*-galactose hydrate 2 : 3 : 4 : 5-tetra-acetate, m.p. 140°, whence α- and β-galactoseptanose penta-acetate (*loc. cit.*). H. W.

***aldehydo*-*d*-β-Galaheptose hexa-acetate.** R. M. Hann and C. S. Hudson (J. Amer. Chem. Soc., 1934, **56**, 2080).—*d*-β-Galaheptose, EtSH, and conc. HCl at room temp. give d-β-*galaheptose Et mercaptal*, m.p. 133° (corr.), $[\alpha]_D^{20}$ +37·8° in H_2O, acetylated (Ac_2O, C_5H_5N) to the *hexa-acetate*, m.p. 105° (corr.), $[\alpha]_D^{20}$ +26·6° in $CHCl_3$, which is converted by $HgCl_2$ in aq. $COMe_2+CdCO_3$ into aldehydo-d-β-*galaheptose hexa-acetate*, m.p. 196° (corr.), $[\alpha]_D^{20}$ +39·9° in $CHCl_3$. H. B.

Thio-sugars. A. L. Raymond (J. Biol. Chem., 1934, **107**, 85—96).—*iso*Propylidenexylose 5-*p*-toluenesulphonate (I) and NaSEt in $COMe_2$, yield 5-*ethylthiol*iso*propylidenexylose* (II), m.p. 66·5—67·5°, $[\alpha]_D^{22}$ −57·5° in EtOH. Acid hydrolysis of (II) gives 5-*ethylthiolxylose*, m.p. 81—82°, $[\alpha]_D^{22}$ −42·2° in EtOH. Similarly, with NaSMe (I) yields 5-*methylthiol*iso*propylidenexylose*, m.p. 91·5—92°, $[\alpha]_D^{22}$ −53·9° in EtOH, hydrolysed to 5-*methylthiolxylose* (III), m.p. 74—75°, $[\alpha]_D^{20}$ −23·0°. The behaviour of these products on oxidation is discussed, as also the rate of glycoside formation, confirming the structures assigned. Neither (III) nor its *osazone*, m.p. 162—163°, $[\alpha]_D^{22}$ −32·8° in C_5H_5N–EtOH, is identical with the natural product from yeast (A., 1925, i, 338; 1926, 52), which thus cannot be 5-methylthiol-xylose, -lyxose, -2-ketoxylose, or -2-ketolyxose. *iso*Propylideneglucose 6-*p*-toluenesulphonate and KSMe in dioxan yield 6-*methylthiol*iso*propylideneglucose*, b.p. 140—155°/0·1 mm., $[\alpha]_D^{22}$ −3·5° to −7·6° in EtOH. This on hydrolysis yields 6-*methylthiolglucose* (IV) as a syrup (p-*bromophenylosazone*, m.p. 184—185°, $[\alpha]_D^{20}$ −48° in C_5H_5N–EtOH), the structure of which is confirmed by its similarity to 6-methylglucose in rate of glucoside formation. 2-Bromomethylglucoside and KSMe in $COMe_2$ give a *methylthiolmethylhexoside*, m.p. 128·5—129·5°, $[\alpha]_D^{20}$ −52·6° in H_2O; the hydrolysis product gives no osazone, whence the SMe probably occupies position 2. H. N. R.

Carbohydrates of grass. Isolation of a polysaccharide of the levan type. S. W. Challinor, W. N. Haworth, and E. L. Hirst (J.C.S., 1934, 1560—1564).—From an aq. extract (freed from protein and insol. polysaccharides) of dried rough-stalked meadow grass (*Poa trivialis*) is isolated a H_2O-sol. *polysaccharide* (I), $[\alpha]_D^{20}$ −41° in H_2O {*Ac* derivative, softens 110°, m.p. indef., $[\alpha]_D^{22}$ +23° in $CHCl_3$; *Me*$_3$ *ether* (II), $[\alpha]_{5780}^{17}$ −60° in $CHCl_3$}, closely resembling levan (III), and giving only fructose (IV) on hydrolysis; (II) similarly hydrolyses to 1 : 3 : 4-trimethylfructose. Examination of the aq.-EtOH extract from which (I) has separated and of its methylation and acetylation products shows the presence of glucose, (IV), a trace of galactose (as mucic acid), and (?) gentiobiose (isolated as heptamethylmethylgentiobioside). (III) contains 10—12 fructofuranose units linked at positions 2 and 6. J. W. B.

Alleged synthesis of starch. M. Rosa and C. H. Liberalli (Rev. Soc. Brasil. Quim., 1933, 4, 313—346).—An exhaustive discussion of the reactions involved leads the authors to condemn the theoretical basis of A. Barreto's alleged synthesis of starch [by treating the acetal prepared from CH_2O and EtOH with excess of MgO; Rev. Chim. Ind. (Rio de Janeiro), 1933, 2, No. 20, 455; 1934, No. 21, 7]. Experimental attempts to repeat the process gave no evidence of the formation of any carbohydrate; the colour reaction with I given by the crude reaction product is not due to starch, but to a hypoiodite of Mg (cf. Petraschenj, A., 1927, 847). E. L.

Importance of Knecht's compound for the nitration of cellulose. C. Trogus (Cellulosechem., 1934, **15**, 104—107).—The ratio $1C_6H_{10}O_5 : 1HNO_3$ for Knecht's compound (I) is confirmed by Schreinemaker's method; the structure $\left[(C_8H_8O_3)\begin{matrix}HO\\HO\end{matrix}\!>\!H\text{---}OH_2\right]NO_3$, is suggested, by analogy with $HNO_3,3H_2O$ (II), since (I) exists (proof by *X*-ray analysis) only in those HNO_3 concns. in which (II) does not occur. (I) may be formed during nitration of cellulose by local alteration in the concn. of the acid and may thus take part in the reaction. R. S. C.

Fractionation of cellulose acetate. W. Herz (Cellulosechem., 1934, 15, 95—99).—Fractional pptn. of cellulose acetate from $COMe_2$ by H_2O gives products which, according to osmotic pressure measurements, have mol. wts. 27,000—80,000. η is recorded for 3 solvents and gives K_m val. in agreement with Staudinger's results. R. S. C.

Preparation of cellulose stearates by Clark and Malm's procedure. I. Schettle and M. Kliutschkin (J. Appl. Chem. Russ., 1934, 7, 558—563).—The H_2O content of air-dry cotton-wool does not interfere with esterification according to Clark and Malm's method; the highest degree of esterification (distearate) is obtained by heating a 1 : 3 : 6 mol. mixture of cellulose, stearic acid, and $(CH_2Cl{\cdot}CO)_2O$ at 100° for 60 hr. R. T.

Resolution of co-ordinated inorganic compounds into optical isomerides. II. Resolution of triethylenediaminezinc chloride and sulphate. P. Neogi and G. K. Mukherjee (J. Indian Chem. Soc., 1934, **11**, 681—685).—Triethylenediaminezinc chloride (I) (d-*tartrate* $+3H_2O$, $[\alpha]_D^{25}$ +181°; d-*camphorsulphonate* $+H_2O$, $[\alpha]_D^{25}$ +18·1°; d-*bromocamphorsulphonate* $+5H_2O$, $[\alpha]_D^{25}$ +42°) is resolved by fractional crystallisation of its *d*-camphornitronate (prep. by interaction with Na *d*-camphornitronate), the d-*triethylenediaminezinc* d-*camphornitronate* $+2H_2O$, $[\alpha]_D^{25}$ +16°, which separates first, being converted into the corresponding *chloride*, $[\alpha]_D^{25}$ +94·2°, and *sulphate*, $[\alpha]_D^{25}$ +87·7°, both racemising completely in 2—3 hr. in solution. Crystallisation of the salt formed from the hydroxide of (I) with nitrocamphor affords l-*triethylenediaminezinc camphornitronate*, $[\alpha]_D^{25}$ −42·6°, converted by dil. HCl into a solution of the non-cryst. *l*-chloride. All $[\alpha]_D$ vals. are in H_2O. J. W. B.

Mechanism of oxidation processes. XL. Hydrolytic fission of amino-acids by charcoal. H. Wieland, I. Drishaus, and W. Koschara [with W. Kapitel] (Annalen, 1934, 513, 203—218; cf. A., 1924, i, 1172).—*dl*-Alanine (I) (2·5% aq. solution) and animal C (II) (as used by Baur, A., 1923, i, 97; 1931, 1366) at 100° in N_2 give [after 8 hr. (when reaction practically ceases)] about 19% of the CO_2 required by the scheme: $NH_2{\cdot}CHMe{\cdot}CO_2H-2H \longrightarrow NH{:}CMe{\cdot}CO_2H \longrightarrow CO_2+MeCHO+NH_3$; the NH_3 and MeCHO are determined also. Contrary to Baur (*loc. cit.*), lactic acid and EtOH are not produced in detectable amounts. The recovered (II) is inactive towards (I), provided the recovery is done in N_2; partial reactivation occurs in presence of O_2. The extent of the above decomp., using (II) previously heated in N_2 at 250—300°, is about 3%. The activity of (II) is not completely lost by previous heating in H_2 at 700—1000°. $H_2C_2O_4$ is also oxidised by (II) to the extent of 3·3% in 1 hr.; much less oxidation occurs using (II) previously heated in N_2 at 700°. Contrary to Wunderly (A., 1924, ii, 841; 1933, 264), aspartic acid is similarly dehydrogenated: $CO_2H{\cdot}CH(NH_2){\cdot}CH_2{\cdot}CO_2H-2H+H_2O \longrightarrow 2CO_2+MeCHO+NH_3$. H. B.

β-Hydroxyglutamic acid. J. M. Gulland and C. J. O. R. Morris (J.C.S., 1934, 1644—1649).—In the neutralisation (Congo-red) of the 25% H_2SO_4 hydrolysate of caseinogen (I) with $Ba(OH)_2$ the whole of the β-hydroxyglutamic acid (II) is adsorbed by the pptd. $BaSO_4$, from which NH_2-acids are eluted with 1% HCl at 25°. After treatment (described) to remove glutamic (III), aspartic (IV), mono-NH_2-carboxylic and basic NH_2-acids, proline and hydroxyproline, decomp. of the Ag salts of the residue affords a gum which extraction with AcOH at room temp. and then EtOH at 50° separates into an EtOH-insol. powder containing (III), pyrrolidonecarboxylic acid and an impure acid containing S and N, and an EtOH-sol. gum [10% of (II) as $CO_2H{\cdot}CH_2{\cdot}C({:}R){\cdot}CH{:}R$ (V) ($R{=}N{\cdot}NHC_6H_4{\cdot}NO_2$-*p*) by oxidation with chloramine-*T* (VI), which is regarded as the only trustworthy test for the presence of (II)], hydrolysis of which with 2*N*-HCl [17% of (II) due to its formation from hydroxypyrrolidinecarboxylic acid] and removal of (III), (IV), and *l*-leucine gives a product from which (II) is separated by H_3PO_4–P_2O_5 at 0°, the Ba salt so obtained decomp. on crystallisation to give cryst. (II)$+H_2O$, similar in properties to Dakin's specimen (A., 1919, i, 150). Determination of (II) is best effected by electrodialysis (improved technique described) of the product obtained by elution of the $BaSO_4$ ppt. with 90% AcOH, the anode liquor being freed from methionine by Bu^{a}OH, and oxidised with (VI), to determine (II) as (V). This method indicates 0·33% of (II) in (I). J. W. B.

Oxidation of cystine with permonosulphuric acid. G. Toennies (J. Amer. Chem. Soc., 1934, 56, 2198).—Oxidation of cystine with 1 and 2 mols. of H_2SO_5 (Gleu, A., 1931, 326) appears to give the mono- and di-sulphoxide, respectively; with 10·7 mol. equivs., 5 O (theoretical amount for oxidation to cysteic acid) are absorbed. The product from cystine perchlorate (in MeCN) and 1 mol. equiv. of H_2SO_5 (in 75% MeOH) probably undergoes dismutation when neutralised (C_5H_5N). H. B.

Separation of isomeric forms of inactive cystine. H. S. Loring and V. du Vigneaud (Proc. Soc. Exp. Biol. Med., **29**, 41—42; Chem. Zentr., 1934, i, 2270).—The product of racemisation of *l*-cystine with conc. acid yields two isomeric forms on fractionation of the hydrochlorides. A. G. P.

Nitration of chitin. P. Schorigin and E. Hait (Ber., 1934, **67**, [*B*], 1712—1714).—H_2SO_4–HNO_3 is unsuitable for the nitration of chitin (I) owing to its hydrolysing action. Better results are obtained by dissolution in HNO_3 (*d* 1·5) and treatment of the product, whereby 1·5 OH groups are esterified with formation of chitin nitrate (II), inflames at 165°. Treatment of (II) with HCO_2H gives sol. and insol. portions which do not differ considerably in chemical constitution. H. W.

Amido- and imido-chlorides of non-aromatic acids. IX. J. von Braun and W. Rudolph (Ber., 1934, **67**, [*B*], 1762—1770; cf. this vol., 393).—In accordance with the electronic theory, the stability of the imido-chlorides, $X{\cdot}CHY{\cdot}CCl{:}N{\cdot}R$, increases when R is changed from Et to $POCl_2$ or SO_2Ph; CO_2Et appears to offer insufficient protection to prevent migration of H, whilst polymerisation occurs when R=CN. Instability towards heat increases in the sequence CCl_3, $CHCl_2$, CH_2Cl, Me. The action of PCl_5 on amides proceeds in accordance with the scheme: $X{\cdot}CO{\cdot}NH_2+PCl_5 \longrightarrow X{\cdot}CCl(NH_2){\cdot}OPCl_4$ $\longrightarrow X{\cdot}C{<}^{O}_{N}{>}PCl_3 \longrightarrow X{\cdot}CCl{:}N{\cdot}POCl_2$. $POCl_3$ is not an intermediate, since $CCl_3{\cdot}CO{\cdot}NH_2$ and $POCl_3$ immediately yield $CCl_3{\cdot}CN$, and $CCl_3{\cdot}CO{\cdot}NH_2$ and PCl_5 afford $CCl_3{\cdot}CCl{:}N{\cdot}POCl_2$ in 100% yield. All acid amides are readily converted into nitriles when warmed with $POCl_3$, and for this purpose 1/2 to 1/3 mol. of $POCl_3$ suffices. Hence for this conversion 1/4 mol. of PCl_5 is adequate, but the advantage of $POCl_3$ rests in its liquid form and easier manipulation and on its smaller liability to attack the OH and CO groups. $PSCl_3$ and amides also yield nitriles, but reaction is more complex than with $POCl_3$. With thioamides and $POCl_3$ the nitriles contain S.

$CH_2Cl{\cdot}CO{\cdot}NH{\cdot}CO_2Et$ and PCl_5 at 100° give unchanged material, PCl_3, $POCl_3$, and the *imido-chloride*, $CHCl_2{\cdot}CCl{:}N{\cdot}CO_2Et$, b.p. 115—118°/11 mm., transformed by cold H_2O into *dichloroacetylurethane*, m.p. 98°, and by NH_2Ph in Et_2O into the *amidine*, $CHCl_2{\cdot}C(NHPh){:}N{\cdot}CO_2Et$, m.p. 143°, b.p. 160°/0·5 mm. $CN{\cdot}NHAc$ and PCl_5 yields mainly $CN{\cdot}N{:}CClMe$, which could not be obtained pure. $SO_2Ph{\cdot}NHAc$ yields the *imido-chloride* $SO_2Ph{\cdot}N{:}CClMe$, b.p. 130°/0·5 mm., which gradually passes into MeCN and $PhSO_2Cl$ and is transformed by NH_2Ph into the *amidine* $SO_2Ph{\cdot}N{:}CMe{\cdot}NHPh$, m.p. 157°. *Benzenesulphonchloroacetamide*, m.p. 106°, from $PhSO_2{\cdot}NH_2$ and $CH_2Cl{\cdot}COCl$ at 140°, yields the *imido-chloride* $SO_2Ph{\cdot}N{:}CCl{\cdot}CH_2Cl$ (I), b.p. 160—164°/0·5 mm., transformed by $NHEt_2$ in C_6H_6 into the *base* $SO_2Ph{\cdot}N{:}C(NEt_2){\cdot}CH_2{\cdot}NEt_2$ (*picrate*, m.p. 145°). The slight lability of H in (I) is shown by the prolonged heating at 120° required for the production of the *imido-chloride* $SO_2Ph{\cdot}N{:}CCl{\cdot}CHCl_2$, b.p. 160°/0·5 mm., converted by H_2O into *benzenesulphondichloroacetamide*, m.p. 137°. Action could not be caused to proceed to the *compound* $SO_2Ph{\cdot}N{:}CCl{\cdot}CCl_3$, b.p. 158°/0·2 mm., m.p. 88°, which is obtained from *benzenesulphontrichloroacetamide*, m.p. 157° (from $PhSO_2{\cdot}NH_2$ and $CCl_3{\cdot}COCl$). $CCl_3{\cdot}CO{\cdot}NH_2$ and PCl_5 at 100° yield the compound $CCl_3{\cdot}CCl{:}N{\cdot}POCl_2$, b.p. 140°/11 mm., m.p. 80°, quantitatively. Contrary to Wallach, the substance $CHCl_2{\cdot}CCl{:}N{\cdot}POCl_2$, b.p. 92—94°/0·3 mm., m.p. 39°, behaves similarly. $CH_2Cl{\cdot}CO{\cdot}NH_2$ and PCl_5 yield the *compound* $CH_2Cl{\cdot}CCl{:}N{\cdot}POCl_2$, b.p. 100°/0·2 mm., which when gradually heated decomposes into $POCl_3$ and (?) $CN{\cdot}CH_2Cl$ and with NH_2Ph in Et_2O gives the *substance* $NHPh{\cdot}CH_2{\cdot}CO{\cdot}NH{\cdot}PO(NHPh)_2$, m.p. 156°. $CMeCl{:}N{\cdot}POCl_2$ could not be obtained in appreciable amount, passing into $POCl_3$ and MeCN. The following transformations are effected by $POCl_3$: $CCl_3{\cdot}CO{\cdot}NH_2$ to $CCl_3{\cdot}CN$; NH_2Bz to PhCN; *o*-$NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}NH_2$ to *o*-$NO_2{\cdot}C_6H_4{\cdot}CN$; lauramide to lauronitrile, b.p. 140—142°/12; adipamide to adipodinitrile; cyclo*pentylacetamide*, m.p. 215°, to cyclo*pentylacetonitrile*, m.p. 35°; methylacetoacetamide to methylacetoacetonitrile, b.p. 68—70°/12 mm. H. W.

Kinetics of alkaline hydrolysis of betaine-amides. D. B. Luten, jun., and T. D. Stewart (J. Amer. Chem. Soc., 1934, **56**, 2151—2158; cf. A., 1932, 1211).—Contrary to the previous assumption (*loc. cit.*) $CN{\cdot}CR_2{\cdot}NR_3I$ (I) are hydrolysed rapidly by dil. alkali to $NH_2{\cdot}CO{\cdot}CR_2{\cdot}\overset{+}{N}R_3$ (II), which then undergo slow hydrolysis to $\overset{-}{C}O_2{\cdot}CR_2{\cdot}\overset{+}{N}R_3$. The simpler (II) hydrolyse according to complex laws (involving fractional exponents); the rate of hydrolysis of the more complex, less reactive (II) is approx. unimol. with respect to each reactant. Variations in ionic strength and temp. have little effect. A reaction mechanism is discussed. $NH_2{\cdot}CO{\cdot}CH_2{\cdot}NMe_3I$ (III), m.p. 198—199° (lit. 191°), $NH_2{\cdot}CO{\cdot}CH_2{\cdot}NEt_3I$ (IV), m.p. 154—156° (lit. 150·5—152·5°), and $NH_2{\cdot}CO{\cdot}CMe_2{\cdot}NMe_3I$, m.p. 234—236°, are prepared by hydrolysis [dil. $Ba(OH)_2$; subsequent neutralisation with H_2SO_4] of the appropriate (I); (III) and (IV) are also obtained from $CH_2I{\cdot}CO{\cdot}NH_2$ and NR_3. H. B.

Condensation of reductone with carbamide. H. von Euler and C. Martius (Arkiv Kemi, Min., Geol., 1934, **11**, **B**, No. 26, 6 pp.).—Condensation of reductone (I) (A., 1933, 937) (2 and 1 mol.) with $CO(NH_2)_2$ (1 mol.) in presence of aq. mineral acids yields *di*- and *mono*-(*βγ-dihydroxyallylidene*)*carbamide*, respectively; the latter, decomp. 180—185°, is stable to cold conc. H_2SO_4 or HCl, hot $POCl_3$, and Ac_2O. $NH_2{\cdot}CO{\cdot}NHPh$ affords the corresponding *Ph* derivative, whilst (I) or its Na derivative [from (I) and NaOEt] in EtOH yields no isolable products when condensed with guanidine, $CS(NH_2)_2$, or ascorbic acid. F. O. H.

Preparation of amino-nitriles. G. A. Menge (J. Amer. Chem. Soc., 1934, **56**, 2197—2198).—OH·CH$_2$·CN and liquid NH$_3$ at room temp. (sealed tube) give about 95% of NH$_2$·CH$_2$·CN (*platinichloride*). Other NH$_2$-nitriles can be prepared similarly. H. B.

Cyanide and ferrocyanide from calcium cyanamide. L. Wöhler, E. Krall, and O. Dornhöfer (Angew. Chem., 1934, **47**, 733—734).—The technical conversion of CaCN$_2$ into alkali cyanide can be effected economically only with the finely-divided fresh dry product. Na$_2$CO$_3$, not NaCl, must be used with C, which is advantageously replaced by CaC$_2$ or Al$_4$C$_3$. Fusion with K$_2$CO$_3$ and Fe filings or, preferably, powdered Fe$_2$O$_3$ effects quant. conversion of CaCN$_2$ into K$_4$Fe(CN)$_6$. H. W.

Molecular compounds of boron trifluoride with water, alcohols, and organic acids. H. Meerwein and W. Pannwitz (J. pr. Chem., 1934, [ii], **141**, 123—148).—Largely a more detailed account of work previously reviewed (A., 1933, 360). The following appears to be new. BF$_3$,2H$_2$O (I), b.p. 58·5—60°/1·2 mm., is also prepared from B$_2$O$_3$ and 40% HF. BF$_3$,H$_2$O gives *cineol*, BF$_3$,H$_2$O,(C$_{10}$H$_8$O)$_2$, m.p. 71—73° (decomp.), and *dioxan*, BF$_3$,H$_2$O,C$_4$H$_8$O$_2$, m.p. 128—130° (decomp.), salts. The following *compounds* are described: BF$_3$,2HCO$_2$H [decomp. rapidly at 75° into (I) and CO], b.p. 43—44°/11 mm.; BF$_3$,2AcOH, b.p. 53—54°/10 mm.; BF$_3$,2EtCO$_2$H, b.p. 60—60·5°/12 mm.; BF$_3$,2Pr$^\alpha$CO$_2$H, b.p. 64°/11 mm.; BF$_3$,2CHMe:CH·CO$_2$H, b.p. 81—82° (partial decomp.)/12·5 mm.; BF$_3$,HCO$_2$H, m.p. −21° to −20°; BF$_3$,AcOH, m.p. 23—24°; BF$_3$,EtCO$_2$H, m.p. 28—29°; BF$_3$,Pr$^\alpha$CO$_2$H, m.p. 29—30°; BF$_3$,CHMe:CH·CO$_2$H, m.p. 35—36°; BF$_3$,NaOH; BF$_3$,KOH; BF$_3$,NaOMe; BF$_3$,KOMe; BF$_3$,BzOH, m.p. 90—91·5° (decomp.); BF$_3$,CH$_2$Ph·CO$_2$H, m.p. 56—59° (decomp.); BF$_3$,H$_2$C$_2$O$_4$, m.p. 57—58° (decomp.); BF$_3$,CO$_2$H·CH:CH·CO$_2$H, m.p. 75—82° (from maleic acid); BF$_3$,CO$_2$H·CH$_2$·CH$_2$·CO$_2$H, m.p. 82—84° (decomp.). Mol. refractions of several of the compounds are determined. H. B.

β-Halogenoethylarsines. A. G. Soare (Bul. Chim. Soc. Române, 1933, **36**, 75—78).—Prolonged agitation of aq. Na$_3$AsO$_3$ with CH$_2$Cl·CH$_2$·OH at ≯ 5° to 10° gives non-cryst. β-*hydroxyethylarsenic acid* (*Ca* salt), which passes into non-cryst. β-*hydroxyethylarsine oxide* (I) when its aq. solution is evaporated in SO$_2$ at 60°. Treatment of (I) with KBr and cold, conc. H$_2$SO$_4$ affords *As* β-*bromoethyl dibromide*, b.p. 110°/25 mm., m.p. 36°, which yields C$_2$H$_4$ quantitatively with warm aq. NaOH. H. W.

Determination of thallium in organic compounds. S. S. Nametkin and N. Melnikov (Z. anal. Chem., 1934, **98**, 414—416).—The substance is dissolved in conc. H$_2$SO$_4$ at 70—80° and oxidised by addition of KMnO$_4$. Excess of KMnO$_4$ is destroyed by H$_2$C$_2$O$_4$ or H$_2$O$_2$ and Br–H$_2$O added. Excess of Br is removed, and Tl determined iodometrically (cf. A., 1928, 725). J. S. A.

Thermal decomposition of organic compounds from the viewpoint of free radicals. IX. Combination of methyl groups with mercury. F. O. Rice and B. L. Evering (J. Amer. Chem. Soc., 1934, **56**, 2105—2107).—The HgAlk$_2$ (I) obtained by combining the fragments formed in the thermal decomp. (method, A., 1932, 1108) of C$_3$H$_8$ or C$_4$H$_{10}$ with Hg is converted by EtOH–HgBr$_2$ into HgAlkBr, and thence by I in aq. KI into AlkI. This and EtOH–NMe$_3$ give NMe$_4$I, thus showing that (I) is largely HgMe$_2$. (I) is accompanied by a small amount of an unstable compound, probably (·HgMe)$_2$. HgMe (Kraus, A., 1913, i, 1314) decomposes when allowed to warm to about room temp.: $2\mathrm{HgMe} \longrightarrow \mathrm{Hg} + \mathrm{HgMe}_2$. Et and higher radicals are not formed in the above decomp. H. B.

Nitration of the monobromotoluenes. M. C. Geerling and J. P. Wibaut (Rec. trav. chim., 1934, **53**, 1011—1030).—Nitration of *o*-C$_6$H$_4$MeBr, containing about 20% of *o*-C$_6$H$_4$Br·OH, which ensures mononitration, with HNO$_3$ at 0° gives (%) 18·2 of 1 : 2 : 3-, 20·15 of 1 : 2 : 4-, 37·3 of 1 : 2 : 5-, and 25·0 of 1 : 2 : 6-NO$_2$-derivatives (thermal analysis). Similarly, nitration of *m*-C$_6$H$_4$MeBr yields (%) 54·45 of 1 : 3 : 6-, 32·55 of 1 : 3 : 4-, and 13·0 of 1 : 3 : 2-NO$_2$-derivatives. The results agree with calc. vals. F. R. S.

Aromatic sulphonyl fluorides. III. W. Steinkopf and R. Hübner (J. pr. Chem., 1934, [ii], **141**, 193—200; cf. A., 1930, 1566; Covic and Gibson, A., 1934, 287).—PhEt and FSO$_3$H give p-*ethylbenzenesulphonyl fluoride*, b.p. 124—125°/14 mm., 238—239° (2-*NO$_2$*-derivative, b.p. 179°/15 mm.), which with MgMeI (I) and MgPhBr (II) affords *di*-p-*ethylbenzenesulphonylmethane* (24% yield), m.p. 131°, and p-*ethyldiphenyl sulphone* (32%), m.p. 91·5—92°, respectively. 1 : 3 : 4-C$_6$H$_3$Me$_2$·SO$_2$F (III) with (I) and (II) gives *di*-(m-4-*xylenesulphonyl*)*methane* (39%), m.p. 155·5—156°, and *phenyl* m-4-*xylyl sulphone* (33%), m.p. 87°, respectively. *m*-Xylene-2 : 4-disulphonyl fluoride and (I) give 2 : 4-dimethanesulphonyl-*m*-xylene (Pollak and Schadler, A., 1918, i, 497) and small amounts of two *compounds*, both C$_{17}$H$_{18}$O$_6$F$_2$S$_4$, m.p. 135° and 272°; with (II), 2 : 4-*dibenzenesulphonyl*-m-*xylene*, m.p. 232—233°, results. The Grignard reagent from (CH$_2$)$_5$Cl$_2$ and (III) afford αε-*di*-(m-4-*xylenesulphonyl*)-*pentane* (27%), m.p. 98°. m-*Chloro*-, b.p. 90°/22 mm. (*NO$_2$*-derivative, m.p. 85°), and m-*bromo-benzenesulphonyl fluoride*, b.p. 122°/23 mm. (*NO$_2$*-derivative, m.p. 104°), are prepared (Sandmeyer) from *m*-NH$_2$·C$_6$H$_4$·SO$_2$F. H. B.

Volume effects of alkyl groups in aromatic compounds. V. Monosulphonation of *p*-cymene. R. J. W. Le Fèvre (J.C.S., 1934, 1501—1502).—Sulphonation of *p*-cymene with 15% oleum at 0—10° occurs mainly (90%) in the 2-position, *i.e.*, *o* to the Me, small amounts of the 3-sulphonate also being formed. The relative amount of 2-substitution and the total yield of (SO$_3$H)$_1$ derivative both decrease with rise in temp. Substitution with ClSO$_3$H also occurs mainly in the 2-position, since with NH$_3$ the product affords the 2-sulphonamide. *p*-Cymene-3-sulphonic acid could not be obtained by oxidation of the 3-SH compound. J. W. B.

Preparation of *m*-fluorobenzotrifluoride. D. Aelony (J. Amer. Chem. Soc., 1934, **56**, 2063).—Thermal decomp. (apparatus used described) of *m*-trifluoromethylbenzenediazonium borofluoride [from *m*-

$NH_2{\cdot}C_6H_4{\cdot}CF_3$ by a modification of Balz and Schiemann's method (A., 1927, 654)] gives m-*fluorobenzotrifluoride*, b.p. 99·5—100·5°/762 mm. $CPhF_3$ is prepared in 75·5% yield by a modification of Swarts' method (A., 1913, i, 841; 1916, i, 133). H. B.

Synthesis of styrene. J. S. Salkind, I. P. Berkovich, and M. K. Amusin (Plast. Massui, 1934, No. 1, 14—20).—PhEt, prepared in 75% yield from C_6H_6 and EtCl, is converted into styrene (75—80% yield) by forming CHClPhMe (I), which is boiled with quinoline. Alternatively (I) is hydrolysed by boiling with 5—10% aq. NaOH, and the CHPhMe·OH dehydrated by heating with 3—5% of $KHSO_4$.

Ch. Abs. (*e*)

Synthesis of some aromatic and hydroaromatic hydrocarbons. S. Landa and J. Čech (Coll. Czech. Chem. Comm., 1934, 6, 423—432).—*αα-Diphenyl-Δ^{a}-hexadecene* (I), b.p. 274—275°/12 mm., m.p. 21·5—22·5°, from αα-diphenylhexadecan-α-ol (modified prep.) and $ZnCl_2$ at 125°, is hydrogenated (Pt-black) in Et_2O to *αα-diphenylhexadecane*, b.p. 279—281°/15 mm., m.p. 24°, which with H_2 and Ni at 100°/85 atm. affords *αα-di*cyclo*hexylhexadecane*, b.p. 269—271°/15 mm., m.p. 18·5—19·5°. Et palmitate with $CH_2Ph{\cdot}MgCl$ gives *α-phenyl-β-benzylheptadecan-β-ol* (II), m.p 28°, and some (III). Dehydration of (II) by $ZnCl_2$ affords *α-phenyl-β-benzyl-Δ^{β}-heptadecene* (III), b.p. 290—292°/16 mm., m.p. 58·5°, which is hydrogenated (Pt) to *α-phenyl-β-benzylheptadecane* (IV), b.p. 294—296°/16 mm., m.p. −34·5° to −35°. (III) or (IV) with H_2 and Ni at 180°/90 atm. gives α-cyclo*hexyl*-β-cyclo*hexylmethylheptadecane*, b.p. 288—290°/17 mm., m.p. −36·5° to −37·5°. The constitutions of (I) and (III) are proved by oxidation with $KMnO_4$; (I) gives $COPh_2$ and pentadecoic acid (V); (III) gives $CO(CH_2Ph)_2$ and (V). (I) and (III) are fluorescent. Physical consts. are recorded for the hydrocarbons. F. S. H. H.

Octachloronaphthalene. II. Chlorination of naphthalene with chlorine. Relative activities of various halogen carriers. V. Schvemberger and V. Gordon (J. Gen. Chem. Russ., 1934, 4, 529—551).—$C_{10}Cl_8$ can be obtained without the use of catalysts by passing Cl_2 over $C_{10}H_8$ without heating for 1 hr., gradually raising the temp. from 100° to 170° for the 2nd—7th hr., and gradually to 200° from the 8th to the 36th hr. The reaction time is shortened to 6 hr. by adding 0·3—1% of $AlCl_3$, $FeCl_3$, $AuCl_3$, $TlCl_3$, $ZrCl_4$, $SbCl_3$, $BiCl_3$, or $TeCl_4$ to the $C_{10}H_8$. UCl_4, AgCl, and $SbCl_5$ are less active than the above, whilst $BeCl_2$, $SiCl_4$, $TiCl_4$, $SnCl_2$, $PbCl_2$, $ThCl_4$, PCl_3, PCl_5, $AsCl_3$, $SeCl_2$, $SeCl_4$, $CrCl_3$, $MnCl_2$, ICl_3, $CoCl_2$, and $NiCl_2$ are inactive. R. T.

Hydrocarbons of high mol. wt. I. Alkylated aromatic hydrocarbons. II. Aliphatic branched-chain hydrocarbons. M. Lerer (Ann. Off. nat. Comb. liq., 1933, 8, 681—733; Chem. Zentr., 1934, i, 1647—1649).—I. The Na additive compound of anthracene reacts readily (best in Et_2O or liquid NH_3) with alkyl halides giving 9 : 10-dialkyl-9 : 10-dihydroanthracenes (I) together with small amounts of 9 : 10-dialkylanthracenes [also from (I) with Pt-black at 280°]; the method may be extended to $C_{10}H_8$. The following are described: 9 : 10-*di*iso*amyl-9 : 10-dihydro-*, b.p. 134—138°/high vac.; 9 : 10-*di*iso*amyl-*, m.p. 134°; 9 : 10-*di-β-octyl-9 : 10-dihydro-*, b.p. 180—190°/high vac.; 9 : 10-*di-β-octyl-*, m.p. 65°; 9 : 10-*diethyl-9 : 10-dihydro-*; 9 : 10-*diethyl-anthracene*, m.p. 145—145·5°; 1 : 4-*di*iso*butyl-1 : 2 : 3 : 4-tetrahydronaphthalene*, b.p. 170—175°/16 mm.; 4 : 4′-*di*iso*butyl-1 : 1′-dinaphthyl*, m.p. 80—81°; 1 : 4-*di*iso*butylnaphthalene*, b.p. 185°/11 mm.; 9 : 10-*dibenzoyl-*, b.p. 195—200°/high vac., and 9-*benzoyl-9 : 10-dihydroanthracene*, m.p. 97·5—98·5°. *d*, *n*, and η are recorded for the liquid products.

II. β-Octyl alcohol (improved prep.) is converted by NaOH into η-methylpentadecan-ι-ol (I), b.p. 158—160°/12 mm., which, on passage over Al_2O_3–asbestos or Cu at 300°, gives *dioctene* (II), $C_{16}H_{32}$, b.p. 142—146°/12 mm., 148°/12 mm. (probably a mixture). A *trioctene* [*η-methyl-ι-*n*-hexyl-Δ^{ι}-* or *-Δ^{κ}-heptadecene*], b.p. 211—214°/13 mm., is similarly prepared from "tricapryl alcohol" (III). (I) with I and red P gives *η-iodo-ι-methylpentadecane*, b.p. 184—188°/12 mm.; this with Na in PhMe affords *ημ-dimethyl-ικ-di-*n*-hexyloctadecane*, b.p. 256°/13 mm. The bromide from (III) and HBr on similar treatment yields *ηπ-dimethyl-ιλμξ-tetra-*n*-hexyldocosane*, b.p. 200—205°/0·003 mm. Mg β-octyl bromide and Me palmitate yield a *mixture*, $C_{32}H_{64}$, b.p. 170—175°/0·1 mm. Attempts to determine the constitution of (II) by oxidation with $KMnO_4$ were fruitless. *d*, n_D^{20}, and η are recorded for most of the liquid products. H. N. R.

Substitution of chlorine in aromatic compounds by amino-groups. I. Preparation of aniline from chlorobenzene. II. Preparation of *p*-nitroaniline from *p*-chloronitrobenzene using copper catalysts. N. N. Voroschcov, jun. (J. Gen. Chem. Russ., 1934, 4, 310—323, 324—327).—I [with V. A. Kobelev; cf. this vol., 1077]. Max. yields (89—90%) of NH_2Ph are obtained from PhCl (1 mol.), NH_3 (5 mols.), and Cu_2O (0·2 mol.) at 200—230°/70 atm.; the by-products are PhOH, 4—5%, and $NHPh_2$, 1—2%. The yield of NH_2Ph increases with increasing abs. and relative $[NH_3]$, of PhOH with increasing [OH′], and of $NHPh_2$ with increasing $[NH_2Ph]$; addition of NH_4Cl retards the reaction. These results point to the mechanism: $PhCl+Cu(NH_3)_2^{\cdot}$ (I) $\longrightarrow PhCl,Cu(NH_3)_2^{\cdot}$ (II); (II) $+NH_3 \longrightarrow$ (I) $+NH_2Ph+HCl$; (II) $+OH' \longrightarrow$ (I) $+PhOH+Cl'$; (II) $+NH_2Ph \longrightarrow$ (I) $+NHPh_2+HCl$; (I) $+Cl' \longrightarrow Cu(NH_3)_2Cl$. The reaction velocity $\propto$ concn. of (I). The catalytic activity of Cu^{I} is > that of Cu^{II}.

II [with M. I. Krilova]. p-$NO_2{\cdot}C_6H_4{\cdot}NH_2$ (III) of 94—97% purity is obtained in 90—98% yield by heating p-$C_6H_4Cl{\cdot}NO_2$ (IV) (1 mol.) with aq. NH_3 (6 mols.) and Cu^{II} [0·1 mol. as $CuSO_4$, $CuCl_2$, or $Cu(OH)_2$], for 30 min. at 217—240°/70 atm. In presence of Cu_2O or Cu smaller yields of less pure (III) are obtained. The velocity of reaction $\propto$ concn. of $Cu(NH_3)_4^{\cdot\cdot}$ and of (IV). R. T.

Preparation of nitrogen-substituted sulphonanilides. G. H. Young (J. Amer. Chem. Soc., 1934, 56, 2167).—p-*Toluenesulphon*-N-n-, m.p. 56°, and -iso-, m.p. 99·5—100°, -*propyl-*, and -sec.-*butyl-*, m.p. 75·5°, -*anilides* are prepared from p-$C_6H_4Me{\cdot}SO_2{\cdot}NHPh$, RBr, and KOH. H. B.

Derivatives of 3 : 5-dinitroaniline. J. J. Blanksma and G. Verberg (Rec. trav. chim., 1934, **53**, 988—1000).—4-*Bromo*-3 : 5-*dinitrobenzoyl chloride*, m.p. 90°, with the appropriate reagent affords *Me*, m.p. 125°, and Et 4-bromo-3 : 5-dinitrobenzoate, 4-*bromo*-3 : 5-*dinitro*-, m.p. 188°, and -3 : 5-dinitro-4-amino-benzamide, and 4-*bromo*-3 : 5-*dinitrobenzazide*, m.p. 116°. The azide with H_2SO_4 yields 4-*bromo*-3 : 5-*dinitroaniline*, m.p. 207° (*Ac* derivative, m.p. 263°), with MeOH forms 4-*bromo*-3 : 5-*dinitrophenylmethylurethane*, m.p. 189°, and with EtOH gives *Et* 4-*bromo*-3 : 5-*dinitrophenylcarbamate*, m.p. 167°. The chloroazide similarly affords *Me*, m.p. 176°, and *Et* 4-*chloro*-3 : 5-*dinitrophenylcarbamate*, m.p. 153°. 2-Chloro-3 : 5-dinitrobenzoyl chloride forms Me and Et esters, 2-chloro-3 : 5-dinitrobenzamide, 3 : 5-*dinitro*-2-*aminobenzamide*, m.p. 284°, and 2-*chloro*-3 : 5-*dinitrobenzazide*, m.p. 64°. The azide is converted into 2-*chloro*-3 : 5-*dinitroaniline*, m.p. 168° (*Ac* derivative, m.p. 153°), *Me*, m.p. 119°, and *Et* 2-*chloro*-3 : 5-*dinitrophenylcarbamate*, m.p. 98°. 2-Bromo-3 : 5-dinitrobenzoyl chloride gives *Me*, m.p. 109°, and *Et* 2-*bromo*-3 : 5-*dinitrobenzoate*, m.p. 74°, and 2-*bromo*-3 : 5-*dinitro-benzamide*, m.p. 216°, and -*benzazide*, decomp. 67°. The azide leads to 2-*bromo*-3 : 5-*dinitroacetanilide*, m.p. 142—143°, solidifying and re-melting at 181°, *Me*, m.p. 123°, and *Et* 2-*bromo*-3 : 5-*dinitrophenylcarbamate*, m.p. 121°, solidifying and remelting at 131°.

Reaction of some of the compounds with NH_2Ph under different conditions results in *Me*, m.p. 188°, and *Et* 3 : 5-*dinitro*-4-*anilinophenylcarbamate*, m.p. 151°, 3 : 5-*dinitro*-4-*aminoacetanilide*, m.p. 234°, 4 : 6-*dinitro*-2-*anilinodiphenylamine*, m.p. 129°, *Me*, m.p. 143°, and *Et* 3 : 5-*dinitro*-2-*anilinophenylcarbamate*, m.p. 102°, and 5 : 7-*dinitro*-1-*phenyl*-2-*methylbenziminazole*, m.p. 192°. F. R. S.

Nitration of 3 : 5-dinitroaniline derivatives. J. J. Blanksma and G. Verberg (Rec. trav. chim., 1934, **53**, 1037—1046).—3 : 5-Dinitrophenylcarbimide, m.p. 89°, gives with the reagent indicated the following products : H_2O, s-*di*-3 : 5-*dinitrophenylcarbamide*, m.p. 306° ; MeOH, *Me* (I), m.p. 127°, and EtOH, *Et* 3 : 5-*dinitrophenylcarbamate* (II), m.p. 83° ; NH_3, 3 : 5-*dinitrophenylcarbamide*, m.p. 206° ; NH_2Me, N-3 : 5-*dinitrophenyl*-N′-*methyl*-, m.p. 179°, and NH_2Et, -*ethylcarbamide* (III), m.p. 155°. 3 : 5-Dinitroaniline with $ClCO_2Me$ gives (I) and with EtNCO yields (III). 3 : 5-Dinitroacetanilide is not nitrated further by HNO_3 or HNO_3–H_2SO_4 at −15°. (III) and HNO_3 yield N′-*nitro*-N-3 : 5-*dinitrophenyl*-N′-*ethylcarbamide*, m.p. 98°. (I) is nitrated (HNO_3) to 3 : 5-*dinitrophenylnitromethylurethane*, m.p. 125° (which with MeOH–NH_3 forms the NH_4 salt of 3 : 5-dinitrophenylnitroamine, decomp. 190°), and *Me* 2 : 3 : 5-*trinitrophenylcarbamate* (IV), m.p. 143°. Similarly (II) and HNO_3 afford 3 : 5-*dinitrophenylnitrourethane*, m.p. 102°, and *Et* 2 : 3 : 5-*trinitrophenylcarbamate* (V), m.p. 118°. (I) is nitrated with HNO_3–H_2SO_4 to (IV) and *Me* 3 : 4 : 5-*trinitrophenylcarbamate*, m.p. 169°, whilst (II) similarly gives (V) and a compound, m.p. 144°. F. R. S.

Preparation of monoguanidines of possible physiological significance. C. E. Braun and W. M. Randall (J. Amer. Chem. Soc., 1934, **56**, 2134—2136).—*S*-Methyl*iso*thiocarbamide sulphate and the appropriate NH_2R in EtOH give γ-*phenylpropyl*-, m.p. 173—174°, δ-*phenylbutyl*-, m.p. 175—176°, *hexahydrobenzyl*-, m.p. 275—276°, decomp. 280—282°, and β-cyclo*hexylethyl*-, m.p. 295—297°, -*guanidine sulphate*. α-Phenyl-α-benzyl-, m.p. 248·5°, and αα-*dibenzyl*-, m.p. 191—192°, -*guanidine hydrochloride* are prepared from $CN{\cdot}NH_2$ and $CH_2Ph{\cdot}NHPh,HCl$ (in EtOH) and $(CH_2Ph)_2NH,HCl$ (in amyl alcohol at 140—150°), respectively. $CS(NH{\cdot}CH_2Ph)_2$, $CH_2Ph{\cdot}NH_2$ (I), and HgO in EtOH give αβγ-tribenzylguanidine (*hydrochloride*, m.p. 203—204°; *trihydrochloride*, m.p. 258—259°), whilst (I) and S-*methylbenzyliso*thio*carbamide hydriodide*, m.p. 103—104° (from $NH_2{\cdot}CS{\cdot}NH{\cdot}CH_2Ph$ and EtOH–MeI) afford αγ-dibenzylguanidine [hydrochloride, m.p. 186° (lit. 176°)]. H. B.

Isomerism of the crystalline liquid *p*-phenetoleazoxybenzoic esters. D. Vorländer and A. Frölich (Ber., 1934, **67**, [*B*], 1556—1571).—*p*-Azoxyphenetole (I) is monomorphic cryst. liquid, and in this state forms mobile droplets, according to *n*, more closely related to the amorphous melt than to the solid crystals. The monomorphic azoxybenzoic esters (II) give viscous rodlets resembling in many respects the solid crystals. The main cause of the differences in the cryst.-liquid phases, in visible crystal structure, and in Röntgen interferences lies in the differing viscosity of the phases. The *p*-phenetoleazoxybenzoic esters (III) are regarded as "bastards" of (I) and (II), and the properties of each parent are developed separately, and not simultaneously. Two cryst.-liquid phases are formed. Depending sharply on temp., (III) have the cryst.-liquid characteristics of either (I) or (II) with slight mutual restrictions. The following details are cited : *p*-azoxyphenetole, amorphous liquid ⇌ (168°) cryst. liquid ⇌ (137°) cryst. solid II ⟶ cryst. solid I (from light petroleum) ; Et *p*-azoxybenzoate, amorphous liquid ⇌ (121°) cryst. liquid ⇌ (113°) cryst. solid II ⟵ cryst. solid I (also cryst. liquid ⟶ cryst. solid I directly) ; p-*phenetoleazoxybenzoic acid*-a, dark yellow needles, -*b*, paler yellow leaflets or plates, m.p. 241° (corr.) to turbid cryst. liquid after softening at 238—239° (corr.), partly vaporising when heated further without attaining the amorphous-liquid phase, and their derivatives ; *Et* ester-a, amorphous liquid ⇌ (115°) cryst. liquid ⇌ (100—102°) cryst. solid ; *Et* ester-b, amorphous liquid ⇌ (112°) cryst. liquid I ⇌ (82—83°) cryst. liquid II ⇌ (74—76°) cryst. solid II (also liquid II ⟶ solid I ⟶ solid II) (respective NO_2-derivatives, m.p. 135° and m.p. 124—126°) ; *chloride*-a, softens at 144°, transparent amorphous melt, 150—152° ; *chloride*-b, softens at 102—104°, viscous cloudy melt, 122—124°, clear amorphous melt, 128—130° ; *allyl* ester-a, having 3 cryst.-solid and 2 cryst.-liquid forms ; *allyl* ester-b, cryst. solid ⇌ (70—72°) cryst. liquid II ⇌ (91°) cryst. liquid I ⇌ (99°) amorphous liquid ; *Me* ester-a, softens at 135°, cloudy, mobile, cryst. liquid at 138°, amorphous liquid at 156° ; *Me* ester-b, softens at 111°, cloudy, mobile, cryst. liquid at 114°, amorphous liquid at 148°. H. W.

Polymethylbenzenes. IX. Addition of ethyl diazoacetate to durene. L. I. Smith and P. O. Tawney. **X. Reaction with aromatic diazonium compounds.** L. I. Smith and J. H. Paden (J. Amer. Chem. Soc., 1934, 56, 2167—2169, 2169—2171).—IX. Slow addition of $CHN_2\cdot CO_2Et$ to durene at 140—145° gives a little Et fumarate, (mainly) *Et* β-2 : 4 : 5-*trimethylphenylpropionate*, b.p. 130—136°/4 mm. [free acid (I), m.p. 96—97° (lit. 92°) (*amide*, m.p. 152—154°)], and tarry material. 2 : 4 : 5-*Trimethylbenzylidenemalonic acid*, m.p. 183—185° (decomp.) [the Et ester, b.p. 182—186°/11 mm., is prepared from 2 : 4 : 5-$C_6H_2Me_3\cdot CHO,CH_2(CO_2Et)_2$, and piperidine], heated at 190—200° gives 2 : 4 : 5-*trimethylcinnamic acid*, m.p. 154—155°, reduced (H_2, PtO_2, 95% EtOH) to (I).

X. 2 : 4 : 6 - *Trinitrobenzeneazo - pentamethylbenzene*, m.p. 176° (decomp.), and -iso*durene*, m.p. 164° (decomp.), prepared by slow addition of C_6HMe_5 (II) and *iso*durene, respectively (in AcOH), to diazotised picramide (III) (in conc. H_2SO_4) [prepared by a slight modification of Blangey's method (A., 1926, 62)] at $< 2°$, are reduced ($SnCl_2$, conc. HCl, AcOH) to amino-pentamethylbenzene (IV) and -*iso*durene (V), respectively. Durene (VI) and bromodurene do not react with (III). Other diazotised amines could not be coupled with (II), (VI), or *s*-$C_6H_3Me_3$. Diazotised (IV) and (II) in AcOH–conc. H_2SO_4 give a *hydrocarbon*, $C_{22}H_{30}$, m.p. 212—213·5°, which is not decamethyldiphenyl (m.p. 239—241°). (II) does not react with diazotised (V), ψ-cumidine, or mesidine. H. B.

Colour of thiol and methylthiol azo-dyes of α- and β-naphthol. A. Luszczak and L. Grün (Monatsh., 1934, 64, 349—360).—The absorption spectra of the following dyes have been determined: 2-4′-nitrobenzeneazo-1-hydroxy-3-thiol-, -3-methylthiol-, -4-thiol-, -4-methylthiol-, -5-thiol-, -5-methylthiol-naphthalene; 1-4′-nitrobenzeneazo-2-hydroxy-6-thiol-, -6-methylthiol-, -7-thiol-, -7-methylthiol-, -8-thiol-, -8-methylthiol-naphthalene. The SH and SMe dyes of the α-series show marked displacement of the absorption bands towards the red and higher extinction in comparison with those of the β-series. The extinction curves of dyes with SH or SMe in the α-position of the $C_{10}H_8$ nucleus are more complex than those of compounds with similar groups in the β-position, whether OH is α- or β-. The position of OH and SH or SMe exerts a very marked and individual influence on the colour of the dyes. H. W.

Relation between absorption spectra and chemical constitution of dyes. VI. Influence of chromophore position in bisazo-dyes. J. A. Funkhouser and W. R. Brode (J. Amer. Chem. Soc., 1934, 56, 2172—2173).—The absorption spectra of 4 mono- and 16 bis-azo-dyes in 30% EtOH, conc. HCl, and 3% NaOH are determined as previously described (cf. A., 1928, 1171); the positions of the max. are tabulated. Comparison of *m*- (I) and *p*- (II) -$NAr{:}N\cdot C_6H_4\cdot N{:}NAr'$ (Ar and Ar′ both contain OH, *e.g.*, Ar=*p*-$OH\cdot C_6H_4\cdot$; Ar′=2-hydroxy-7-sulpho-α-naphthyl) shows that (II) have more intense and better defined absorption bands; introduction of CO_2H into Ar or Ar′ produces broader but less intense bands. The spectra of (I) are similar to the spectra obtained by addition of the bands of $NAr{:}NPh$ and $NPh{:}NAr'$; (II) show a distinct shift in the intensity distribution with intensified bands (hyperchromic effect) at lower frequencies (hypsochromic effect). *p*-Coupling of N:N groups promotes an effect similar to the conjugation of chromophores (III) to form a single (III) in the mol.; *m*-substituted (III) do not influence each other appreciably. Bisazo-dyes have broader and less sharply defined bands than monoazo-dyes of similar structure. H. B.

Absorption spectra of azo-compounds.—See this vol., 1287.

Formation of certain aromatic hydrazines. A. J. Berlin (J. Gen. Chem. Russ., 1934, 4, 728—732).—When SO_2 is passed through a suspension of NH_2Ph (I) in aq. NaOH and $NaNO_2$ at 0—5°, the reactions $2(I)+HNO_2 \longrightarrow PhN_2\cdot NHPh$ (II) $\longrightarrow$ $NHPh\cdot NH_2$ (III)+(I) take place, whilst when the solution is not cooled (II) decomposes to yield PhOH, N_2, and (I). With *o*-anisidine in place of (I), 2-*hydrazinoanisole-5-sulphonic acid*, $+0{\cdot}5H_2O$, decomp. 232—235°, is obtained. R. T.

Action of bases on nitrophenylhydrazines: 2 : 4-dinitrophenylhydrazine. A. K. Macbeth and J. R. Price (J.C.S., 1934, 1637—1639).—2 : 4-$(NO_2)_2C_6H_3\cdot NH\cdot NH_2$ with boiling aq. NH_3 (*d* 0·945) gives 70% of 6-nitro-1-hydroxy-1 : 2 : 3-benztriazole (I), 17% of *m*-$C_6H_4(NO_2)_2$ (II), 5% of an amorphous acid (III), and a trace of *mm*′-dinitroazoxybenzene (IV). With boiling 10% aq. N_2H_4 82·5% of (I), 1% of (II), and 1% of (III), with boiling 10% N_2H_4–EtOH 90% of (I) are formed. With 0·04—0·37*N*-aq. $Ba(OH)_2$ at 60° traces of NH_3 are formed; the amount of (I) decreases from 70 to 16%, whilst that of (II) and (IV) increases from 10 to 27 and 10·5 to 49%, respectively, with increasing concn. 0·1*N*-NaOH gives the same result as 0·1*N*-$Ba(OH)_2$. With 0·2—7·5*N*-aq. NaOH at 15±2° the amount of (I) is a min. (8·5%) and those of (II) and (IV) are a max. (33 and 52%, respectively) at about 2·4*N*, whilst the amount of (III) increases with increasing concn. (12% at 7·5*N*). R. S. C.

Influence of *o*-substituents on the reactivity of aromatic compounds. G. Lock (Oesterr. Chem. Ztg., 1934, 37, 159—161, 167—170).—A crit. summary of lit. data relating to the effect of *o*-substituents on reactions, in which the superposition of steric and chemical (polar) factors, and the variation of the effect in different reactions, are discussed. J. W. B.

Derivatives of 3 : 5- and 4 : 6-dibromo-*o*-phenetidine. E. Bureš and B. Tusarová (Časopis českoslov. Lék., 1934, 14, 1—14; Chem. Zentr., 1934, i, 2581—2582).—3 : 5-*Dibromo-o-phenetidine* (I), m.p. 57° (*hydrochloride*, decomp. > 100°; *sulphate*, unstable; *picrate*, m.p. 145°; Ac_2 derivative, m.p. 108°; Bz_1 derivative, m.p. 151°; N-*Et* derivative, b.p. 152°), is prepared by treating *o*-phenetidine with Br in AcOH. From the diazotised base are obtained (by heating) 3 : 5-*dibromophenetole*, b.p. 268° (4-NO_2-derivative, m.p. 128°) (with H_2SO_4 and Na_2SO_4) 3 : 5-*dibromo*-2-*hydroxyphenetole* (fuming liquid), and (Sandmeyer) 2-*chloro*-3 : 5 -*dibromophenetole*, m.p. 46°; 2 : 3 : 5-

tribromophenetole, m.p. 72°, and 3 : 5-*dibromo*-2-*iodophenetole*, m.p. 62°. The *Ac* derivative, m.p. 79°, of *o*-phenetidine with Br in AcOH gives 4 : 6-*dibromo*-2-*acetamidophenetole*, m.p. 141°, hydrolysed to 4 : 6-*dibromo*-o-*phenetidine* (II), m.p. 60° (*hydrochloride*, decomp. > 150°; Ac_2 derivative, m.p. 151°; Bz_1 derivative, m.p. 159°; N-Me_2 derivative, liquid). From (II) by diazotisation the following are prepared : 4 : 6-*dibromophenetole*, m.p. 270—272°; 2-NO_2-derivative, m.p. 46°; 2-*OH*-derivative, a fuming liquid resembling PhOH; 2-*Cl*-derivative, slightly fuming crystals, m.p. 61°; 2-*Br*-derivative, m.p. 73°; 2-*I*-derivative, m.p. 69°. R. N. C.

Condensation products from phloroglucinol and aromatic amines. [Diaryldiaminophenols.]—See B., 1934, 954.

Constituents of *Ginkgo biloba*, L., fruit. I—III. S. Furukawa (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 24, 304—313, 314—319, 320—324).—I. Ginkgol Me ether (I) (cf. A., 1928, 1291) in $CHCl_3$ at 0° with O_3 during 30 hr. followed by hydrolysis affords *n*-heptoic acid and its aldehyde, $H_2C_2O_4$, and azelaic acid, which indicates the presence of a pentadecenyl group. Dihydroginkgolic acid with $COMe_2$–$KMnO_4$ gives impure palmitic acid (also obtained from dihydroginkgol), which is probably identical with *cyclo*gallipharic acid (cf. A., 1904, i, 587). When heated, ginkgol affords *m*-cresol [oxidised to *m*-$OH{\cdot}C_6H_4{\cdot}CO_2H$, which is also obtained by oxidation of (I)] and a mixture of aliphatic hydrocarbons, which indicates that OH is *m* to the pentadecenyl side-chain (cf. A., 1907, i, 1032).

II. Bilobol (II) (A., 1928, 1291) with MeI in boiling EtOH–NaOEt affords a Me_2 ether, b.p. 250—252°/6 mm., oxidised by O_3 in $CHCl_3$ at 0° to the same products as (I). Dihydrobilobol with $KMnO_4$ affords palmitic acid. Dry distillation of (II) affords probably orcinol or β-orcinol.

III. Et *m*-methoxybenzoylacetate (prep. described) with tridecyl iodide in boiling EtOH–NaOEt during 5 hr. affords a product, hydrolysed to m-*methoxyphenyl tetradecyl ketone*, b.p. 250—258°/10 mm., which is reduced (Clemmensen) to m-*methoxypentadecylbenzene*, m.p. 22°, and demethylated to dihydroginkgol.

J. L. D.

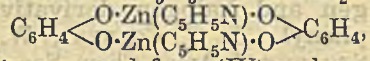
Cationoid reactivity of aromatic compounds. II. Action of potassium cyanide on 1-nitroso-β-naphthol and 1-benzeneazo-β-naphthol. W. Bradley and R. Robinson (J.C.S., 1934, 1484—1489; cf. A., 1932, 622).—Cationoid activity of 1-nitroso-β-naphthol (I) is shown by its reaction with aq. KCN at 80—90° to form 1-*amino*-2-*hydroxy*-4-*cyanonaphthalene* (II). 1-Benzeneazo- (III) and 1-*p*-sulphobenzeneazo-β-naphthol similarly give (II), indicating that these compounds probably have the hydrazone structure. Five other hydroxyazo-compounds react similarly, two only slowly, and four not at all. (II), m.p. 200—201° (decomp.) (*hydrochloride*, by dry HCl gas in Et_2O), is insol. in HCl and unstable in air or dil. aq. NaOH, reduces Fehling's solution, and cannot be diazotised or smoothly hydrolysed, but its structure is shown by the following reactions. It gives a Ac_3 derivative (IV) (by hot Ac_2O–C_5H_5N), m.p. 163—164°, by Me_2SO_4–aq. NaOH 1-*dimethylamino*-2-*methoxy*-4-*cyanonaphthalene*, m.p. 93—93·5° (sol. in dil. HCl; hydrolysed by cold, conc. H_2SO_4 or hot 33% NaOH to 4-*dimethylamino*-3-*methoxy*-1-*naphthoamide*, m.p. 183°, further hydrolysed by hot conc. HCl to the acid), and with CrO_3–H_2SO_4 4-*cyano*-1 : 2-*naphthaquinone*, m.p. 175—176° (decomp. slowly by aq. NaOH). This quinone affords 4-*cyano*-1 : 2-*benzphenazine*, m.p. 247°, hydrolysed by hot 40% NaOH to 1 : 2-*benzphenazine*-4-*naphthoic acid*, m.p. 305°, and is reduced (SO_2 in hot EtOH) to 4-*cyano*-1 : 2-*dihydroxynaphthalene*, m.p. 210—211°, the Me_2 *ether*, m.p. 109° (obtained by MeI and K_2CO_3 in hot $COMe_2$; Me_2SO_4–aq. NaOH gives a *substance*, m.p. > 300°), of which with hot 25% KOH gives 3 : 4-*dimethoxy*-1-*naphthoic acid*, m.p. 161—161·5°. (IV) and hot, dil. KOH yield 1-*acetamido*-2-*hydroxy*-4-*cyanonaphthalene*, m.p. 224° [*K* and *Na* salts; oxidised ($KMnO_4$) to *o*-$C_6H_4(CO_2H)_2$], the *Me ether* (V) (by MeI–K_2CO_3–$COMe_2$), m.p. 275°, of which is also obtained [Sandmeyer; $K_2Ni(CN)_4$] from 1-*acetamido*-4-*amino*-2-*methoxynaphthalene* (VI), m.p. 196°. 1-Nitro-2-methoxynaphthalene with Zn–EtOH–conc. HCl gives 2-methoxy-α-naphthylamine, m.p. 55° (lit. 54° and 84°), the Ac derivative, m.p. 178—179° (lit. 175°), of which with HNO_3 (*d* 1·42) in AcOH at < 5° gives the 4-NO_2-derivative, m.p. 251°, indifferent to Zn–HCl or Na_2S, but reduced to (VI) by hot aq. $Na_2S_2O_4$. (VI) in C_6H_6 with aq. CrO_3–H_2SO_4 yields 2-*methoxy*-1 : 4-*naphthaquinone*, m.p. 184—185° (lit. ? 146—147°), also obtained by hydrolysis and subsequent oxidation of (V). A by-product in the formation of (II) from (III) is a *substance*, probably $C_{17}H_{13}O_2N_3$, m.p. 235° (decomp.) [*Me ether*, m.p. 206° (sinters at 196°; decomp. 215°)]. (I) and *p*-$C_6H_4Me{\cdot}SO_2H$ in EtOH give 1-*amino*-2-p-*toluenesulphonyloxy*-4-*naphthyl*-p-*tolylsulphone*, m.p. 151—152°, which by alkaline hydrolysis and subsequent acetylation yields 1-*diacetamido*-2-*acetoxy*-4-*naphthyl*-p-*tolylsulphone*, m.p. 191—192°.

R. S. C.

Derivatives of hydroxydiphenyls. II. Nitrogen and halogen derivatives of 4-hydroxydiphenyl. J. C. Colbert, W. Meigs, and A. H. Stuerke (J. Amer. Chem. Soc., 1934, 56, 2128—2130; cf. this vol., 291).—3-Chloro-4-hydroxydiphenyl (I), b.p. 176·6°/5 mm. (cf. *loc. cit.*) [*Me ether*, m.p. 93° (all m.p. are corr. unless stated otherwise)], and HNO_3 in AcOH give 3-*chloro*-5-*nitro*-4-*hydroxydiphenyl*, m.p. 89—90° [4′-*Br*-derivative, m.p. 193—194°; the *hydrochloride* and Bz_2 derivative of the corresponding NH_2-derivative have m.p. 180° (decomp.) and 181—182°, respectively], the structure of which is established by chlorination in AcOH to 3 : 4′-*dichloro*-5-*nitro*-4-*hydroxydiphenyl*, m.p. 190—192° (uncorr.) [the *hydrochloride* and Bz_2 derivative of the corresponding NH_2-compound have m.p. 210° (decomp.) and 217—218°, respectively], which is also prepared from 3-nitro-4-hydroxydiphenyl (II) (*benzoate*, m.p. 111°) and Cl_2 in AcOH. The structure of (II) is established since acetylation and benzoylation of the NH_2-derivative causes rearrangement (A., 1925, i, 808). (I) is also nitrated to 3-*chloro*-5 : 4′-*dinitro*-4-*hydroxydiphenyl*, sublimes at 200°. 3 : 5-Dichloro-4-hydroxydiphenyl, b.p. 188·7°/5 mm. (cf. *loc. cit.*) (*Me ether*, m.p. 54°; 4′-*Br*-derivative, m.p. 136·5—138°), and HNO_3 in AcOH give the 4′-NO_2-derivative, m.p. 214—215°.

4-Hydroxydiphenyl (2 : 4-*dinitro*-, m.p. 115°, and 2 : 4 : 6-*trinitro*-, m.p. 224°, -*phenyl ethers*) and Cl_2 in AcOH give Cl-, Cl_2-, or Cl_3-derivatives according to the time of reaction (cf. *loc. cit.*); more prolonged chlorination affords a mixture containing Cl_5-, m.p. 115—118° (uncorr.), and Cl_7-, m.p. 142—145° (uncorr.), -derivatives. H. B.

Polymorphism of aromatic disulphides. I. Chmelnitzkaja and V. Michels (J. Gen. Chem. Russ., 1934, **4**, 452—455).—When reduced with N_2H_4 ($(p\text{-}NO_2\cdot C_6H_4\cdot S\cdot)_2$ yields two *forms* of $(p\text{-}NH_2\cdot C_6H_4\cdot S\cdot)_2$ (I), m.p. 83° [Ac_2 derivative (II), m.p. 216°], and m.p. 143—144° (Ac_2 derivative, m.p. 181—182°). (II) is converted into Ginsberg's γ-form, m.p. 122°, by exposure to light. A fourth form, m.p. 172°, of (II) is obtained by heating (I) successively with 30% $NaHSO_3$ and Ac_2O. R. T.

Pyrocatechol complex salts and their constitution. G. Spacu and M. Kuraš (J. pr. Chem., 1934, [ii], **141**, 201—217).—The complexes $[M^{II}(O\cdot C_6H_4\cdot O)_2]H_2(C_5H_5N)_2$, described by Weinland and Sperl (A., 1926, 165), are best formulated as $[(C_5H_5N)_2M(O\cdot C_6H_4\cdot OH)_2]$ (*A*). The *Zn* salt (I) (*A*, M=Zn) is obtained (i) from $o\text{-}C_6H_4(OH)_2$ (II), $ZnCl_2$, and C_5H_5N in H_2O, (ii) as the *monohydrate* from (II) and aq. $[(C_5H_5N)_2Zn](NO_3)_2,2H_2O$, and (iii) as the *dihydrate* from (II) and aq. $[(C_5H_5N)_2Zn](OAc)_2$. Dry (I) is converted by dry NH_3 into the *complex*, $[(NH_3)_2Zn(O\cdot C_6H_4\cdot OH)_2]$. (II), $ZnCl_2$, and $(\cdot CH_2\cdot NH_2)_2$ in H_2O give the *complex* $[enZn(O\cdot C_6H_4\cdot OH)_2]$, also obtained from (II) and $(Zn\,en_3)Cl_2,2H_2O$ in aq. NaOAc. The *Cd* (III) (*A*, M=Cd) and *Ni* (*A*, M=Ni) complexes are also prepared. The *complex*, $[enCd(O\cdot C_6H_4\cdot OH)_2]$, is obtained from $(Cd\,en_3)Cl_2$ and (II). (II) and $Zn(OAc)_2$ in H_2O give the *salt*, $OH\cdot C_6H_4\cdot O\cdot Zn\cdot OAc(+H_2O)$ (IV), whilst $Cd(OAc)_2$ and (II) in EtOH afford the *salt*, $OH\cdot C_6H_4\cdot O\cdot Cd\cdot OAc$ [converted by aq. C_5H_5N into (III)]. $ZnCl_2$ (1 mol.), (II) (2 mols.), and an excess of C_5H_5N in hot H_2O give the *complex*,  $C_6H_4{<}\begin{matrix}O\cdot Zn(C_5H_5N)\cdot O\\ O\cdot Zn(C_5H_5N)\cdot O\end{matrix}{>}C_6H_4$, colourless [*monohydrate*, prepared from (IV) and aq. C_5H_5N at 100°]; when the reaction mixture is cooled slowly in the dark, a red *complex* (V) of the same composition as (I) is obtained. (V) loses 1 mol. of C_5H_5N at 70° and decomposes from 150°. The complex obtained from (II), $ZnSO_4$, and C_5H_5N using Weinland and Sperl's method (*loc. cit.*) contains Zn and N in the ratio 1 : 2·47; the use of more dil. solutions gives a *complex* of the composition $4[Zn(O\cdot C_6H_4\cdot O)_2]H_2(C_5H_5N)_2+C_6H_4(OH)_2$. (II), $[Co(NH_3)_6]Cl_3$, and C_5H_5N in aq. NaOAc afford the *complex*, $[(C_5H_5N)_2Co(O\cdot C_6H_4\cdot OH){:}(O\cdot C_6H_4\cdot O)]$. H. B.

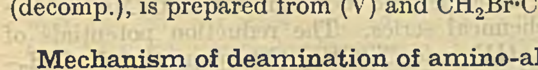
Halogen hydroxo- and pyrocatechol hydroxo-salts of bivalent heavy metals.—See this vol., 1317.

Homologues of resorcinol. R. Robinson and R. C. Shah (J.C.S., 1934, 1491—1498).—Additional evidence is cited to confirm the nuclear methylation of β-resorcylic acid by MeI–KOH (J.C.S., 1895, **67**, 900). Et_2 glutaconate does not condense with Me ketones. The Na derivative of Et_2 α-acetoglutarate and $Pr^{a}COCl$ in Et_2O lead to a mixture of γ-aceto- and γ-butyro-butyric (I) acids. Et *C*-butyrylacetoacetate (modified prep.) is hydrolysed (NH_3–Et_2O) to Et butyrylacetate, which with NaOEt and $CH_2Cl\cdot CH_2\cdot CO_2Et$ gives Et_2 butyroglutarate, whence only a poor yield of (I) was obtained. Et butyrobutyrate is best cyclised by NaOEt in Et_2O, giving 2-*ethyldihydroresorcinol*, m.p. 175—177° (decomp.), which with Br under most conditions gives tars, but affords (excess Br; cold $CHCl_3$) a Br_2-, m.p. 75—77°, and [cold AcOH; Br (3 mols.); NaOAc (3 mols.)] a Br_3-derivative, m.p. 92—94° (decomp.). Nuclear alkylation of resacetophenone (II) (improved prep.) is best effected by KOH (4 mols.) and MeI (5 mols.) under stated conditions; the resulting 2-hydroxy-4-methoxy-3-methylacetophenone, m.p. 80—82°, is reduced (Clemmensen) to 6-*methoxy*-3-*ethyl*-o-*cresol*, b.p. 128—131°/15 mm. (p-*nitrobenzoyl* derivative, m.p. 135—137°), which with hot HBr (*d* 1·7) gives 2-*methyl*-4-*ethylresorcinol*, m.p. 88—90° [Me_2 *ether*, b.p. 115—118°/15 mm., oxidised ($KMnO_4$; 70—80°) to 2 : 6-*dimethoxy*-3-*ethylbenzoic acid*, m.p. 114—120°, or, finally, to an *acid*, m.p. 200—205° (decomp.)]. Ethylation of (II) affords in poor yield a mixture of *O*-Et_2 and *C*-Et-*O*-Et derivatives. β-Resorcylaldehyde gives a mixture of *O*-Et_2-aldehyde and some 2-*hydroxy*-4-*ethoxy*-3-*ethylbenzaldehyde*, m.p. 58—60°, and β-resorcylic acid gives a similar mixture. *Me* β-*resorcylate* (by MeOH–H_2SO_4, not by HCl), m.p. 118—119°, affords similarly, but smoothly, *Me* 2-*hydroxy*-4-*ethoxy*-3-*ethylbenzoate* (III), m.p. 52—53°, *Me* 2-*hydroxy*-4-*ethoxybenzoate*, m.p. 77—79°, *Me* 2 : 4-*diethoxybenzoate* (IV), m.p. 51—54°, and a mixture of (III) and (IV), which is best separated by way of the respective acids, (V) and (VI). (V) is hydrolysed and decarboxylated by hot HI (*d* 1·7) to 2-*ethylresorcinol*, m.p. 95—97°, which gives (Gattermann) 2 : 4-*dihydroxy*-3-*ethylbenzaldehyde*, $+0{\cdot}5H_2O$, m.p. 115—118° [2 : 4-*dinitrophenylhydrazone*, m.p. 295° (decomp.); *pyrylium* salt with 5 : 6-dimethoxy-1-hydrindone and HCl in AcOH], reduced (Clemmensen) to 4-*methoxy*-2-*ethylresorcinol*, m.p. 98—99°. The last-mentioned substance is probably identical with the dihydric phenol obtained from citrinin (A., 1931, 1092), but the latter decomposes when kept (m.p. 65—70° after 2—3 years). 4-Ethylresorcinol gives (Gattermann) 2 : 4-*dihydroxy*-5-*ethylbenzaldehyde*, m.p. 130—131° [2 : 4-*dinitrophenylhydrazone*, m.p. 279° (decomp.)], reduced to 6-*methyl*-4-*ethylresorcinol*, m.p. 60—63°, b.p. 150—155°/20 mm. Orsacetophenone is reduced to 5-*methyl*-4-*ethylresorcinol*, $+1{\cdot}5H_2O$, m.p. 72—82°, $+0{\cdot}25H_2O$, and anhyd., m.p. 75—80°. Zn for Clemmensen reductions is activated by pulverising and treating three times with hot HCl. R. S. C.

Derivatives of protocatechuic acid from safrole; rearrangement of the acyl group. K. Ono and M. Imoto (J. Chem. Soc. Japan., 1934, 55, 517—524).—Heating of 30 g. of safrole with 17 g. of KOH and 30 g. of MeOH at 200—208° for 3 hr. in an autoclave gave 3 g. of *iso*safrole and 27 g. of a mixture of 3 : 4- (I) and 4 : 3-$C_6H_3(OH)(O\cdot CH_2\cdot OMe)\cdot CH{:}CHMe$ (II). The Ac and Bz derivatives of (I) and (II) were prepared and their oxidation products investigated. Ch. Abs. (*e*)

Catalytic action of Japanese acid earth. V. Action on methyl*cyclo*hexanols and menthol. H. Inoue (Bull. Chem. Soc. Japan, 1934, 9, 353—363; cf. A., 1927, 51).—Ring-fission of 2- (I), 3-, and 4-methyl*cyclo*hexanol (II) in presence of Japanese acid earth at 250—350° proceeds similarly to that of *cyclo*hexanol, (I) giving most and (II) least *cyclo*pentane derivatives. Menthol yields similarly at 250° methyl*cyclo*pentane, menthene (III), menthane, *p*-cymene, *iso*propyl- and methyl*iso*butyl-*cyclo*pentane (IV); at 350° *cyclo*pentane, (III), and (IV) are the main products. R. S. C.

Aromatic alcohols and thiolacetic acid. B. Holmberg (J. pr. Chem., 1934, [ii], 141, 93—112).—$CPhRR'\cdot OH$ and $SH\cdot CH_2\cdot CO_2H$ (I) in (usually) 2*N*-HCl at 100° (bath) give $CPhRR'\cdot S\cdot CH_2\cdot CO_2H$ (II) in addition to $SH\cdot CH_2\cdot CO_2\cdot CPhRR'$; cinnamyl alcohol (III) and benzilic acid (IV) react similarly, but acids analogous to (II) are not obtained from $CH_2Ph\cdot CRR'\cdot OH$, $CH_2Ph\cdot CH_2\cdot CH_2\cdot OH$, or mandelic acid. Thus, $CH_2Ph\cdot OH$ gives $CH_2Ph\cdot S\cdot CH_2\cdot CO_2H$; $CHPhMe\cdot OH$ affords $CHPhMe\cdot S\cdot CH_2\cdot CO_2H$, m.p. 64—66° [also prepared from (I) and CHPhMeBr in aq. EtOH–NaOH] [corresponding *sulphoxide*, m.p. 115—117° (decomp.), and *sulphone*, m.p. 112—113°]; $CPhMe_2\cdot OH$ yields β-*phenyl*iso*propylthiolacetic acid*, m.p. 72—74°; $CHPh_2\cdot OH$ furnishes *benzhydrylthiolacetic acid*, m.p. 129—130° [*Na* salt ($+4H_2O$)]; $CPh_2Me\cdot OH$ gives impure $CPh_2Me\cdot S\cdot CH_2\cdot CO_2H$; $CPh_3\cdot OH$ affords $CPh_3\cdot S\cdot CH_2\cdot CO_2H$ [*Na* salt ($+5H_2O$)]; (III) yields cinnamylthiolacetic acid [corresponding *sulphoxide*, m.p. 124—125° (decomp.) (previous sintering)]; (IV) furnishes *carboxymethylthioldiphenylacetic acid*, $CO_2H\cdot CH_2\cdot S\cdot CPh_2\cdot CO_2H$, m.p. 194—196° (decomp.). The following are prepared from (I) and the appropriate bromide: β-*phenylethylthiolacetic acid* (V), m.p. 56—58° [corresponding *sulphoxide*, m.p. 104—105° (slow) and 108—109° (rapid heating), and *sulphone*, m.p. 77—78°]; γ-phenylpropylthiolacetic acid, an oil [corresponding *sulphoxide*, m.p. 114—115° (decomp.)]; *carboxymethylthiolphenylacetic acid*, $CO_2H\cdot CH_2\cdot S\cdot CHPh\cdot CO_2H$, m.p. 133—135°. (V) is best prepared by addition of (I) to styrene either alone or in AcOH; addition occurs slowly in C_6H_6. β-*Phenylethylthetinacetic acid*,



$CO\langle{}^{CH_2}_{O}\rangle S(CH_2\cdot CH_2Ph)\cdot CH_2\cdot CO_2H$, m.p. 112—113° (decomp.), is prepared from (V) and $CH_2Br\cdot CO_2H$. H. B.

Mechanism of deamination of amino-alcohols. I. Amino-alcohols derived from phenyl α-amino-β-phenylethyl ketone. A. K. Mills. **II. Amino-alcohols derived from α-aminopropiophenone hydrochloride.** A. K. Mills and J. Grigor (J.C.S., 1934, 1565—1568, 1568—1570).—I. $COPh\cdot CH_2\cdot CH_2Ph$ [prepared in quant. yield by hydrogenation (Pt-black) of the chalkone in EtOH] in MeOH gives the oximino-derivative, reduced by $SnCl_2$ to *Ph α-amino-β-phenylethyl ketone hydrochloride* (I), m.p. 228—229° (decomp.), which with $CH_2Ph\cdot MgBr$ affords β-*amino-αβ-dibenzyl-α-phenylethyl alcohol*, m.p. 96—97° [*hydrochloride*, m.p. 251—252° (decomp.)]. This with $NaNO_2$ in cold 25% AcOH gives $CH_2Ph\cdot CHPh\cdot CO\cdot CH_2Ph$. β-*Amino-αγ-diphenyl-α-p-tolyl-*n*-propyl alcohol* [from (I) and p-$C_6H_4Me\cdot MgBr$], m.p. 134—135° [*hydrochloride*, m.p. 218—219° (decomp.)], gives on deamination $CH_2Ph\cdot CHPh\cdot CO\cdot C_6H_4Me$-*p*; β-*amino-αγ-diphenyl-α-(α-naphthyl)-*n*-propyl alcohol* (similarly prepared), m.p. 165—166° [*hydrochloride*, m.p. 229—230° (decomp.)], affords similarly α-*naphthyl αβ-diphenylethyl ketone*, m.p. 68—69°, also obtained from α-$C_{10}H_7\cdot CO\cdot CH_2Ph$, Na, and CH_2ClPh in EtOH. The migration of Ph in each of the above cases is contrary to the behaviour of *s*-pinacones on dehydration and indicates that org. groupings do not possess a definite "migrational aptitude."

II. α-Aminopropiophenone hydrochloride [by hydrogenation (Pd–C) of oximinopropiophenone, m.p. 113—114°, in Et_2O–HCl] and 1-$C_{10}H_7\cdot MgBr$ give β-*amino-α-phenyl-α-1-naphthyl-*n*-propyl alcohol*, m.p. 160° [*hydrochloride*, m.p. 253—254° (decomp.)], which with $NaNO_2$ in cold, dil. AcOH gives α-*naphthyl α-phenylethyl ketone*, m.p. 49·5—50·5° (*oxime*, m.p. 160·5—161·5°), also obtained from α-$C_{10}H_7\cdot CO\cdot CH_2Ph$, NaOEt, and MeI in EtOH. β-*Amino-α-phenyl-α-benzyl-*, m.p. 69·5° (*hydrochloride*, m.p. 235—236°), and -α-*methyl-*n*-propyl alcohol*, m.p. 82—83° (*hydrochloride*, m.p. 244°), similarly prepared, give with HNO_2 $CH_2Ph\cdot CO\cdot CHPhMe$, b.p. 175°/12—13 mm. (oxime, m.p. 83—84°), and $CHPhMe\cdot COMe$, b.p. 94—96°/12—13 mm. (semicarbazone, m.p. 172—173°). Migration of Ph is thus the normal reaction (cf. lit.). R. S. C.

Sterol group. XIX. Constitution of ergosterol. J. L. Dunn, I. M. Heilbron, R. F. Phipers, K. M. Samant, and F. S. Spring (J.C.S., 1934, 1576—1581; cf. A., 1933, 1290).—Reasons (see original for details) are adduced for believing that ergosterol has the OH at position 3 and the ethylenic linkings at 5 : 6 and 8 : 9. Methoxycholestene, m.p. 82—83°, best prepared by methylation of cholestanol, with CrO_3 in AcOH at 80° gives the acid, $C_{27}H_{46}O_4$, m.p. 195°. *Me ergostanylxanthate*, m.p. 109—110°, $[\alpha]_D^{21}$ —3·6° in $CHCl_3$, at 200—210°/vac. affords *ergostene*, $C_{28}H_{48}$, m.p. 86—87°, oxidised by CrO_3 to the acid, $C_{28}H_{48}O_4$, m.p. 218—219° (Me_2 ester, m.p. 82—83°). Cholestenediol diacetate (prep. from cholestanetriol diacetate), m.p. 124—125°, could not be dehydrated. Ergostadienetriol I (*A*) readily loses H_2O, best in Ac_2O at 100°, to give dehydroergosterol. Ergostanedionol is reduced (Clemmensen in AcOH) to *ergostene*, m.p. 78°, hydrogenation of which affords ergostane, m.p. 82°. (*A*) and CrO_3 give first ergostadienedionol, m.p. 249°, and then a *substance*, $C_{28}H_{40}O_4$, m.p. 204—205° (*monoxime*, m.p. 165—167°). Ergostadienedionol and KOH–MeOH give a little (?) *ergostatrienedione*, $C_{28}H_{40}O_2$, m.p. 145—146°. The product, $C_{29}H_{46}O_3$, from methoxyergostadienediol and $Pb(OAc)_4$ has m.p. 130—131° (lit. 105—106°). Structures are assigned to the OH-derivatives. R. S. C.

Chemistry of the algæ. I. Algal sterol, fucosterol. I. M. Heilbron, R. F. Phipers, and H. R. Wright (J.C.S., 1934, 1572—1576).—*Fucus vesiculosus* contains chlorophyll, carotenoids, n-$C_{31}H_{64}$, and two pectins, which yielded *fucosterol* (I) (0·2% of dry wt.), $C_{29}H_{48}O$, m.p. 124°, b.p. 220—230°/0·2 mm., $[\alpha]_D^{20}$ —38·42° in $CHCl_3$ {*acetate*, m.p. 118—119°, $[\alpha]_D^{20}$

—43·8° in $CHCl_3$ [*tetrabromide*, m.p. 133° (decomp.), unstable]; *propionate*, m.p. 105—106°; *benzoate*, m.p. 120°, monotropic; *digitonide*, m.p. 223—225°}, hydrogenated (PtO_2) in EtOAc–AcOH to fucostanol (=stigmastanol). (I) occurs, at least partly, free and contains two ethylenic linkings in the nucleus (Br and BzO_2H titrations; O_3 does not give $CHMe_2\cdot CHEt\cdot CHO$); it occurs also in *Pelvetia canaliculata* and, with sitosterol, in *Nitella opaca*, Agh, and is probably the characteristic algal sterol. Biological relations are indicated. R. S. C.

Calosterol.—See this vol., 1276.

Diazotisation of anæsthesine (ethyl *p*-aminobenzoate). M. A. Schwarz (Gazzetta, 1934, **64**, 518—521).—Diazotisation of *p*-$NH_2\cdot C_6H_4\cdot CO_2Et$ in dil. HCl at 2°, adding 1 mol. $NaNO_2$ all at once, yields *p*-$OH\cdot C_6H_4\cdot CO_2Et$ and *Et diazoaminobenzene*-4 : 4′-*dicarboxylate* (I) (yellow), m.p. 152—154°, converted by *p*-$NH_2\cdot C_6H_4\cdot CO_2Et$ and a little HCl into *Et aminoazobenzene*-3 : 4′-*dicarboxylate* (II) (red), m.p. 114°. In presence of NaOAc addition of $NaNO_2$ to a solution of *p*-$NH_2\cdot C_6H_4\cdot CO_2Et$ at 70° (then rapidly cooling) yields a mixture of (I) and (II). R. K. C.

Preparation of anæsthesine. E. A. Tzofin and A. G. Radushkevich (Khim. Farm. Prom., 1934, No. 1, 23—25).—*p*-$NO_2\cdot C_6H_4\cdot CO_2H$ is refluxed with EtOH and H_2SO_4, and the product neutralised and reduced by Fe filings and AcOH. Ch. Abs. (*e*)

Fission of disulphides by alkali. I. Behaviour of αα′-disulphidobisphenylacetic acid. A. Schöberl, E. Berninger, and F. Harren (Ber., 1934, **67**, [*B*], 1545—1550).—Treatment of $CHPhCl\cdot CO_2H$ or $CHPhBr\cdot CO_2H$ with hot aq. Na_2S_2 leads to $OH\cdot CHPh\cdot CO_2H$, whilst in cold solution αα′-*disulphidobisphenylacetic acid* (I) $(CO_2H\cdot CHPh)_2S_2$, m.p. 218°, and an *isomeride*, m.p. (indef.) 141°, are obtained; they are also prepared by oxidation of $SH\cdot CHPh\cdot CO_2H$ by I. (I) is readily decomposed by alkali to $SH\cdot CHPh\cdot CO_2H$, H_2S, and $COPh\cdot CO_2H$ [identified as the phenylhydrazone, m.p. 163° (decomp.), and 2 : 4-dinitrophenylhydrazone, m.p. 194°]. Reaction is therefore : $[CO_2H\cdot CHPh\cdot S\cdot]_2+H_2O \longrightarrow SH\cdot CHPh\cdot CO_2H+OH\cdot S\cdot CHPh\cdot CO_2H$. $COPh\cdot CO_2H$ is formed from (I) by the action of O_2 in alkaline solution, but is not an oxidation product, the gas being used mainly for the conversion of Na_2S_2 into $Na_2S_2O_3$; the simultaneous production of BzOH is unexplained. H. W.

Hydrolysis of phenylalanine.—See this vol., 1314.

Synthesis of γ-chloro-α-phenyl-α-alkylbutyronitriles. R. Hastings and J. B. Cloke (J. Amer. Chem. Soc., 1934, **56**, 2136—2138).—γ-*Chloro*-α-*phenyl*-α-*methyl*-, b.p. 109—111°/3—4 mm., -α-*ethyl*-, b.p. 115—116·5°/3—4 mm., -α-n-*propyl*-, b.p. 121—123°/3—4 mm., and -α-n-*butyl*-, b.p. 133—135°/3—4 mm., -*butyronitrile* are prepared by successive treatment of $CHPhAlk\cdot CN$ (from $CHNaPh\cdot CN$ and Me_2SO_4, Et_2SO_4, PrBr, and BuBr in Et_2O) with $NaNH_2$ and $(\cdot CH_2Cl)_2$ in C_6H_6; the yields are about 22%. H. B.

Perkin's cinnamic acid synthesis. F. Böck, G. Lock, and K. Schmidt (Monatsh., 1934, **64**, 399—414).—When the aldehyde (1 mol.), NaOAc (0·7 mol.), and Ac_2O (2·1 mols.) are heated at 150° until reaction commences and then for 7—8 hr. at 180—200°, the presence of Cl in the aldehyde mol. increases the yield of the cinnamic acid in all cases, particularly when Cl is at 2 or 2 and 6. Under these conditions or at lower temp. the presence of NO_2 favours the yield. The presence of Me has the opposite effect. The influence of time, temp., and ratio of reactants in the case of PhCHO, NaOAc, and Ac_2O is described. The following -cinnamic acids are described: *o*-chloro-, m.p. 211°; *m*-chloro-, m.p. 165°; *p*-chloro-, m.p. 247°; 2 : 5-*dichloro*-, m.p. 194·5° (corr.), whence β-2 : 5-*dichlorophenylpropionic acid*, m.p. 181° (corr.); 2 : 6-dichloro-, m.p. 196°; 2 : 3 : 6-*trichloro*-, m.p. 189°; *o*-nitro-, m.p. 242°; *m*-nitro-, m.p. 201°; *p*-nitro-, m.p. 288°; 2 : 4-dinitro-, m.p. 179° [improved prep. of 2 : 4-$(NO_2)_2C_6H_3\cdot CHO$]; *o*-methyl-, m.p. 169°; *m*-methyl-, m.p. 118°; *p*-methyl-, m.p. 199°; 2 : 4 : 6-*trimethyl*-, m.p. 176° (*Ba* salt; *Et* ester, m.p. 40°), in very small yield by Perkin's reaction, more conveniently obtained by hydrolysis of the crude ester from mesitylaldehyde, Na, and EtOAc, and converted by Br in CS_2 or AcOH into *bromotrimethylstyrene*, m.p. 53°. 2 : 4 : 6-$(NO_2)_3C_6H_2\cdot CH{:}CH\cdot CO_2H$ could not be obtained. H. W.

Course of the semi-hydrogenation of the acetylenic linking from the stereochemical viewpoint. E. Ott [with V. Barth and O. Glemser] (Ber., 1934, **67**, [*B*], 1669—1674; cf. A., 1927, 441).—Parallelism exists between the "activity" of a reducing catalyst and the reduction potential of metals. Reduction of $CPh{:}C\cdot CO_2H$ (I) by Zn, dil. aq. NH_3, and NH_4Cl gives 10% of *allo*- (II) and 90% of *trans*- (III) -cinnamic acid. Mn affords mainly (II) with 4% of (III), whereas the less noble metals Mg, Ba, and Na, in accordance with Le Chatelier's principle, do not yield (III), but 50% of unchanged (I) and 50% of $CH_2Ph\cdot CH_2\cdot CO_2H$. Metals nobler than Zn give (III) exclusively, as shown particularly by Cr powder and HCl–AcOH. Combination of Zn with nobler metals (Ag, Au, Cu) gives pairs occupying a place between Zn and Mn with respect to reduction potential. The phenomenon is probably analogous to overvoltage. Zn–Ag and Zn–Cu are the most active pairs, yielding 24% and 37%, respectively, of (II) from (I). The reduction potentials of the reducing catalysts Co, Ni, Pt, Pd, all lie in a very narrow region corresponding with a position intermediate between Zn and Mn in the electrochemical series. The reduction potentials of $Cr(OH)_2$ (IV) and $Ti(OH)_3$ (V) suspended in NH_3–NH_4Cl–H_2O are of the same order of magnitude, (IV) yielding a mixture of (II) and (III) from (I), whereas (V) gives solely (II). H. W.

Synthesis of isomeric phenylbutadienecarboxylic acids. H. Lohaus (Annalen, 1934, **513**, 219—229).—*cis*-α-Bromocinnamaldehyde (I) (von Auwers *et al.*, A., 1931, 222; 1932, 271), $CN\cdot CH_2\cdot CO_2Me$, and piperidine or MeOH–NaOMe give *Me* (Δ^{γ}-cis-) γ-*bromocinnamylidenecyanoacetate* (II), m.p. 133°, also obtained [together with (III)] from *Me* γδ-*dibromo*-α-*cyano*-δ-*phenyl*-Δ^{α}-*butene*-α-*carboxylate*, m.p. 98° [from $CHPh{:}CH\cdot CH{:}C(CN)\cdot CO_2Me$ (III) and Br in $CHCl_3$], by spontaneous decomp. in Et_2O or by the action of Et_2O–$NHEt_2$. (I) does not similarly condense with

$CN\cdot CH_2\cdot CO_2Et$; *Et γ-bromocinnamylideneacetate*, m.p. 75°, is obtained from $CHBrPh\cdot CHBr\cdot CH{:}C(CN)\cdot CO_2Et$ and Et_2O–$NHEt_2$. Reduction (Zn dust, 90% MeOH) of (II) gives the non-cryst. impure *Me* (Δ^{γ}-cis-)*cinnamylidenecyanoacetate*, decomp. about 80° (not sharp). Supplementary details are given (cf. von Auwers and Müller, A., 1924, i, 44) for the prep. of γ-bromo-β-hydroxy-γ-benzylidenebutyric and γ-bromocinnamylideneacetic acid (IV), m.p. 142°. (IV) is considered to have the Δ^{α}-*trans*-Δ^{γ}-*cis* configuration. Reduction (Zn dust, 80—90% EtOH) of (IV) (as Na salt) affords some Δ^{α}-trans-Δ^{γ}-cis-*cinnamylideneacetic acid* (V) (*iso-cinnamylideneacetic acid*), m.p. 128°, and (mainly) the *trans-trans*-acid (VI), m.p. 165°. Reduction (Zn dust, 90% MeOH) of the Me ester of (IV) gives (mainly) the Me ester, solidifies at —13°, of (V); hydrolysis (MeOH–KOH) of this gives (VI) and a little (V). H. B.

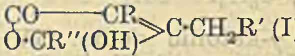
Preparation of chaulmoogra derivatives. I. Substituted amines and amides. J. H. Payne, R. Wrenshall, and K. van H. Duker (J. Amer. Chem. Soc., 1934, 56, 2126—2128).—β-Iodoethyl chaulmoograte [from chaulmoogryl chloride (I) and $CH_2I\cdot CH_2\cdot OH$ (II) at 0°] and NMe_3 in C_6H_6 at 100° (sealed tube) give *chaulmoogrylcholine iodide*, decomp. about 150°, which with AgCl in MeOH affords the *chloride*, softens and decomp. about 65°. *Di-iododihydrochaulmoogrylcholine iodide*, decomp. about 210°, and *chloride*, melts partly at 54°, decomp. > 185°, are similarly prepared from β-iodoethyl di-iododihydrochaulmoograte [from (I), (II), and I]. *Chaulmoogr*-p-*phenetidide*, m.p. 115°, and -p-*carbethoxyanilide*, m.p. 94—95°, and *dihydrochaulmoogr-anilide*, m.p. 94°, -p-*phenetidide*, m.p. 117°, and -p-*carbethoxyanilide*, m.p. 120—121°, are described. H. B.

Mechanism of the formation of choleic acids. E. Chargaff and G. Abel (Biochem. J., 1934, 28, 1901—1906).—Choleic acids (I) formed from deoxycholic acid and fatty acids with branched chains are much more labile than those formed from normal fatty acids. (I) from fatty acids substituted in the β-position are more stable than from α-substituted acids. If the quotient mol. wt. of longer chain/mol. wt. of shorter chain is > 6·3, the corresponding (I) has a normal co-ordination no. Smaller quotients correspond with lower co-ordination no. Many halogenated fatty acids do not form (I). The following compounds appear to be new: *methylnonylmalonic acid*, m.p. 94—95° (*Et* ester, b.p. 147—148°/5 mm.), loses CO_2 to yield *α-methylundecoic acid*, b.p. 125—127°/6 mm. The following are described: *α-butyl*-n-*hexoic acid-tetracholeic acid*, m.p. 147—148°; *β-methyl*-n-*nonoic acid-hexacholeic acid*, m.p. 170·5°; *α-ethyl*-n-*decoic acid-tetracholeic acid*, m.p. 176°; *α-methyl*-n-*undecoic acid-tetracholeic acid*, m.p. 179°; *α-ethyl*-n-*hexadecoic acid-octacholeic acid*, m.p. 178—179°.
A. E. O.

Organic reactions with boron fluoride. VII. Rearrangement of *iso*propyl salicylate and condensation of propylene with salicylic acid. W. J. Croxall, F. J. Sowa, and J. A. Nieuwland (J. Amer. Chem. Soc., 1934, 56, 2054—2056).—Slow passage of C_3H_6 (1·25 mols.) into o-$OH\cdot C_6H_4\cdot CO_2H$ and BF_3 in heptane and fractionation of the resulting esters gives o-$OH\cdot C_6H_4\cdot CO_2Pr^{\beta}$ (I), b.p. 120—122°/18 mm., Pr^{β} 3-*iso*propylsalicylate, b.p. 147—149°/18 mm. [the free acid, m.p. 72°, heated to 200° affords o-$C_6H_4Pr^{\beta}\cdot OH$ (II)], and Pr^{β} 3 : 5-di*iso*propylsalicylate (III), b.p. 163—165°/18 mm. (free acid, m.p. 115·2°, decarboxylated to 2 : 4-$C_6H_3Pr^{\beta}_2\cdot OH$); the following reactions occur: o-$OH\cdot C_6H_4\cdot CO_2H + C_3H_6 \longrightarrow$
o-$OH\cdot C_6H_4\cdot CO_2Pr^{\beta} \longrightarrow OH\cdot C_6H_3Pr^{\beta}\cdot CO_2H \xrightarrow{C_3H_6}$
$OH\cdot C_6H_3Pr^{\beta}\cdot CO_2Pr^{\beta} \longrightarrow OH\cdot C_6H_2Pr^{\beta}_2\cdot CO_2H \longrightarrow$ $OH\cdot C_6H_2Pr^{\beta}_2\cdot CO_2Pr^{\beta}$. (III) is obtained in almost quant. yield when the reaction is allowed to go to completion. (I) heated with BF_3 gives 3-*iso*propylsalicylic acid (not isolated) and a little of the 5-derivative; thermal decomp. of the mixture of acids affords (II) (and a little p-$C_6H_4Pr^{\beta}\cdot OH$) H. B.

Reactions of γ-ketonic acids. IV. Ketonic esters. E. P. Kohler and W. D. Peterson (J. Amer. Chem. Soc., 1934, 56, 2192—2197).—Bromination of β-*p*-chlorobenzoyl-α-phenylpropionic [γ-keto-α-phenyl-γ-*p*-chlorophenylbutyric] acid gives a mixture [separable as previously described (this vol., 1217) for the Cl-free analogue] of β-*Br*-derivatives, m.p. 183° (I) and 216° (II) (cf. A., 1926, 1140), esterified (MeOH–H_2SO_4 or Et_2O–CH_2N_2) to *Me* esters, m.p. 145° and 133°, respectively. These are converted by MeOH–NaOAc or –C_5H_5N into mixtures (proportions varying with conditions) of cis- (III), m.p. 93°, and trans- (IV), m.p. 109°, -*Me* β-p-*chlorobenzoyl-α-phenylacrylates*. (III) and (IV) are reduced (catalytically) at the same rate, give the same *dibromide*, m.p. 136° [converted by aq. KI into (III)], and with MeOH–NH_2OH,AcOH afford 6-keto-5-phenyl-3-*p*-chlorophenyl-1 : 2-oxazine (V) (*loc. cit.*). (III) and NH_2OH,HCl in C_5H_5N also give (V); (IV) similarly affords *Me γ-oximino-α-phenyl-γ-*p*-chlorophenylcrotonate*, m.p. 130° (VI) (main product) and 105°, which are probably *syn* and *anti* forms [both are hydrolysed to the same *acid*, m.p. about 220° (decomp.), which with MeOH–H_2SO_4 gives (VI)]. Addition of MgMeI to (III) in cold Et_2O–C_6H_6, and decomp. of the Mg complex with cold acid in Et_2O gives *Me γ-hydroxy-α-phenyl-γ-*p*-chlorophenyl-*Δ^{α}*-pentenoate*, m.p. 107° [oxidised ($KMnO_4$, $COMe_2$) to $BzCO_2Me$ (VII) and p-$C_6H_4Cl\cdot COMe$ (VIII)], and *α-phenyl-γ-*p*-chlorophenyl-γ-methylcrotonolactone* (IX), m.p. 94° [oxidised ($KMnO_4$, $COMe_2$] to *αβ-dihydroxy-α-phenyl-γ-*p*-chlorophenyl-γ-valerolactone*, m.p. 182°, and thence to (VII) and (VIII)]. Reduction of (IX) affords *α-phenyl-γ-*p*-chlorophenyl-γ-valerolactone*, m.p. 105°, also prepared (together with an *isomeride*, m.p. 120°) from Me β-*p*-chlorobenzoyl-α-phenylpropionate and MgMeI with subsequent hydrolysis (MeOH–NaOH). MgMeI and (IV) give *Me* trans-*γ-hydroxy-α-phenyl-γ-*p*-chlorophenyl-*Δ^{α}*-pentenoate*, m.p. 105° [free *acid* (X), m.p. 134°], also oxidised to (VII) and (VIII). (III) and (IV) are both hydrolysed (MeOH–NaOH or AcOH–HCl) to cis-γ-p-*chlorobenzoyl-α-phenylacrylic acid* (XI), two forms, m.p. 132° and 102° (re-solidifying with m.p. 132°), which with MgMeI affords (IX). trans-γ-p-*Chlorobenzoyl-α-phenylacrylic acid* (XII), m.p. 135° [which with MgMeI gives (X)], is obtained together with (XIII) (below) from β-*p*-chlorobenzoyl-α-phenyl-β-propiolactone [from (II)] and NaOAc in AcOH–Ac_2O; (XII) is also formed similarly in small yield from the isomeric lactone from (I). (XI) and AcOH–Ac_2O give *γ-acetoxy-α-phenyl-γ-*p*-chlorophenylcrotonolactone* (XIII), m.p. 110°, also formed (at a much slower rate) from (XII). (XI) and MeOH–H_2SO_4 afford (III) (about 40%) and *γ-methoxy-α-phenyl-γ-*p*-chlorophenylcrotonolactone*, m.p. 73° (about 60%) [also obtained from (XIII) and MeOH]. The changes occurring in the production of mixtures of (III) and (IV) from (I) and (II) are discussed.

H. B.

Reactions of γ-ketonic acids. C. F. H. Allen, J. B. Normington, and C. V. Wilson (Canad. J. Res., 1934, **11**, 382—394).—Reaction with RMgX has been employed to differentiate between the open-chain (1 mol. addition for each atom of active H) and lactol  $\left.\begin{array}{l}\mathrm{CO}\text{———}\mathrm{CR}\\ \mathrm{O\cdot CR''(OH)}\end{array}\right>\mathrm{C\cdot CH_2R'}$ (I) (2 mols. addition for each atom of active H) structures of various substituted γ-keto-αγ-diaryl-β-arylmethyl-Δ^{α}-butenoic acids, prepared by methods previously described (A., 1932, 1031; 1933, 610). The following *acids*, $R''\cdot CO\cdot C(CH_2R')\colon CR\cdot CO_2H$, or *lactols* [as (I)] are new: R=R′=*Ph* and R″=*mesityl*, m.p. 250° (decomp.), p-C_6H_4Cl, m.p. 144° (*acid chloride*, m.p. 150°; reduced by Zn–80% AcOH to *γ-keto-α-phenyl-γ-*p*-chlorophenyl-*β*-benzylbutyric acid*, m.p. 173—174°), p-*tolyl*, m.p. 133°, and p-$C_6H_4\cdot CO_2H$, m.p. 240° (*Me* ester, m.p. 137°); R=*Ph*, R′=o-C_6H_4Cl, and R″=p-C_6H_4Cl, m.p. 147°; R=*piperonyl*, R′=*Ph*, R″=p-C_6H_4Cl, m.p. 153°, and *Ph*, m.p. 138°; R=*anisyl*, R″=*Ph*, R′=o-$C_6H_4\cdot OMe$, m.p. 126°, o-C_6H_4Cl, m.p. 154°, and α-*furyl*, m.p. 121°. It is concluded that the differences are due to *cis–trans* isomerism, the *cis*-acid giving rise to esters of both open-chain and cyclic forms, the latter being impossible with the *trans*-acid. Confirmatory evidence of structure accrues from the action of AcCl, which gives chlorides with the lactols but fails to react with the open-chain acids. The same tests are applied to a series of *γ-keto-αγ-diarylbutyric acids*, $R'\cdot CO\cdot CH_2\cdot CHR\cdot CO_2H$, some of which give evidence of cyclic forms, and of which the following are new: R=*Ph*, R′=p-C_6H_4F, m.p. 161° (*nitrile*, m.p. 102°; *Me* ester, m.p. 101°), p-C_6H_4Br, m.p. 160°, p-*tolyl*, m.p. 152° (*nitrile*, m.p. 80°; *Me* ester, m.p. 112°), *mesityl*, m.p. 172° (*nitrile*, m.p. 77—78°; *Me* ester, m.p. 60—61°); R=*piperonyl*, R′=p-C_6H_4Cl, m.p. 190° (*nitrile*, m.p. 129°; *Me* ester, m.p. 109°); the *Me* esters when R=*Ph*, R′=p-C_6H_4Ph, m.p. 157° (*nitrile*, m.p. 176°), p-$C_6H_4\cdot NO_2$, m.p. 104° (*nitrile*, m.p. 155°), p-$C_6H_4\cdot CO_2Me$, m.p. 110° (*nitrile* of R′=*p*-$C_6H_4\cdot CO_2H$, m.p. 239°), and 4-*chloro*-m-*tolyl*, m.p. 80° (*nitrile*, m.p. 76—77°); and when R=*piperonyl*, R′=*Ph*, m.p. 121°. With AcCl *dimerides* of γ-keto-α-phenyl-γ-*p*-chlorophenyl-, m.p. 235°, -γ-phenyl-, m.p. 295°, -γ-*p*-fluorophenyl-, m.p. 247°, and γ-p-*tolyl*-, m.p. 270° (all decomp.), -butyric acid, are obtained. No evidence of cyclic forms of *γ-keto-γ-*p*-chlorophenyl-* (II), m.p. 131° (*Me* ester, m.p. 63°), and *-γ-mesityl-*+0·5H_2O (III), m.p. 107°, *-butyric acid*, and of other derivatives of the type $R\cdot CO\cdot CH_2\cdot CH_2\cdot CO_2H$, was obtained, and with AcCl all [except (III), which affords the *enol acetate*, m.p. 288—290°] give unsaturated lactones, (II) affording *γ-*p*-chlorophenylcrotonolactone*. With AcCl *cyclo*hexanone gives *cyclo*hexenyl acetate. Mechanisms are discussed and it is considered probable that lactone formation in ketonic acids occurs by dehydration of an enolic form, and hence the formation of angelica lactones from lævulic acid (IV) is not evidence for a cyclic structure, (IV) being almost certainly open-chain. The following new compounds are also prepared: 4-*chloro*-m-*tolyl*, b.p. 195—200°/6 mm. (*dibromide*, m.p. 117°), 4-iso*propyl*-o-*tolyl*, b.p. 205—210°/12 mm. (*dibromide*, m.p. 140—141°), *mesityl* (*dibromide*, m.p. 131°) and *p*-fluorophenyl, m.p. 76—77°, *styryl ketone*, and *piperonylidene*-p-*chloroacetophenone*, m.p. 128°; p-*chlorobenzoyl*-3 : 4-*methylenedioxybenzoylmethane*, m.p. 151° [*Cu* derivative, m.p. 290—292° (decomp.)], *benzoylmesitoylmethane*, m.p. 84° [*Cu* derivative, m.p. 185° (decomp.)], *α-bromobenzylidene*-2 : 4 : 6-*trimethylacetophenone*, m.p. 73°, 3-p-*chlorobenzoyl*-5-*piperonyl*isoo*xazole*, m.p. 180°, and 5-*phenyl*-3-*mesityl*isoo*xazole*, m.p. 76°. All m.p. are corr.

J. W. B.

Phenolic acids. V. Reaction of 3 : 5-dinitro-β-resorcylic acid with sugars. P. P. T. Sah and K. C. Meng (Sci. Rep. Nat. Tsing Hua Univ., 1934, **2**, 343—346).—3 : 5-Dinitro-β-resorcylic acid gives a red coloration with *d*-glucose, maltose, and lactose in alkaline solution. There is no quant. relationship between the depth of colour and the concn. of the sugar.

H. N. R.

Hexahydroterephthalic acids. R. Malachowski and J. Jankiewiczówna (Ber., 1934, **67**, [*B*], 1783—1788).—*p*-$C_6H_4(CO_2H)_2$ is reduced by Na–Hg to the H_4-stage, esterified, and the ester is hydrogenated (PtO_2) and then hydrolysed with 10% HCl. The mixture of acids [*cis*- (I) : *trans*- (II) -hexahydroterephthalic acid=5 : 1] is purified through the Ca salts giving (I), m.p. 170—171° [*Me* ester, m.p. 14°, *Ca* (+2·5H_2O) salt, less sol. in hot than in cold H_2O], and (II), m.p. 312—313° [*Ca* salt (+2·5H_2O)]. The acid, m.p. 166—167°, contains 94% of (I) and 6% of (II) and cannot be separated into its components by crystallisation from H_2O; it differs in cryst. form from homogeneous (I). Treatment of (I) with Ac_2O at 100° affords the *polymeric* cis-*anhydride* (III) (?) $OAc\cdot[C_8H_{10}O_3]_9\cdot Ac$, m.p. (indef.) 105—110°, transformed at 230° into the *polymeric* trans-*anhydride* (IV), m.p. (indef.) 262—270°. Distillation of (III) or (IV) under diminished pressure and with very rapid cooling of the vapour gives Ac_2O and the *monomeric anhydride*, m.p. 150—160°, which is very unstable and polymerises when melted or warmed in C_6H_6 in presence of a trace of NaOH. Hydrolysis by H_2O or 10% HCl leads to (I).

H. W.

Preparation of phthalimido-compounds. R. Weisz and K. Lányi (Magyar chem. Fol., 1933, **39**, 153—155; Chem. Zentr., 1934, i, 2746).—Phthalimido-compounds are prepared by boiling phthalimide with EtONa in EtOH for 2 hr., and then adding the appropriate halogen derivative. Alkyl halides have no action. Aryl α-bromoalkyl ketones, $CH_2Cl\cdot CO_2Et$, and $CHMeBr\cdot CO_2Et$ react smoothly, but α-bromo-fatty esters containing side-chains are ineffective. Ca and Mg phthalimides give poorer yields than Na. *Benzylphthalimide*, m.p. 116°, *Ph α-phthalimidoethyl ketone*, m.p. 87—88°, *Et phthalimidoacetate*, m.p. 112—113°, and *Et α-phthalimidopropionate*, m.p. 61—63°, are described. R. N. C.

Stereochemistry of diphenyls. XXXVII. Resolution of substituted diphenylbenzenes. A. E. Knauf, P. R. Shildneck, and R. Adams. **XXXVIII. Resolution of 2 : 2′-dibromodiphenyl-4 : 4′-dicarboxylic acid.** N. E. Searle and R. Adams (J. Amer. Chem. Soc., 1934, **56**, 2109—2111, 2112—2114).—XXXVII. *cis*-3 : 6-Dibromo-2 : 5-di-(3-bromo-2 : 4 : 6-trimethylphenyl)quinol (A., 1931, 348, 1049) and *l*-menthoxyacetyl chloride in C_6H_6–C_5H_5N give a mixture (separable by fractional crystallisation from $COMe_2$) of the *dimenthoxyacetates*, m.p. 141—143° and 155°, of d- (I), m.p. 289—290°, $[\alpha]_D^{16}$ +13·4° in EtOAc, and l- (II), m.p. 290—291°, $[\alpha]_D^{25}$ −16·2° in EtOAc, -3 : 6-*dibromo*-2 : 5-*di*-(3-*bromo*-2 : 4 : 6-*trimethylphenyl*)*quinol*, respectively. (I) and (II) are obtained from the esters by hydrolysis (aq. EtOH–NaOH in H_2), subsequent treatment with $SnCl_2$–HCl in aq. $COMe_2$, and final crystallisation (C_6H_6). (I) and (II) are oxidised (*p*-benzoquinone in EtOH) to l-, m.p. 283—284°, $[\alpha]_D^{16}$ −26·5° in $CHCl_3$, and d-, m.p. 284—285°, $[\alpha]_D^{28}$ +36·74° in $CHCl_3$, -3 : 6-*dibromo*-2 : 5-*di*-(3-*bromo*-2 : 4 : 6-*trimethylphenyl*)-p-*benzoquinone*, respectively, which are reduced ($SnCl_2$, C_5H_5N) to (I) and (II), respectively. The *dimenthoxyacetate* of *trans*-3 : 6-dibromo-2 : 5-di-(3-bromo-2 : 4 : 6-trimethylphenyl)quinol exists in 2 cryst. modifications, m.p. 167—168° (from light petroleum) and 145—146°, re-solidifying with m.p. 167—168° (both forms are obtained from $COMe_2$ or EtOH); hydrolysis of either form gives an inactive product. *cis*- and *trans*-2 : 5-Dibromo-3 : 6-di-*m*-4-xylylquinol (A., 1930, 1588) (*dimenthoxyacetates*, m.p. 120—124° and 154°, respectively) could not be resolved.

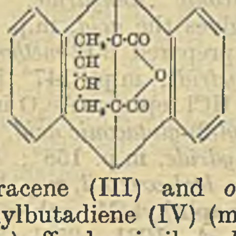
XXXVIII. Tetrazotised Et 2 : 2′-diaminodiphenyl-4 : 4′-dicarboxylate and $Hg(NO_3)_2$ in aq. HBr give the tetrazonium di(mercuribromide) (III). Hydrolysis (aq. EtOH–KOH) of the product obtained by thermal decomp. [method essentially that of Schwechten (A., 1932, 1244)] of dry (III) in presence of dry KBr affords 2 : 2′-*dibromodiphenyl*-4 : 4′-*dicarboxylic acid*, m.p. 310—312°, which is resolved by brucine into d- (IV), m.p. 311—313°, $[\alpha]_D^0$ (in 7 : 3-dioxan–MeOH) +17·4° (max. by extrapolation) ⟶ 0° [*brucine* salt, m.p. 210—220°, $[\alpha]_D^0$ (in $CHCl_3$) +27·2° (max.) ⟶ +1·9°], and l-*forms* (V), m.p. 311—313°, $[\alpha]_D^0$ (in dioxan–MeOH) −17·8° (max.) ⟶ 0° [*dibrucine* salt, m.p. 197—207°, $[\alpha]_D^0$ (in $CHCl_3$) −15·7° (max.) ⟶ 0°]. (IV) and (V), obtained by decomp. of the salts with EtOH–conc. HCl at −65°, racemise more readily than the corresponding I_2-acids (A., 1933, 608). 2 : 2′-Dibromo-4 : 4′-diaminodiphenyl (*di*-d-*bromocamphorsulphonate*, m.p. 297—300°, and d-*camphorsulphonate*, m.p. 218—219°, which do not exhibit mutarotation at 0° or 25°), prepared from $(m\text{-}C_6H_4Br\cdot NH\cdot)_2$ (in Et_2O) and conc. HCl, could not be resolved. H. B.

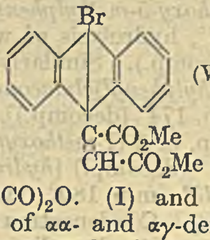
Solubility relationships amongst optically isomeric salts. IV. Salts of 6 : 6′-dinitrodiphenic acid, a new type of resolving agent. A. W. Ingersoll and J. R. Little (J. Amer. Chem. Soc., 1934, **56**, 2123—2126).—*dl*-6 : 6′-Dinitrodiphenic acid (I) (improved prep.; cf. Kenner and Stubbings, J.C.S., 1921, **119**, 593) [*d*-, m.p. 199° (corr.), and *dl*-, m.p. 206—208° (corr.), -α-phenylethylamine and *d*-α-*p*-tolylethylamine, m.p. 211·5—213° (corr.), salts] is resolved by *d*-α-phenylethylamine into the *d*-acid (II), m.p. 231—231·5° (corr.), $[\alpha]_D^{25}$ +127° in MeOH [dl-, m.p. 207—208°, and d- (+$COMe_2$), m.p. ($COMe_2$-free) 217—219° (corr.), -*α-phenylethylamine*, *dl*-α-*p*-tolylethylamine, m.p. 197·5—198° (corr.), and *dl*-α-anisylethylamine salts], and impure *l*-acid (III), m.p. 228—229°, $[\alpha]_D^{25}$ −111° in MeOH [*d*-α-phenylethylamine salt, m.p. 204—205° (corr.)]. (III), purified through the *l*-phenylethylamine salt, is obtained with $[\alpha]_D^{27}$ −126° in MeOH. (I) could not be resolved by *d*-α-*p*-tolylethylamine. *dl*-α-Phenylethylamine (but not the *p*-tolyl- or anisyl-ethylamines) is resolved by (II); *dl*-α-fenchylamine is similarly partly resolved. Solubility data (cf. A., 1932, 263) for the above salts are given. H. B.

Formation of cyclic compounds from diphenyl derivatives. III. Optical resolution of 6-nitro-6′-acetamidodiphenic acid and formation of 5-nitrophenanthridone-4-carboxylic acid therefrom. S. Sako (Bull. Chem. Soc. Japan, 1934, 9, 393—402; cf. this vol., 520).—6 : 6′-Dinitro-2 : 2′-dimethyldiphenyl is reduced by Na_2S in EtOH at 50° to 6-nitro-6′-amino-2 : 2′-dimethyldiphenyl (I), m.p. 124—125° (lit. 122—123°), distils in vac., or by an excess of Na_2S at 100° mainly to 4 : 5-*dimethylphenazone oxide*, m.p. 153°. The *Ac* derivative, m.p. +0·5C_6H_6, 92°, and anhyd., 103—104°, of (I) is oxidised (aq. $KMnO_4$; $MgSO_4$; 100°) to dl-6-*nitro*-6′-*acetamidodiphenic acid*, decomp. 229° (sinters at 130°), giving *strychnine H* salts, of the *l*-, m.p. 273° (decomp.), $[\alpha]_D^{20}$ −73° in MeOH, and *d*-, m.p. +MeOH, 175° (decomp. 273°), and, anhyd., decomp. 273°, $[\alpha]_D^{20}$ +36·5° in MeOH, -acids, and the *distrychnine* salt, +2MeOH, m.p. 174°, decomp. 207°, $[\alpha]_D^{20}$ +11·9° in MeOH, of the *d*-acid, whence were obtained the d- and l-*acids*, $[\alpha]_D$ ±122·1° in H_2O, m.p. (impure) 93° (decomp.). The NH_4 salt of the *d*-acid is stable to hot H_2O, but the acid is racemised by cold, conc. HCl. The active acid with hot H_2SO_4 slowly gives inactive 5-*nitrophenanthridone*-4-*carboxylic acid* (II), m.p. > 330°. This is not rigid proof of the planar configuration of (II), which is, however, probable on other grounds. R. S. C.

Syntheses in the hydroaromatic series. XXII. Anthracene–C_4O_3 [acetylenedicarboxylic anhydride] adduct, its use in diene syntheses, and synthesis of phthalic and dihydrophthalic acids. O. Diels and W. Friedrichsen (Annalen, 1934, **513**, 145—155).—Anthracene–acetylenedicarboxylic anhydride (I) (A., 1931, 848) and butadiene in C_6H_6 at 100° (sealed tube) give a 1 : 1-*adduct* (II), m.p. 212°, which undergoes thermal decomp. to 9 : 10-dihydroanthracene (III) and $o\text{-}C_6H_4(CO)_2O$. (I) and dimethylbutadiene (IV) (mixture of αα- and αγ-derivatives) afford a similar *adduct*, m.p. 197°, which when heated under atm. pressure decomposes to anthracene

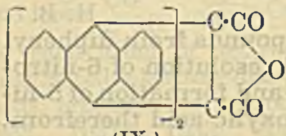
(II.)





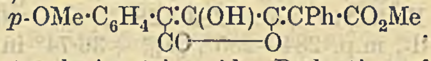
(VII.)

(V), (III), and (after hydrolysis) a *dimethylphthalic acid*, m.p. 194° (*anhydride*, m.p. 124°); thermal decomp. in a vac. gives (V) and a *dimethyldihydrophthalic acid*, m.p. 145° (*anhydride*, m.p. 99°). An isomeric *dimethyldihydrophthalic acid*, m.p. 184° (*anhydride*, m.p. 100°), is prepared by hydrolysis (EtOH–KOH) of the product from equimol. amounts of (IV) and Me acetylenedicarboxylate (VI). *Adducts*, $C_{25}H_{22}O_3$, m.p. 199—200°, and $C_{23}H_{16}O_3$, m.p. 279—280°, are prepared from (I) and ααγ-trimethylbutadiene and *cyclo*pentadiene, respectively. 9-Bromoanthracene and (VI) give the *Me₂* ester (VII), m.p. 178° {free acid, m.p. 215° [anhydride, m.p. 240°, which forms an *adduct*, $C_{21}H_{19}O_3Br$, m.p. 192°, with (IV)]}. 9 : 10-Dibromoanthracene (VIII) does not react with (VI), but with maleic anhydride gives the 9 : 10-endo-*maleic anhydride*-9 : 10-*dibromoanthracene*, m.p. 263° [converted by short heating with quinoline into (VIII)]. (I) heated in $PhNO_2$ or PhOH gives CO, CO_2, and the *compound* (IX), m.p. 360°, which is stable towards KOH, conc. HNO_3, Ac_2O, NH_2Ph, and quinoline. H. B.


(IX.)

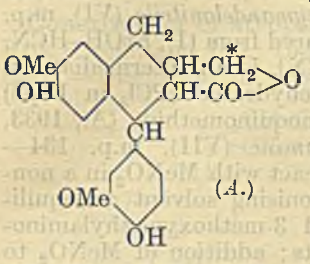
***b*-Dinitro-α-truxillic acid and the di- and tetranitro-γ-truxillic acids.** F. Schenck (Ber., 1934, **67**, [*B*], 1690—1695).—Treatment of γ-truxillic anhydride (I) with Ac_2O and HNO_3 (*d* 1·4) at 100° affords pp′-*dinitro-γ-truxillic acid* (II), decomp. 308—310° (*Me₂*, m.p. 196·5—197°, and *Et₂*, m.p. 147—147·5°, esters; *Me H* ester, m.p. 214—215°), oxidised to $p\text{-}NO_2\cdot C_6H_4\cdot CO_2H$ in 53% yield, *α-dinitro-γ-truxillic acid*, decomp. 265° (corresponding *anhydride*, decomp. 253°), transformed by NaOH–MeOH into *Me H α-dinitro-γ-truxillate*, m.p. 179—180°, and thence by MeOH–H_2SO_4 into *Me₂ α-dinitro-γ-truxillate*, m.p. 111—112° (from MeOH–H_2O) or m.p. 136—137° (after desiccation over P_2O_5), and b-*dinitro-γ-truxillic acid*, decomp. 265° (*Me₂* ester, m.p. about 102—104°). (III) is not identical with *b*-dinitro-α-truxillic acid, which is isomerised by boiling Ac_2O to pp′-*dinitro-γ-truxillic anhydride*, m.p. about 232°. Nitration of (I) with fuming HNO_3 and conc. H_2SO_4 under defined conditions leads to 2 : 4 : 2′ : 4′-*tetranitro-γ-truxillic acid*, decomp. 238° (*Ba* salt), which is oxidised to 2 : 4-$C_6H_3(NO_2)_2\cdot CO_2H$; the *anhydride*, *Me₂*, m.p. 188—189°, *Et₂*, m.p. 180—181°, and *Et H*, m.p. 207—208°, esters are described. H. W.

β-Arylglutaconic acids. I. Synthesis. G. R. Gogte (Proc. Indian Acad. Sci., 1934, **1**, (A), 48—59).—6-Methylcoumarin-4-acetic acid refluxed with 20% aq. NaOH and subsequently treated with Me_2SO_4 at 80—90° and boiling Ac_2O yields β-(2-*methoxy-5-methylphenyl*)*glutaconic anhydride*, m.p. 117°, hydrolysis of which gives the *acid*, m.p. 169° (decomp.). Similarly was prepared β-(2-*methoxy-4-methylphenyl*)*glutaconic anhydride*, m.p. 147° [*acid*, m.p. 174° (decomp.)]. Dil. HCl replaces Ac_2O in the prep. of β-(1-*methoxynaphthyl*-2)-*glutaconic acid*, m.p. 161° (decomp.) [*hydroxyanhydride*, m.p. 158°; *semianilide*, m.p. 180° (decomp.); *hydroxyanil*, m.p. 199—200°]. Condensation of α-naphthyl Me ether with acetonedicarboxylic acid (cf. A., 1931, 1055) affords β-(1-*methoxynaphthyl*-4)-*glutaconic acid*, decomp. 199° [*hydroxyanhydride*, m.p. 156°; *semianilide*, m.p. 176—177° (decomp.); *hydroxyanil*, m.p. 223—224°]. β-Naphthacoumarin-4-acetic acid on treatment with aq. NaOH, Me_2SO_4, etc. yields two β-(2-*methoxynaphthyl*-3)-*glutaconic acids*, (*a*), m.p. 186° (decomp.) and (*b*), m.p. 162° (decomp.). Both give the same *hydroxyanil*, m.p. 196—197°, and, on heating, *hydroxyanhydride* (I), m.p. 135° (from which the *semianilide*, m.p. 172°, is obtained), and an *isomeride* of the latter, m.p. 172°; (*b*) with Ac_2O readily yields (I) [which on hydration readily reverts to (*b*)], whilst (*a*) is unchanged. Hence (*a*) is the *trans* and (*b*) the *cis* form of the acid. F. O. H.

Constitution of pinastric acid. M. Asano and Y. Kameda (Ber., 1934, **67**, [*B*], 1522—1526; cf. Koller *et al.*, A., 1933, 508).—$p\text{-}OMe\cdot C_6H_4\cdot CH_2\cdot CN$, $Et_2C_2O_4$, and NaOEt afford *Et cyano*-p-*anisylpyruvate*, m.p. 93—95°, converted by $CH_2Ph\cdot CN$ and NaOEt into *p*-methoxydiphenylketipinonitrile, which is hydrolysed to *p*-methoxypulvinic anhydride (I). Treatment of (I) with KOH–MeOH leads to the compound (II)  $p\text{-}OMe\cdot C_6H_4\cdot\underset{CO\text{———}}{C}{:}C(OH)\cdot\underset{O}{C}{:}CPh\cdot CO_2Me$, identical with natural pinastric acid. Reduction of (II) with Zn and AcOH gives Me γ-keto-α-phenyl-δ-*p*-anisyl-*n*-valerate (semicarbazone, m.p. 142—144°). $CH_2Ph\cdot CO_2Na$, $p\text{-}OMe\cdot C_6H_4\cdot CH{:}CH\cdot CHO$, and Ac_2O at 150—155° give α-*phenyl*-δ-p-*anisyl*-$\Delta^{\alpha\gamma}$-*pentadienoic acid* (III), m.p. 192—193° (*Na* and *K* salts), and α-*phenyl*-Δ-p-*anisyl*-$\Delta^{\alpha\gamma}$-*butadiene*, m.p. 158—159°. (III) is transformed by reduction in boiling AcOH–EtOH with Na–Hg followed by bromination and treatment of the product with NaOAc at 100° into α-*phenyl*-γ-p-*methoxybenzylcrotonolactone*, m.p. 115·5—116·5°, converted by KOH–MeOH into γ-keto-α-phenyl-δ-*p*-anisylvaleric (*p*-methoxyhydrocornicularic) acid, m.p. 103—104° [*semicarbazone*, m.p. 191° (decomp.); *Me* ester, m.p. 56—57°, and its *semicarbazone*, m.p. 144—145°]. Condensation of $CHPh{:}CH\cdot CHO$ with $p\text{-}OMe\cdot C_6H_4\cdot CH_2\cdot CO_2Na$ in presence of Ac_2O gives δ-*phenyl*-α-p-*anisyl*-$\Delta^{\alpha\gamma}$-*pentadienoic acid*, m.p. 209—210°, whence α-p-*anisyl*-γ-*benzylcrotonolactone*, m.p. 102—103°, γ-keto-δ-phenyl-α-*p*-anisylvaleric (*p*′-methoxyhydrocornicularic) acid, m.p. 146—147° [*semicarbazone*, m.p. 146—147° (decomp.); *Me* ester, m.p. 63—64°, and its *semicarbazone*, m.p. 173—174°]. H. W.

Structure of "sulphite-liquor lactone." H. Erdtman (Annalen, 1934, **513**, 229—239).—The α-dimethyl-lactone (I), $C_{22}H_{24}O_6$ (*Br₂*-derivative, m.p. 183—184°), of Holmberg (A., 1921, i, 850) is oxidised ($KMnO_4$, aq. $COMe_2$) to 4 : 5 : 3′ : 4′-tetramethoxy-2-benzoylbenzoic acid (II) (Haworth and Mavin, A., 1931, 954), an alkali-insol. substance, m.p. 166—167° [2 : 4-*dinitrophenylhydrazone* (?), m.p. 250—252° (decomp.)], and resinous materials. Oxidation (alkaline NaOBr) of (I) affords (II) [the diveratroylacetic acid of Holmberg (B., 1928, 185)], the so-called 3 : 4-diveratrylfuran (*loc. cit.*), and a dibasic acid (III), $C_{22}H_{24}O_8$ (Holmberg's "dimethoxytruxinic acid"), m.p. 192—193°, $[\alpha]_D^{20}$ +39·3° in $COMe_2$. Oxidation ($KMnO_4$, $COMe_2$) of (III) gives the same products as (I). (I) could not be reduced (H_2, PtO_2, EtOH–AcOH). (II) is converted by conc. H_2SO_4 and fuming

HNO_3 into 2 : 3 : 6 : 7-tetramethoxyanthraquinone and trinitroveratrole, respectively. (III) gives an *anhydride*, m.p. 204—205° (rapid heating); its *Me_2 ester*, m.p. 148—149°, is dehydrogenated [$Pb(OAc)_4$ in AcOH] to Me 6 : 7-dimethoxy-1-3′ : 4′-dimethoxyphenylnaphthalene-2 : 3-dicarboxylate, m.p. 165—167°. (III) is (probably) 6 : 7-dimethoxy-1-3′ : 4′-dimethoxyphenyl-1 : 2 : 3 : 4-tetrahydronaphthalene-2 : 3-dicarboxylic acid. "Sulphite-liquor lactone" (Holmberg, A., 1921, i, 25, 849; *loc. cit.*) is probably *A* or *A* with CO and CH_2* interchanged; it does not occur as such in wood, but probably arises by cyclisation of a diarylbutene. H. B.


(*A*.)

Imines. G. Mignonac (Ann. Chim., 1934, [xi], 2, 225—294).—Imines are products of hydrogenation of nitriles or oximes or of dehydrogenation (in presence of metals) of bases, but their isolation is often impossible owing to secondary reactions. One mol. of the imine, reacting as $CH_2R\cdot CH{:}NH$, with a second mol., reacting as $CHR{:}CH\cdot NH_2$ (imine–enamine tautomerism), forms NH_3 and substances, $CH_2R\cdot CH{:}N\cdot CH{:}CHR$, which either condense further with imine to yield, *e.g.*, $CHPh(N{:}CHPh)_2$ (I), or may be further reduced to Schiff's bases (*A*) or *sec.*-amines. (*A*) may, however, also be formed (*e.g.*, from aromatic aldimines) by hydrolysis of the imine and condensation of the resulting aldehyde with the amine formed by reduction of another portion of imine. Thus, addition of 1 mol. of H_2 to PhCN, *o*- or *p*-$C_6H_4Me\cdot CN$ in Et_2O in presence of Ni at room temp. gives the primary base, unchanged nitrile, a little aldehyde, and (*A*); PhCN gives also some (I). The following are incidentally described: p-*toluylidene*-p-*methylbenzylamine*, m.p. 84°, b.p. 156—157°/3 mm., and the corresponding o-o-*compound*, b.p. 170—171°/5 mm.; *benzylidenebenzylamine* (II), b.p. 142—143°/4 mm. Similarly, addition of 1 mol. of H_2 to $CHPh{:}NOH$ in abs. EtOH in presence of Ni gives $CH_2Ph\cdot NH_2$, (II), and a little PhCHO, whilst much PhCHO is formed in 50% EtOH; the PhCHO does not arise by hydrolysis of the oxime, since the catalyst is necessary for its formation. Reduction of the appropriate ketoximes led, however, to isolation of the imines themselves; thus are obtained *Ph Me ketimine hydrochloride*, cryst., hygroscopic, *Ph Et ketimine hydrochloride*, m.p. 145° (block) (*Ac* derivative of the imine, m.p. 126°) [with some of the Schiff *base*, $CHPhEt\cdot N{:}CPhEt$, b.p. 170—171°/9 mm. (*hydrochloride*, m.p. 174°)], $CPh_2{:}NH$, and *Ph $C_{10}H_7$ ketimine*, m.p. 68—69°. *cyclo*Hexanoneoxime resembles the aldoximes in giving *cyclo*hexanone (50—60%) and cyclo*hexyliminocyclohexane*, b.p. 117—118°/9 mm. [*hydrochloride*, m.p. 180° (decomp.)].

Passage of $CH_2Ph\cdot CH_2\cdot NH_2$ (III) in N_2 over Ni at 190—230° gives H_2, NH_3, PhCN, and unchanged (III); if steam is added to the mixture, base, NH_3, and 10—15% of $CH_2Ph\cdot CHO$ are obtained; PrCHO (25—30%), PhCHO (40%), and *p*-$C_6H_4Me\cdot CHO$ (35%) are obtained similarly from the corresponding amines; if anhyd. NH_3 is added to the mixture at 225°, there is more rapid evolution of H_2 and much $CH_2Ph\cdot CH{:}NH$ is isolated, together with unchanged (III) and $CH_2Ph\cdot CN$. These results prove the existence of an equilibrium between (III), the nitrile, imine, and H_2 in presence of Ni. The imines were themselves isolated (20 and 70% yields, respectively) by passage of $CHPhEt\cdot NH_2$ (at 240—250°) or $CHPh_2\cdot NH_2$ (at 260°) in N_2 over Ni (no added NH_3); NH_2Pr gave only NH_3 and unidentified products. $CH_2Ph\cdot CH{:}NH,HCl$, m.p. 180—183°, gives in air the *carbonate* (IV), m.p. 101—103°, of (III) (cf. lit.), and by dissolution in H_2O affords $CH_2Ph\cdot CN$ and (III). (IV) in air gives some $CH_2Ph\cdot CHO$. $CHPh{:}NH,HCl$ [best obtained from (I) and HCl in EtOH], m.p. 181—182°, with dry NH_3–Et_2O at room temp. or −40° give NH_4Cl and (I); the free imine could not be isolated (cf. lit.). The stability of ketimines varies greatly according to the nature of the ketone. Hydrogenation of (I) (Ni) in abs. EtOH at $< 40°$ gives $CH_2Ph\cdot NH_2$ (about 1 mol.) and (II) (about 1 mol.); the first products are, however, (II) and $CHPh{:}NH$, since in 98% EtOH the imine is partly hydrolysed and the resulting aldehyde condenses to re-form (I); this in turn is further reduced, so that the final product contains little amine and much (II). R. S. C.

Reactive methyl group in toluene derivatives. I. Oxidation with selenium dioxide and cleavage of benzylpyridinium halides. C. H. Fisher (J. Amer. Chem. Soc., 1934, 56, 2056—2057).—*p*-$NO_2\cdot C_6H_4\cdot CHO$ is obtained in 56% yield when equimol. amounts of *p*-$NO_2\cdot C_6H_4\cdot CH_2Br$ and SeO_2 in EtOH are heated at 140—150° (the EtOH is allowed to distil). CH_2PhCl (no solvent) heated with SeO_2 gives 49% of PhCHO and 3% of BzOH; CH_2Ph_2 (I) similarly affords 47% of $COPh_2$; $CHPh_3$ (II) furnishes 15% of $CPh_3\cdot OH$; *p*-$NO_2\cdot C_6H_4Me$ (III) gives a little *p*-$NO_2\cdot C_6H_4\cdot CO_2H$ (IV). (I), (II), (III), and 4 : 4′-dinitrodiphenylmethane are unaffected by SeO_2 in boiling EtOH. *p*-Nitrobenzylpyridinium chloride and bromide are converted by aq. NaOBr into (IV); reaction occurs very rapidly and probably proceeds through an intermediate Br-derivative. Benzylpyridinium chloride similarly gives resinous products. H. B.

Oxidation of organic compounds as a means of investigating their constitution. II. C. Cattaneo (Gazzetta, 1934, 64, 509—517; cf. this vol., 653).—$CH_2Ph\cdot CHO$ and aq. H_2O_2 combine at room temp. to give the "*perhydrate*" $2CH_2Ph\cdot CHO,H_2O_2$, m.p. 69—70° (decomp.), which decomposes very slowly in presence of H_2O yielding HCO_2H, $CH_2Ph\cdot OH$, and $CH_2Ph\cdot CHO$ by "perhydrolysis." At 50° the interaction of $CH_2Ph\cdot CHO$ and H_2O_2 yields CO_2, CO, and O_2, whilst at 95° H_2 and CH_4 are also formed, and $CH_2Ph\cdot CO_2H$, BzOH, PhCHO, and HCO_2H are produced. $CH_2Ph\cdot CO_2H$ and aq. H_2O_2 at 95° yield CO_2, O_2, BzOH, PhCHO, and HCO_2H, and treatment of the solution with $KMnO_4$ yields a little $BzCO_2H$, indicating that $OH\cdot CHPh\cdot CO_2H$ is formed by a process of α-oxidation. R. K. C.

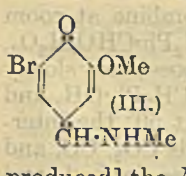
Compounds of bivalent carbon. IX. Chlorodiphenylacetaldehyde diethyl acetal and its adaptability to carbon monoxide acetal fission. H.

Scheibler and A. Schmidt (Ber., 1934, **67**, [*B*], 1514—1518; cf. this vol., 1201).—Hydroxydiphenylacetaldehyde Et_2 acetal, b.p. 140°/2 mm., obtained from MgPhBr and $(OEt)_2CH{\cdot}CO_2Et$, is converted by $SOCl_2$ and C_5H_5N into *chlorodiphenylacetaldehyde Et_2 acetal* (I), b.p. 136°/1 mm., which with C_5H_5N yields $CHPh_2{\cdot}CO_2Et$. Addition of (I) to MgPhBr in Et_2O leads to loss of PhCl and formation of a compound, $(OEt)_2CH{\cdot}CPh_2{\cdot}MgBr$, which affords $:C(OEt)_2$ (recognised by conversion into HCO_2H) and CH_2Ph_2 (yield 35·7%). H. W.

Cannizzaro's reaction. G. Lock (Monatsh., 1934, **64**, 341—348; cf. A., 1933, 504).—Treatment of $3:4\text{-}C_6H_3(OH)_2{\cdot}CHO$ with KOH–MeOH–MeI gives a mixture of 3-hydroxy-4-methoxy- (I), 4-hydroxy-3-methoxy-, and 3 : 4-dimethoxy-benzaldehyde. 2-Bromo-3-hydroxy-4-methoxybenzaldehyde (II) (simplified prep. from (I)] is very slowly transformed by 25% KOH at 100° into *2-bromo-3-hydroxy-4-methoxybenzyl alcohol* (III), m.p. 151—152° after softening, and *2-bromo-3-hydroxy-4-methoxybenzoic acid*, m.p. 214—215° (corr.). 2-Bromo-3 : 4-dimethoxybenzaldehyde, m.p. 86°, from (II), Me_2SO_4, and KOH, similarly affords *2-bromo-3 : 4-dimethoxybenzyl alcohol* (IV), m.p. 82·5°, and 2-bromo-3 : 4-dimethoxybenzoic acid, m.p. 203—204° (corr.). (IV) is obtained also by methylation of (III). *2 : 6-Dibromo-3 : 4-dimethoxybenzaldehyde*, m.p. 137·5°, is converted by 50% KOH at 100° into HCO_2H and *3 : 5-dibromoveratrole*, m.p. 34°, transformed by HI (*d* 1·7) at 100° into pyrocatechol. H. W.

Vanillin synthesis. H. O. Mottern (J. Amer. Chem. Soc., 1934, **56**, 2107—2108).—$o\text{-}OMe{\cdot}C_6H_4{\cdot}OAc$ and $AlCl_3$ at $< 5°$ give 4-hydroxy-3-methoxyacetophenone, oxidised [$PhNO_2$ (1 mol.) and aq. NaOH (3 mols.) at 100°] to 4-hydroxy-3-methoxyphenylglyoxylic acid, which when heated with $p\text{-}C_6H_4Me{\cdot}NMe_2$ at 170° affords vanillin. H. B.

Mechanism of condensation of aromatic hydroxyaldehydes with nitromethane in presence of organic bases. S. P. Makarov (J. pr. Chem., 1934, [ii], **141**, 77—90).—5-Bromovanillin (I) and EtOH–NH_2Me (1·2 mols.) in cold $CHCl_3$ give *5-bromo-α-methylamino-4-hydroxy-3-methoxybenzyl alcohol* (II), m.p. 93—95° (loss of H_2O), re-solidifying with m.p. 211°, which is hydrolysed (acid; alkali) to (I), and when heated at 85—90° in a vac. loses 1 mol. of H_2O and affords *5-bromo-3-methoxymethylaminoquinomethide* (III), m.p. 211°, decomp. 214—215°. (III) is also obtained from (I) and NH_2Me in warm EtOH. (II) does not react with cold $MeNO_2$; in the hot [whereby (III) is produced] the *NH_2Me* salt (IV), decomp. 150°, of *5-bromo-ω-nitro-4-hydroxy-3-methoxystyrene* (V), m.p. 189—190° (decomp.) (*NH_4*, decomp. 145—150°, and *Ba* salts), results. It is probable that $MeNO_2$ first adds to (III) forming α-nitro-β-methylamino-β-5-bromo-4-hydroxy-3-methoxyphenylethane, which then isomerises to (IV) or gives (V) + NH_2Me. (V) is also formed from (I), $MeNO_2$, and NH_2Me (trace) in EtOH at 70—75°. (II) and EtOH–HCN afford *α-methylamino-α-(5-bromo-4-hydroxy-3-methoxyphenyl)acetonitrile*, m.p. 93—94° [formed by addition of HCN to (III)], hydrolysed (acid; alkali) to (I); *5-bromo-4-hydroxy-3-methoxymandelonitrile* (VI), m.p. 106—107° (decomp.) [prepared from (I), EtOH–HCN, and a little K_2CO_3 or KCN], is an intermediate in the hydrolysis. (VI) is dehydrated (PCl_3 in Et_2O) to 5-bromo-3-methoxycyanoquinomethide (A., 1933, 716). *Vanillylidenemethylamine* (VII), m.p. 134—135° (decomp.), does not react with $MeNO_2$ in a non-ionising solvent. In an ionising solvent an equilibrium between (VII) and 3-methoxymethylaminoquinomethide (VIII) results; addition of $MeNO_2$ to (VIII) gives (after acidification) ω-nitro-4-hydroxy-3-methoxystyrene (*Ba* salt). (VII) and Et_2O–HCN afford *α-methylamino-α-(4-hydroxy-3-methoxyphenyl)-acetonitrile*, m.p. 132°. H. B.


(III.)

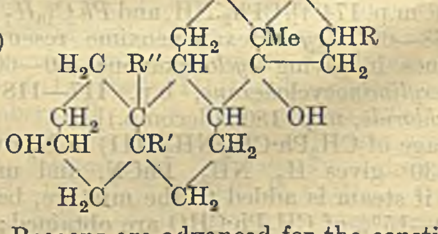
o-Aldehydocarboxylic acids. I. New general method of synthesising phthalonic acids. Synthesis of ψ-opianic and m-opianic acids. S. N. Chakravarti and M. Swaminathan (J. Indian Chem. Soc., 1934, **11**, 715—719).—Oxidation of homophthalic acids with SeO_2 in boiling xylene affords phthalonic acids in good yields. Thus 5 : 6- (I) and 4 : 6-dimethoxyhomophthalic acid afford, respectively, ψ- (II) and *m*-opianic acid (isolated as their NH_2Ph salts), and homophthalic acid gives phthalonic acid. When heated with 4 mols. of PCl_5 and $POCl_3$ at 140—150° (I) affords *3 : 3 : 4 : 4-tetrachloro-5 : 6-dimethoxy-3 : 4-dihydro*iso*coumarin*, m.p. 128°, hydrolysed by MeOH–KOH to (II). J. W. B.

Condensation of polyhydric alcohols, sugars, and hydroxy-acids with aldehydes.—See this vol., 1330.

***X*-Ray crystallographic measurements on derivatives of cardiac aglucones.** J. D. Bernal and D. Crowfoot (Chem. and Ind., 1934, 953—956).—Measurements are recorded for *lactone* 135 (I), digitaligenin (dianhydrogitoxigenin) [II], digitoxigenin (III), gitoxigenin (IV), and digoxigenin (V). (I) is free from OH and is prepared by dehydration of digoxigenin and reduction of the product; it is therefore isomeric or identical with the lactone, $C_{23}H_{36}O_2$, of Windaus and Stein. The data obtained for (I) and (IV) exclude many of the chemically permissible configurations which might be given to the framework of the cardiac aglucones, whereas those obtained for (II), (III), and (V) supply no certain information. H. W.

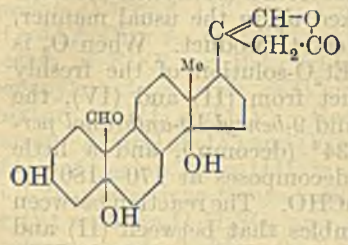
Constitution of vegetable heart poisons. R. Tschesche (Angew. Chem., 1934, **47**, 729—732).—A lecture. Reasons are advanced for the constitutions I (R=H; R′=OH; R″=CHO) and (R=OH;

(I.)



R′=H; R″=Me) for strophanthidin and gitoxigenin, respectively. H. W.

Constitution of strophanthidin. II. G. A. R. Kon (Chem. and Ind., 1934, 956—958; cf. this vol., 1007).—Discussion of possible formulæ for strophanthidin (I) in the light of the results of Bernal *et al.* (see above) indicates the annexed structure as the most probable. The arguments are valid only if the formation of 3′-methyl*cyclo*pentenophenanthrene from (I) and uzarigenin can be regarded as proof of a sterol-like skeleton, and is not due to re-arrangement in the course of dehydrogenation; also that the latter does not involve the elimination or wandering of Me groups other than those attached to quaternary C atoms. H. W.



Jute lignin. IV. Dioxymethylene group in lignin. P. B. Sarkar (J. Indian Chem. Soc., 1934, **11**, 691—700).—CH_2O (I) has been obtained from five lignocelluloses (II) and from the lignins obtained from them, the $O·CH_2·O$ group being a common constituent of lignin (III). The best yield of (I) [determined by the dimedon method, which is the only one applicable to (III), and is shown to be trustworthy] is obtained by distillation with 28% H_2SO_4, more conc. or weaker acids giving lower vals. The max. yield (2·78%) of (I) is obtained from (III) prepared by the action of 42% HCl at 20° for 24 hr., prolonged exposure of (II) to strong acids, higher temp., and subsequent acid boiling reducing the yield of (I), due to resin formation with phenolic substances. The reducing action of (III) is due to the two *o*-OH groups set free during isolation. Allowing for this loss of (I) the true % is 3·61, whence the mol. wt. of (III) is 830. The presence of $O·CH_2·O$ in (III) is confirmed by treatment of a sample, from which (I) has been removed, with CH_2I_2 at 140—150°, the product again giving similar amounts of (I). Since (I) also gives an insol. compound with phloroglucinol the lower yield of furfuraldehyde in delignified jute [(I) having been thus removed] is explained. J. W. B.

Manufacture of cyclic α-cyanoketimines and cyclic α-cyanoketones.—See B., 1934, 953.

Ammono-ketone alcohols. I. Benzophenoneimine. G. E. P. Smith, jun., and F. W. Bergstrom (J. Amer. Chem. Soc., 1934, **56**, 2095—2098).—The additive compound from PhCN and MgPhBr with liquid NH_3 in Et_2O gives (cf. Cornell, A., 1929, 173) $CPh_2{:}NH$ (I) [hydrochloride, m.p. > 310°; picrate, m.p. 281—282° (slow decomp.)], which with $NHPh·NH_2$ at 60—70° and NH_2Ph (excess allowed to distil) affords *benzophenone-phenylhydrazone*, m.p. 138—139°, and *-anil*, m.p. 112—113°, respectively. (I) and NH_2OH in liquid NH_3 give $CPh_2{:}N·OH$, whilst (I) and anhyd. HCN in EtOH afford *α-cyanobenzhydrylamine*, m.p. 101—102°, which is converted by KNH_2 (1 mol.) in liquid NH_3 into (I) and KCN. N-*Phenyl*-N′-*benzhydrylidenecarbamide*, m.p. 160—162° (decomp.) [from (I) and PhNCO in C_6H_6], is hydrolysed by repeated crystallisation from 95% EtOH to $COPh_2$ and $NH_2·CO·NHPh$. (I) with $NaNH_2$ (1 mol.) and KNH_2 (2 mols.) in liquid NH_3 gives *salts*, $CPh_2{:}NNa$ and $CPh_2(NHK)_2$, respectively, which could not be freed from NH_3. Deep red solutions are obtained from (I) and Na or K in liquid NH_3; subsequent hydrolysis (H_2O) gives $COPh_2$ and $CHPh_2·NH_2$ (II) [*hydrochloride*, m.p. 290—292° (decomp.)] (in about 50% yield, irrespective of the excess of Na used). (I) is not reduced by MgPhBr, probably owing to the insolubility of the resulting complex. (I) and $Mg+MgI_2$ in C_6H_6 give the *complex*, $(CPh_2{:}NH)_2,MgI_2$; when the reaction mixture is evaporated and then treated with liquid NH_3, (II) and $CPh_2{:}N·CHPh_2$ are obtained. Reduction of (I) to an ammono-benzpinacol or -benzpinacolin has not been accomplished. H. B.

Side-chain chlorination of *pp*′-dimethylbenzophenone. II. 4 : 4′-Tetrachlorodimethylbenzophenone. E. Connerade (Bull. Soc. chim. Belg., 1934, **43**, 447—461; cf. A., 1933, 1051).—4 : 4′-Dimethylbenzophenone and Cl_2 (slightly > 4 mols. at 140°) yields a product, from which MeOH isolates a *Cl_4-compound*, m.p. 109·5° (probably partly nuclear-substituted). The main product, from which the Cl_5-derivative is removed by ligroin, is 4 : 4′-*tetrachlorodimethylbenzophenone* (I), identified by hydrolysis to benzophenone-4 : 4′-dialdehyde. (I) with LiPh yields Ph_2 and polymeric products of the type $[{:}CH·C_6H_4·CO·C_6H_4·CH{:}]_n({:}CH·C_6H_4·CO·C_6H_4·CHO)_2{:}$ (II), $n=3$, m.p. 190—195°; (III), $n=4$; (IV), $n=11$. These are coloured and fluorescent in solution. (I) with $AlCl_3$ yields 4 : 4′-*dibenzylbenzophenone*, as a gum (oxidised to 4 : 4′-*dibenzoylbenzophenone*, m.p. 227°), and *bis*-4 : 4′-*dibenzylbenzophenone*, $[·CHPh·C_6H_4·CO·C_6H_4·CHPh·]_2$, a gum, oxidised to *triphenyl*-4 : 4′-*dimethylbenzophenone* (?) and a *product*, $C_{54}H_{40}O_6$, m.p. 157°. (I) with MgPhBr yields Ph_2 and a *resin*, $C_{42}H_{65}O_5$. H. N. R.

Pinacol–pinacolin rearrangement. VI. Rearrangement of symmetrical aromatic pinacols. W. E. Bachmann and J. W. Ferguson (J. Amer. Chem. Soc., 1934, **56**, 2081—2084).—*s*-Pinacols, OH·CRR′·CRR′·OH, prepared usually by reduction (Zn, AcOH; $Mg+MgI_2$; exposure to sunlight in $Pr^{\beta}OH$ for 1—2 months) of CORR′ or, occasionally, from $(·COR)_2$ and MgR′X, are rearranged by AcCl in AcOH–C_6H_6 or (more generally) I in AcOH to mixtures of COR·CRR′R′ and COR′·CRRR′, which are analysed by fission with MeOH–KOH to $RCO_2H+R'CO_2H$. The relative migration aptitudes of the groups studied are (Ph=1): phenetyl 500, anisyl 500, *m*-anisyl 1·6 (mean val.), *p*-C_6H_4Cl 0·66, *m*-C_6H_4Cl 0; vals. previously deduced (cf. A., 1932, 515, 737; this vol., 292) for other groups are also given. The relative migration aptitudes of R and R′ can be predicted from the vals. of these groups with respect to a third (mutual) group. 4 : 4′-*Diethoxy*-, m.p. 141—142°, 4 : 4′-*diethoxy*-4″ : 4‴-*dimethyl*-, m.p. 168—169°, 3 : 3′-dimethoxy-, m.p. 140—142° (lit. 139°), 3 : 3′-*dimethoxy*-3″ : 3‴-, m.p. 139—140°, and -4″ : 4‴-, m.p. 160—162°, *-dimethyl*-, 3 : 3′-*dimethoxy*-4″ : 4‴-*diphenyl*- (I), m.p. 172—173°, 4 : 4′-*dimethoxy*-3″ : 3‴-*dimethyl*-, m.p. 144—145°, 4 : 4′-

dichloro-4'' : 4'''-*dimethoxy*- (II), m.p. 181—182°, 4 : 4'-dichloro-4'' : 4'''-dimethyl-, and 3 : 3'-*dichloro*-4'' : 4'''-*diphenyl*- (III), m.p. 174—175°, -*benzpinacols* are described. 3-*Methoxy*-4' : 4''-*diphenyltriphenylmethane*, m.p. 149—149·5°, isolated from the fission products of the mixture of pinacolins from (I), is also prepared by reduction (HCO_2H) of the carbinol from 3-methoxy-4'-phenylbenzophenone and *p*-$C_6H_4Ph\cdot Li$. 4-*Chloro*-4' : 4''-*dimethoxytriphenylmethane*, m.p. 65—66°, obtained similarly from (II), is prepared by reduction (Zn dust, AcOH) of the carbinol from $CO(C_6H_4\cdot OMe\text{-}p)_2$ and *p*-$C_6H_4Cl\cdot MgBr$, whilst 3-*chloro*-4' : 4''-*diphenyltriphenylmethane*, m.p. 144—145° [from (III)], is obtained by reduction (HCO_2H) of the carbinol from 4 : 4'-diphenylbenzophenone and *m*-$C_6H_4Cl\cdot MgI$. *p*-$C_6H_4Me\cdot COCl$, PhOEt, and $AlCl_3$ in CS_2 give 4-*ethoxy*-4'-*methylbenzophenone*, m.p. 84—85°; 4-ethoxybenzophenone, m.p. 47° (lit. 38—39°), is prepared from BzCl. *m*-$OMe\cdot C_6H_4\cdot CN$ with MgPhBr and *m*-$C_6H_4Me\cdot MgBr$ (IV) affords 3-methoxy-, b.p. 185°/4 mm., m.p. 38—40°, and 3-*methoxy*-3'-*methyl-benzophenone*, b.p. 212—213°/22 mm., respectively. *p*-$OMe\cdot C_6H_4\cdot CHO$ and (IV) give 4-*methoxy*-3'-*methylbenzhydrol*, m.p. 51—52°, oxidised (CrO_3, AcOH) to 4-*methoxy*-3'-*methylbenzophenone*, b.p. 238—240°/35 mm., also prepared from *p*-$OMe\cdot C_6H_4\cdot CN$ and (IV). *m*-$C_6H_4Cl\cdot COCl$, Ph_2, and $AlCl_3$ in CS_2 afford 3-*chloro*-4'-*phenylbenzophenone*, m.p. 106—107°; 3-*chloro*-4'-*methylbenzophenone*, m.p. 97—98°, is similarly prepared from PhMe. H. B.

Reversibility of the Friedel–Crafts condensation. Styryl methyl and distyryl ketones. C. F. Woodward, G. T. Borcherdt, and R. C. Fuson (J. Amer. Chem. Soc., 1934, **56**, 2103—2105; cf. this vol., 774).—*p*-Chlorostyryl Me ketone (I), m.p. 58—59·5° (lit. 51°), prepared by Walther and Rätze's method (A., 1902, i, 466), PhCl, and $AlCl_3$ in the cold give ββ-*di*-p-*chlorophenylethyl Me ketone* (II), m.p. 91—92·5° (*semicarbazone*, m.p. 180—181°), oxidised ($Na_2Cr_2O_7$, AcOH) to 4 : 4'-dichlorobenzophenone. *p*-$C_6H_4Me\cdot CH{:}CH\cdot COMe$ (III) and PhMe similarly afford ββ-*di*-p-*tolylethyl Me ketone* (IV), m.p. 73·5—74° (*semicarbazone*, m.p. 140—141·5°), whilst $CHPh{:}CH\cdot COMe$ (V) and PhCl yield (under appropriate conditions) β-*phenyl*-β-p-*chlorophenylethyl Me ketone* (VI), b.p. 180—182°/4 mm. (*semicarbazone*, m.p. 155·5—157°). (I)—(VI) treated with C_6H_6, $AlCl_3$, and HCl (cf. A., 1933, 1170) give ββ-diphenylethyl Me ketone (VII) in 33—92% yield; (VII) and PhCl similarly afford (mainly) (VI) and (II). Interruption of the reaction between *di*-o-*chlorostyryl ketone* (VIII), m.p. 124—125°, C_6H_6, and $AlCl_3$ gives β-*phenyl*-β-o-*chlorophenylethyl* o-*chlorostyryl ketone* (IX), m.p. 144° [also prepared from (VIII) and MgPhBr]; more prolonged reaction affords di-ββ-diphenylethyl ketone (X), which is also obtained from MgPhBr and $CHPh{:}CH\cdot CO\cdot CH_2\cdot CHPh_2$ (XI). (X) is also formed from C_6H_6, $AlCl_3$, and (IX), (XI), and distyryl, di-*p*-chlorostyryl, and di-*p*-methylstyryl ketones. H. B.

Additions to conjugated systems in anthracene series. I. Action of magnesium phenyl bromide on methyleneanthrone. P. L. Julian and A. Magnani (J. Amer. Chem. Soc., 1934, **56**, 2174—2177).—Contrary to Bergmann (A., 1930, 903), 9-benzylideneanthrone (I) (obtained by passing dry HCl into anthrone+PhCHO at 100°) and MgPhBr (II) give a *compound*, $C_{27}H_{20}O$, m.p. 147°, and only a little anthraquinone (III). In agreement with Bergmann (*loc. cit.*), the product from 9-methyleneanthrone (IV) and (II), when worked up in the usual manner, affords (III) as the sole cryst. product. When O_2 is passed into the moist Et_2O-solution of the freshly prepared reaction product from (II) and (IV), the fluorescence disappears and 9-*benzyl*-10-*anthranol peroxide* (V), m.p. 133—134° (decomp.), and a little (III) are isolable. (V) decomposes at 170—180° to (III), $CH_2Ph\cdot OH$, and PhCHO. The reaction between (II) and (IV) thus resembles that between (II) and αβ-unsaturated ketones (Kohler, A., 1906, i, 753). Reduction (H_2, Pd, EtOH) of (I) gives 9-*benzylanthrone* (VI), m.p. 91—92°, and some (III) (separates when the Et_2O-extract is kept); passage of O_2 through the freshly prepared reduced solution affords (III) and $CH_2Ph\cdot OH$. (VI) could not be prepared from the dibromide, m.p. 138° (lit. 148°), of (I) by Bach's method (A., 1890, 1144); (I) and (III) are obtained. H. B.

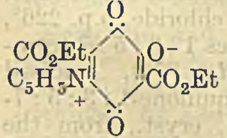
Condensation of phenols with unsaturated ketones or aldehydes. I. β-Naphthol and vinyl methyl ketone. S. A. Miller and R. Robinson (J.C.S., 1934, 1535—1536).—$CH_2{:}CH\cdot COMe$, β-$C_{10}H_7\cdot OH$, and NaOEt or KOEt in cold, dry EtOH give β-2-*hydroxy*-1-*naphthylethyl Me ketone* (I), m.p. 84° (*ferrichloride* of *Ac* derivative, cryst.), the *Me ether*, m.p. 54°, b.p. 205°/10 mm., of which was also obtained by hydrogenation (Pd) in AcOH at 30—40° of 2-*methoxy*-1-*naphthylideneacetone*, m.p. 146·5—147·5°, b.p. 195—205°/1 mm. (prepared from $COMe_2$ and the aldehyde by NaOH). (I), best with chloranil and hot $POCl_3$, gives 2-*methyl*-5 : 6-*naphtha*-(1 : 2)-*pyrylium ferrichloride*, m.p. 151°. R. S. C.

Highly activated carbonyl group. Dimesityl triketone. R. C. Fuson, J. F. Matuszeski, and A. R. Gray (J. Amer. Chem. Soc., 1934, **56**, 2099—2101).—Di-2 : 4 : 6-trimethylbenzoylmethane (I) is oxidised (SeO_2, dioxan) to *di*-2 : 4 : 6-*trimethylphenyl triketone* (II), m.p. 111—112·5°, and a compound, m.p. 201—202°. (II) is also obtained (i) as a by-product in the oxidation (HNO_3) of γ-hydroxy-αβδ-triketo-αδ-di-2 : 4 : 6-trimethylphenylbutane (this vol., 895), (ii) by the action of alkali on di-2 : 4 : 6-trimethylphenyl tetraketone (III) (*loc. cit.*), or (iii) (most conveniently) by prolonged heating of (III) in AcOH (or EtOH). (II) and $NH_2\cdot CO\cdot NH\cdot NH_2$ give mesitylglyoxalsemicarbazone (this vol., 525); with NH_2OH, a *compound*, m.p. 180—181°, which appears to be isomeric with mesitylglyoxaloxime, results. (II) is decomposed by hot 10% NaOH to 2 : 4 : 6 : 2' : 4' : 6'-hexamethylbenzil, 2 : 4 : 6-$C_6H_2Me_3\cdot CO_2H$, and 2 : 4 : 6-$C_6H_2Me_3\cdot CH(OH)\cdot CO_2H$. (I) does not react with *p*-$C_6H_4Cl\cdot CHO$ in aq. EtOH–NaOH. (I), $Bu^{\alpha}O\cdot NO$, and HCl in Et_2O give a *compound*, $C_{21}H_{33}O_3N$, m.p. 153—154°, which could not be hydrolysed (EtOH–H_2SO_4 or –HCl). Cryst. products could not be obtained from (I) and $Pb(OAc)_4$ in AcOH. H. B.

Reduction of α-hydroxy-αβ-dibenzoylethylene and dibenzoylethylene oxide and chlorohydrin.

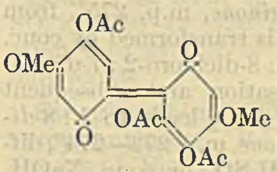
R. E. LUTZ and F. N. WILDER (J. Amer. Chem. Soc., 1934, 56, 2065—2067).—Reduction ($Na_2S_2O_4$ in boiling 85% EtOH) of α-hydroxy-αβ-dibenzoylethylene (I) or αβ-dibenzoylethylene chlorohydrin (II) gives approx. equal amounts of αβ-dibenzoylethane (III) and αβ-*dibenzoylethyl alcohol* (IV), m.p. 87·5° (corr.) [*acetate* (V), m.p. 116° (corr.), obtained by the action of cold AcCl or Ac_2O at 75°; chloride, prepared by the action of $SOCl_2$ or BzCl (cold or at 50°)]. αβ-Dibenzoylethylene oxide (VI) similarly affords a 2 : 1 mixture of (III) and (IV). Reduction [Zn dust (large excess), AcOH] of (IV) and (VI) at 35°, and the acetate of (II) at the b.p., gives (III) in each case. (IV) heated at 150° passes into *trans*-αβ-dibenzoylethylene. (IV) or (V) with Ac_2O–H_2SO_4 and AcCl–H_2SO_4 affords 3-acetoxy- and 3-chloro-2 : 5-diphenylfuran, respectively. The production of (III) and (IV) from (I) is considered to involve the following reactions: $COPh{\cdot}CH_2{\cdot}CH(COPh){\cdot}OH$ (IV) $\longleftarrow$ $[OH{\cdot}CPh{:}CH{\cdot}C(OH){:}CPh{\cdot}OH]$ $\xleftarrow{H_2}$ $COPh{\cdot}CH{:}C(COPh){\cdot}OH \xrightarrow{H_2} [H_2O + COPh{\cdot}CH{:}C{:}CPh{\cdot}OH] \longrightarrow [({:}CH{\cdot}COPh)_2] \longrightarrow ({\cdot}CH_2{\cdot}COPh)_2$ (III). Related types of reduction are discussed briefly. H. B.

Action of pyridine on ethyl 2 : 5-dichloro-*p*-benzoquinone-3 : 6-dicarboxylate and derivatives of terephthalic acid. H. LIEBERMANN and D. LISSER (Annalen, 1934, 513, 180—189).—Et 2 : 5-dichloro-*p*-benzoquinone-3 : 6-dicarboxylate and C_5H_5N in cold $COMe_2$ give the *betaine* (I) of *Et 2-hydroxy-5-pyridinium*-p-*benzoquinone*-3 : 6-*dicarboxylate*, m.p. 194° (decomp.), which is formed by hydrolysis (traces of H_2O present in the reagents or formed by autocondensation of $COMe_2$ by the C_5H_5N) of the first formed di(pyridinium chloride) and subsequent elimination of HCl from the hydroxyphenylpyridinium chloride. (I) is reduced (aq. $Na_2S_2O_4$) to *Et* 2 : 3 : 5-*trihydroxyterephthalate*, m.p. 116° [Ac_3 derivative, m.p. 100°; free *acid*, m.p. 247° (decomp.)]. The product obtained from (I) and boiling MeOH or EtOH is reduced ($Na_2S_2O_4$ in aq. $COMe_2$) to Et tetrahydroxyterephthalate, m.p. 178°. *Et* 2-*hydroxy*-5-*phenoxy*-p-*benzoquinone*-3 : 6-*dicarboxylate*, m.p. 128—130° [from (I) and PhOH in aq. $COMe_2$], is similarly reduced to *Et* 2 : 3 : 5-*trihydroxy*-6-*phenoxyterephthalate*, m.p. 128° (Ac_3 derivative, m.p. 128°; free *acid*, m.p. > 280°), whilst *Et* 5-*anilino*-2-*hydroxy*-p-*benzoquinone*-3 : 6-*dicarboxylate*, m.p. 160° [from (I) and NH_2Ph in aq. $COMe_2$], similarly gives *Et* 6-*anilino*-2 : 3 : 5-*trihydroxyterephthalate*, m.p. 102°. (I) and fuming HCl at 45° afford *Et* 5-*chloro*-2-*hydroxy*-p-*benzoquinone*-3 : 6-*dicarboxylate*, m.p. 98° [*Ac* derivative (II), m.p. 107°], reduced to *Et* 6-*chloro*-2 : 3 : 5-*trihydroxyterephthalate*, m.p. 110° [Ac_3 derivative, m.p. 104°; 3-*Ac* derivative, m.p. 85°, prepared by reduction of (II)]. 2 : 4 : 5-*Trihydroxy*-3 : 6-*dicarbethoxyphenylpyridinium bromide*, m.p. 202° (decomp. from 170°), is obtained from (I) and 48% HBr. H. B.



(I.)

Dehydrogenation of phenols. IV. Reactive positions of 4 : 4′-dimethoxydiquinone and oxidative coupling of 4-ethylpyrogallol. H. ERDTMAN (Annalen, 1934, 513, 240—250).—Prolonged treatment of 4 : 4′-dimethoxydiquinone (4 : 4′-dimethoxydiphenyl-2 : 5 : 2′ : 5′-diquinone) (this vol., 184) with AcOH–conc. H_2SO_4 gives 2 : 3 : 6 : 2′ : 3′ : 6′-hexa-acetoxy-4 : 4′-dimethoxydiphenyl (I) (cf. *loc. cit.*) and (probably) 1 : 4 : 5 : 6-*tetra-acetoxy*-2 : 7-*dimethoxydiphenylene oxide* (II), m.p. 255—256°; the quinone (*A*) is probably an intermediate [addition of AcOH affords (I); rearrangement gives (II)]. Hydrolysis (EtOH–H_2SO_4) of (I) and subsequent methylation (Me_2SO_4, KOH) gives 2 : 3 : 4 : 6 : 2′ : 3′ : 4′ : 6′-*octamethoxydiphenyl*, m.p. 146—147° (5 : 5′-Br_2-derivative, m.p. 113—114°), also prepared from 4-*iodo*-1 : 2 : 3 : 5-*tetramethoxybenzene*, m.p. 52—53° [from 1 : 2 : 3 : 5-$C_6H_2(OMe)_4$, I, and HgO at 70—75°], and Cu-bronze at 230°. (II) is similarly converted into *hexamethoxydiphenylene oxide*, m.p. 126—127·5°. (I) is unaffected by prolonged treatment with AcOH–conc. H_2SO_4; 6-hydroxy-2 : 7-dimethoxydiphenylene oxide-1 : 4-quinone similarly gives (mainly) the acetate and a little 1 : 4 : 6-triacetoxy-2 : 7-dimethoxydiphenylene oxide (*loc. cit.*).



(*A*.)

4-Ethylpyrogallol (III) is oxidised [air in aq. $Ba(OH)_2$] to 4 : 5 : 6 : 4′ : 5′ : 6′-*hexahydroxy*-3 : 3′-*diethyldiphenyl*, m.p. 235—237° (decomp.) (*hexa-acetate*, m.p. 168—169°), which readily absorbs O_2 in 2*N*-NaOH or -KOH, converted by successive methylation and bromination into 2 : 2′-*dibromo*-4 : 5 : 6 : 4′ : 5′ : 6′-*hexamethoxy*-3 : 3′-*diethyldiphenyl*, m.p. 98—101°. Clemmensen reduction of 6-acetyl-4-ethylpyrogallol [from (III), AcOH, and $ZnCl_2$ at 145°] gives 4 : 6-diethylpyrogallol (*triacetate*, m.p. 106—108°), which is readily oxidised (O_2 in alkali); cryst. products could not be isolated. 1 : 2 : 3-$C_{10}H_5(OH)_3$ is oxidised (O_2 in aq. MeOH–$NaHCO_3$+Na_2CO_3) to an impure *hydroxynaphthaquinone*, m.p. 263—265° (decomp.), reductive acetylation of which affords 1 : 2 : 3-$C_{10}H_5(OAc)_3$. H. B.

Preparation and properties of hexachloro-1 : 4-naphthaquinone. V. SCHVEMBERGER and V. GORDON (J. Gen. Chem. Russ., 1934, 4, 695—703).—Hexachloro-1 : 4-naphthaquinone (I), m.p. 222—222·5°, b.p. 412—415°/758 mm., is obtained from $C_{10}Cl_8$ and conc. HNO_3, or from 1 : 4-naphthaquinone and $SbCl_5$ in presence of I. Fuming HNO_3 oxidises (I) to tetrachlorophthalic acid, H_2O has no action, aq. or EtOH–KOH yields NaCl and unidentified products, PCl_3 converts (I) into $C_{10}Cl_8$, and H_2SO_4 dissolves (I) but does not decompose it. R. T.

Photolysis of halogenated anthrahydroquinones. A. E. GOLDSTEIN [with J. H. GARDNER] (J. Amer. Chem. Soc., 1934, 56, 2130—2131).—Halogenoanthraquinones are reduced ($Na_2S_2O_4$ in 20% NaOH), the resulting solutions exposed in absence of air to light from a 500-watt lamp, and then oxidised (air); anthraquinone is thus obtained from its 1- and 2-Cl- and -Br-derivatives, whilst 1-hydroxyanthraquinone is formed from its 4-Cl-derivative. The ease of removal of halogen is: 1- > 2- and Br > Cl. H. B.

Preparations in the anthracene series. R. Scholl and K. Ziegs (Ber., 1934, 67, [*B*], 1746—1750).—1 : 8-Dichloro-2 : 7-dimethylanthraquinone (I), m.p. 196—197°, is purified with difficulty when prepared from 2 : 7-dimethylanthraquinone (I), SO_2Cl_2, and I in $PhNO_2$ and is better obtained by addition of the tetrazotised 1 : 8-$(NH_2)_2$-compound (III) to CuCl–HCl. 1 : 8-*Dichloro*-2 : 7-*di*-ω-*chloromethylanthraquinone*, m.p. 285°, is obtained by the action of Cl_2 on (II) in conc. H_2SO_4 containing I at 100°. 1 : 8-*Dichloro*-2 : 7-*di*-ω-*bromomethylanthraquinone*, m.p. 275°, from (I) and Br in $PhNO_2$ at 170°, is transformed by conc. H_2SO_4 at 130—135° into 1 : 8-dichloro-2 : 7-dialdehydoanthraquinone. Diazotisation and subsequent treatment of (III) with $KCu(CN)_3$ leads to 1 : 8-*dicyano*-2 : 7-*dimethylanthraquinone*, m.p. 272—274°, difficultly hydrolysed by 80% H_2SO_4 or conc. NaOH. *Anthraquinone*-2 : 7-*dicarboxyl chloride* is converted by *m*-xylene and $AlCl_3$ at 60—65° into 2 : 7-*di*-m-4′-*xyloylanthraquinone*, m.p. 163—164°. Oxidation of (I) with HNO_3 (*d* 1·1) at 210—220° or by pptd. MnO_2 and conc. H_2SO_4 at 55—60° gives 1 : 8-*dichloroanthraquinone*-2 : 7-*dicarboxylic acid*, m.p. 318° (decomp.) after darkening at about 300° (Me_2 ester, m.p. 193·5—194°), slowly converted by NaOH and NH_3 into the 1 : 8-$(OH)_2$- and 1 : 8-$(NH_2)_2$-compounds, respectively. Treatment of the *acid chloride* with C_6H_6 and $AlCl_3$ leads to 1 : 8-*dichloro*-2 : 7-*dibenzoylanthraquinone*, m.p. 236°, converted by NH_3–EtOH–H_2O at 170—175° into 1 : 8-*diamino*-2 : 7-*dibenzoylanthraquinone*, m.p. 266—267°. 1 : 8-*Dianilino*-, m.p. 263°, 1 : 8-*di*-p-*toluidino*-, m.p. about 240°, and 1 : 8-*diphenoxy*-, m.p. 235°, -2 : 7-*dibenzoylanthraquinone* are described.

H. W.

1 : 3 : 5 : 8-Tetrahydroxy-2-methylanthraquinone. E. H. Charlesworth and R. Robinson (J.C.S., 1934, 1531—1533).—*p*-$C_6H_4Me\cdot COCl$ and $ClSO_3H$ give a little 4-*carboxytoluene*-3-*sulphonyl chloride*, m.p. 110°. Attempts to prepare 3 : 5-dihydroxy-*p*-toluic acid (I) by the method of Mitter *et al.* (A., 1928, 764) gave only *m*-$OH\cdot C_6H_4\cdot CO_2H$. (I) (modified prep.), $+0{\cdot}5H_2O$, m.p. 260°, gives (Me_2SO_4) the Me_2 *ether*, m.p. 215°, of which with $CCl_3\cdot CH(OH)_2$ and H_2SO_4 yields 3 : 5-*dimethoxy*-4-*methyl*-α-*trichloromethylphthalide*, m.p. 133—134°, hydrolysed by hot 20% NaOH to 3 : 5-*dimethoxy*-4-*methylphthalide*-α-*carboxylic acid*, m.p. 173—174°, which with Cu chromite and quinoline at 150—160° gives 3 : 5-*dimethoxy*-4-*methylphthalide* (II), m.p. 158°. 3 : 5-Dimethoxy-*p*-toluic acid, CH_2O, and HCl give a *Cl*-compound, m.p. 131°. (II) and alkaline $KMnO_4$ afford 3 : 5-*dimethoxy*-4-*methylphthalic acid*, m.p. 195—196° (decomp.), the *anhydride*, m.p. 166°, of which with *p*-$C_6H_4(OMe)_2$ and $AlCl_3$ in CS_2 gives a product, converted directly by H_2SO_4 at 150° into 1 : 3 : 5 : 8-*tetrahydroxy*-2-*methylanthraquinone*, m.p. 276—277° (Ac_4 derivative, m.p. 223°), not identical with catenarin. R. S. C.

Hydroxy- and chloro-derivatives of 2-methylanthraquinone. G. J. Marriott and R. Robinson (J.C.S., 1934, 1631—1635).—3 : 6-Dichlorophthalic anhydride (I), *o*-$C_6H_4Me\cdot OMe$, and $AlCl_3$ give 3 : 6-*dichloro*-2-(4′-*methoxy*-3′-*methylbenzoyl*)*benzoic acid*, m.p. 182—183°, which with 10% oleum and H_3BO_3 at 130° (10 min.) or conc. H_2SO_4 and H_3BO_3 at 140—150° (15 min.) gives 5 : 8-*dichloro*-2-*methoxy*-1-(or 3-)*methylanthraquinone*, m.p. 246—247°; some demethylation also occurs to give the 2-*OH*-compound, m.p. about 298°, also obtained in poor yield from *o*-cresoldichlorophthalein, 3 : 6-dichlorophthalic acid, and H_2SO_4 at 110—115°. The above results are contrary to the statements of Walsh *et al.* (J.C.S., 1910, 97, 691). (I) and *o*-cresol with $AlCl_3$ give 3 : 6-*dichloro*-2-(2′-*hydroxy*-3′-*methylbenzoyl*)*benzoic acid* (II) (54% yield), m.p. 197° (*Ca* salt), and o-*cresol*-3 : 6-*dichlorophthalein*, m.p. 268°. (II), also obtained in 12% yield by H_3BO_3 at 160—170°, with 20% oleum and H_3BO_3 affords (max. yield 40%) 5 : 8-*dichloro*-1-*hydroxy*-2-*methylanthraquinone*, m.p. 196—197° (*Ac* derivative, m.p. 191°). This, best (poor yield) with NaOMe in MeOH at 135—145° or with Cu-bronze at 100—105°, gives 1 : 5-*dihydroxy*-2-*methylanthraquinone*, m.p. 187° (Ac_2 derivative, m.p. 220°), and, by the former method, also a little 1 : 5 : 6-$(OH)_3$-compound. Catenarin (III) with $SnCl_2$ gives the *anthrone*, $C_{15}H_{12}O_4$, decomp. 230°, the amorphous Ac_2 derivative of which by oxidation (CrO_3) and acetylation affords a little 1 : 8-*diacetoxy*-2-*acetoxymethylanthraquinone*, m.p. 182°. Absorption spectra (described) confirm the above structures. (III) is either 1 : 4 : 8- or 1 : 5 : 8-trihydroxy-2-hydroxymethylanthraquinone. R. S. C.

Tautomerism of anthraquinone-1-carboxyl chlorides. VII. Tautomerism of anthraquinone-1 : 3 : 5 : 7- and -1 : 4 : 5 : 8-tetracarboxyl chlorides. R. Scholl, K. Meyer, and A. Keller (Annalen, 1934, 513, 295—304; cf. this vol., 1104).—The $C_6H_3Me_2\cdot CO_2H$ obtained from *p*-xylene, $(\cdot COCl)_2$, and $AlCl_3$ in CS_2 at 0° (cf. Liebermann, A., 1912, i, 464) is converted ($SOCl_2$) into the chloride, b.p. 226°, which with $AlCl_3$ at 115—120° gives 1 : 3 : 5 : 7-tetramethylanthraquinone (Seer, *ibid.*, 276), oxidised [HNO_3 (*d* 1·1) at 210°] to anthraquinone-1 : 3 : 5 : 7-tetracarboxylic acid [*chloride* (I), cryst., from the acid and PCl_5 in C_6H_6], *m*-Xylene (II), (I), and $FeCl_3$ in $PhNO_2$ at 60—70° give 30% of 1 : 3 : 5 : 7-*tetra*-m-4′-*xyloylanthraquinone*, m.p. > 355° (darkens at 315°), whilst (I), PhCl, and $AlCl_3$ at 75° afford 28% of 1 : 3 : 5 : 7-tetra-*p*-chlorobenzoylanthraquinone (not investigated) and 13% of 3 : 7-*di*-p-*chlorobenzoyl*-9 : 10-*di*-p-*chlorophenylanthracene*-1 : 5-*dicarboxylic acid* (III), m.p. > 350° (formed by reduction of the intermediate dilactone of 9 : 10-dihydroxy-3 : 7-di-*p*-chlorobenzoyl-9 : 10-di-*p*-chlorophenyl-9 : 10-dihydroanthracene-1 : 5-dicarboxylic acid). (III) is converted by conc. H_2SO_4 at 50° into the blue 5′ : 5″-dichloro-3 : 7-di-*p*-chlorobenzoyl*hetero*coerdianthrone (7′ : 7″) (for structure of parent compound, see A., 1932, 617). 5 : 8-*Dicyano*-1 : 4-*dimethylanthraquinone*, m.p. 309° (darkening) [from the 5 : 8-Cl_2-derivative, m.p. 313—314° (lit. 244°), and CuCN in $CH_2Ph\cdot CN$], is hydrolysed (dil. HCl at 200°) to 1 : 4-*dimethylanthraquinone*-5 : 8-*dicarboxylic acid*; with dil. HNO_3 at 200—210°, *anthraquinone*-1 : 4 : 5 : 8-*tetracarboxylic acid* [*chloride* (IV)] results. (II), (IV), and a little $FeCl_3$ give 49% of 1 : 4 : 5 : 8-*tetra*-m-4′-*xyloylanthraquinone*, m.p. 320° (darkening), and about 35% of an inseparable mixture of lactones. 1 : 4 : 5 : 8-*Tetra*-p-*toluoylanthraquinone*, m.p. 350° (slow decomp.), is obtained in 56% yield from (IV), PhMe, and $AlCl_3$ in cold $PhNO_2$. The reactions with (I) and (IV) often give inseparable mixtures of CO-, lactonic, and ketolactonic acids, ketolactone, tetraketone, and the original acid.

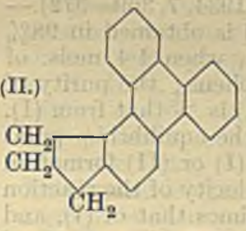
p-C_6H_4ClMe, $(\cdot COCl)_2$, and $AlCl_3$ in CS_2 at room temp. give 2-chloro-5-methylbenzoic acid (40%) [chloride, b.p. 165—167°/85 mm., which could not be converted (method: Seer, *loc. cit.*) into a dichlorodimethylanthraquinone] [oxidised ($KMnO_4$) to 4 : 1 : 3-$C_6H_3Cl(CO_2H)_2$] and a *dichlorodimethylbenzophenone*, m.p. 70°. H. B.

Preparation of ketols by means of mixed aminomagnesium compounds. J. Cologne (Bull. Soc. chim., 1934, [v], **1**, 1101—1114; cf. A., 1932, 499; 1933, 698, 1277).—The condensation proceeds best with 2 mols. of ketone and 1 mol. of $NPhMe\cdot MgBr$ (I); Mg compounds derived from $NHEt_2$ and piperidine are unsuitable. The following are described: γ-methylheptan-γ-ol-ε-one, b.p. 85—86°/14 mm. (semicarbazone, m.p. 124—125°), from COMeEt, βδθ-trimethylnonan-δ-ol-ζ-one, b.p. 81—82°/2 mm. (*semicarbazone*, m.p. 135—136°), from $COMeBu^{\beta}$, the *semicarbazone*, m.p. 197°, of δ-methyl-γ-ethylheptan-γ-ol-ε-one from $COEt_2$, and *γεη-trimethyl-δ-ethylnonan-δ-ol-ζ-one*, b.p. 104—105°/3 mm., from δ-methylhexan-γ-one. Treatment of the product from fluorenone and (I) with pinacolin, $COEtBu^{\gamma}$, $COPr^{\beta}_2$, or COPhMe gives δ-(*9-hydroxy-9-fluorenyl*)-ββ-*dimethylbutan-γ-one*, m.p. 95°, δ-(*9-hydroxy-9-fluorenyl*)-ββ-*dimethylpentan-γ-one*, m.p. 92°, δ-(*9-hydroxy-9-fluorenyl*)-βδ-*dimethylpentan-γ-one*, m.p. 127°, and ω-(*9-hydroxy-9-fluorenyl*)-*acetophenone*, m.p. 112°, respectively, in yields of 60—80%. An intermediate ketone–aminomagnesium compound is formed. F. S. H. H.

Perylene and its derivatives. A. Zinke, F. Stimler, and E. Reuss (Monatsh., 1934, **64**, 415—425).—The yield of perylene-3 : 10-quinone is greatly improved by adding MnO_2 to the mixture of α-dinaphthol and $AlCl_3$ at 160—170° and oxidising the crude product (I) with dil. CrO_3. (I) is converted into perylene, m.p. 273°, when distilled with Zn dust. 2 : 11-*Dihydroxyperylene*-3 : 10-*quinone* (II) is obtained from β-naphthaquinone (III) and $AlCl_3$ at 140—150° or, similarly, from 2-dinaphthyldiquinone, m.p. 310°, prepared by warming (III) with dil. H_2SO_4 and oxidation of the product with $K_2Cr_2O_7$. Treatment of (II) with H_2SO_4 and MnO_2 gives *phenanthrene-1 : 8 : 9 : 10-tetracarboxylic dianhydride*. (II) and BzCl in boiling $PhNO_2$ afford 2 : 11-*dibenzoyloxyperylene-3 : 10-quinone*, m.p. 317°, whilst reduction and subsequent benzoylation of (II) yields 2 : 3 : 10 : 11-*tetrabenzoyloxyperylene*, m.p. 278—279°. (II) and *o*-$C_6H_4(NH_2)_2$ in boiling $PhNO_2$–AcOH give the *diazine*, $C_{32}H_{18}N_4$. H. W.

Compounds of petroleum. III. Mode of formation of naphthenic acids. J. von Braun and H. Wittmeyer (Ber., 1934, **67**, [*B*], 1739—1746).—The possibility is discussed that naphthenic acids (I) are formed by oxidation during the refining of petroleum by acid and alkali. Petroleum is therefore exhaustively extracted with liquid SO_2 and extract (II) and residue (III) are treated separately with alkali. The ratio of (I) in (II) and (III) is 3 : 1, but the assumption that this is due to acids differing in kind is not warranted. The isolation of individuals from (II) and (III) is impossible, but comparison of the acid mixtures of similar b.p. from (II) and (III) by conversion into the amines and NH_4 bases followed by degradation of the latter shows that *tert.* dimethylated amines and olefines (IV) are produced in similar amount. Oxidation of (IV) affords ketones and acids (V) in similar proportion and of like physical properties, and from (V) similar amines are derived. The pre-existence of (I) in petroleum is therefore established. Treatment of (I) from various sources with SO_2 at −10° to −20° does not lead to a clean separation into groups of constitutively closely related individuals. H. W.

Strophanthin. XXXI. Dehydrogenation of strophanthidin. R. C. Elderfield and W. A. Jacobs (J. Biol. Chem., 1934, **107**, 143—154; cf. this vol., 657).—The products obtained by dehydrogenation of strophanthidin (I) depend on the conditions; caution is therefore necessary in interpreting the results. (I) with Se at 320—340° yields a hydrocarbon, $C_{18}H_{16}$, m.p. 125—126° (corr.) [picrate, m.p. 118—119°; $C_6H_3(NO_2)_3$ derivative, 148—150°; $C_6H_2Me(NO_2)_3$ derivative, m.p. 93—94°], identical with that isolated by Diels *et al.* (A., 1928, 169). Preliminary pyrolysis of (I) at 340—360°, followed by Se dehydrogenation at 320—340°, yields a small amount of a mixture (?) of hydrocarbons, m.p. 123—124° [picrate, m.p. 128—130°; $C_6H_3(NO_2)_3$ derivative, m.p. 150—152°], yielding a little of a quinone on oxidation. Dehydrogenation of (I) at 340—360° and fractional crystallisation of the product yields: (*a*) a *hydrocarbon*, $C_{21}H_{16}$, m.p. 295—297°, possibly *cyclo*pentanotriphenylene (II); (*b*) Diels' hydrocarbon, $C_{18}H_{16}$; (*c*) a *hydrocarbon* (III), $C_{16}H_{14}$, m.p. 124—125° (*picrate*, m.p. 140—141°), yielding, on oxidation, a *quinone*, $C_{16}H_{12}O_2$, m.p. 208—209° (*quinoxaline*, m.p. 150°); and (*d*) a *hydrocarbon* (IV), $C_{16}H_{14}$, m.p. 127° (*picrate*, m.p. 126—127°; $C_6H_3(NO_2)_3$ *derivative*, m.p. 151—153°), yielding on oxidation a *quinone*, m.p. 203—205° (*quinoxaline*, m.p. 168—171°). (III) and (IV) are regarded as di-methyl- or -ethyl-phenanthrenes; their formation, and that of (II), is discussed. *iso*-Strophanthic acid, after preliminary decarboxylation at 200°, on dehydrogenation with Se at 320—340° yields a mixture from which a *hydrocarbon*, $C_{16}H_{14}$ (?), m.p. 140—142° [*picrate*; $C_6H_3(NO_2)_3$ *derivative*, m.p. 128—129°], can be isolated. H. N. R.



(II.)

Grayanotoxin, the active principle of *Leucothoe grayana*. I. S. Miyajima and S. Takei (Bull. Inst. Phys. Chem. Res. Japan, 1934, **13**, 1234—1244).—From *L. grayana*, Maxim., were isolated *p*-methoxycinnamic acid and *grayanotoxin-I* (I), m.p. 249°, *-II* (II), $C_{20}H_{32}O_5$, m.p. 190—191°, and *-III* (III), m.p. 210—235°. These are not alkaloids or glucosides. Deacetylation of (I), $C_{20}H_{30}O_2(OH)_3\cdot OAc$, gives (III), $C_{20}H_{34}O_6,0\cdot 5H_2O$. The toxicity to fish is in the order (III)>(I)>(II), it being < that of rotenone or pyrethrin. F. O. H.

Resins of mastic and Manila elemi. P. Casparis and P. Naef (Pharm. Acta Helv., 1934, **9**, 19—23; Chem. Zentr., 1934, i, 3350).—α-Masticoresin is hydrolysed by KOH–EtOH to *α-masticoresinol* and *α-masticoresinic acid* (both gums); β-masticoresin resists hydrolysis. The following are described: *menthyl*, m.p. 70—72°, and *amyrin anthraquinone*-2-*carboxylate*, m.p. 263—265°, and *amyrin* 3 : 5-*dinitrobenzoate*, m.p. 220—221·5° (*α-naphthalide*, m.p. 202—203°). H. N. R.

Use of *l*-menthoxyacetyl chloride for resolution of amino-acids. D. F. Holmes and R. Adams (J. Amer. Chem. Soc., 1934, **56**, 2093—2094).—*l*-Menthoxyacetyl chloride (I) and *dl*-NH_2·CHR·CO_2H (II) in 5% NaOH give mixtures (separable by crystallisation from 60% EtOH or a 3 : 1 mixture of high-boiling petroleum and EtOAc) of the diastereoisomeric *l*-menthoxyacetyl derivatives; subsequent hydrolysis (20% HBr–EtOH) affords *d*- and *l*-(II) (when R is Me, Pr^{β}, and Ph). The following are described: l-*menthoxyacetyl-glycine*, m.p. 155—156°, -d- and -l-*alanine*, m.p. 147—148° and 117—118°, respectively, -d- and -l-*valine* (III), m.p. 156—157·5° and 93—96°, respectively, -d- and -l-*phenylglycine* (IV), m.p. 162° and 113—116°, respectively, and -dl-*phenylalanine*, m.p. 100—101°; β-$C_{10}H_7$ l-*menthoxyacetate*, m.p. 108—109·5° [from β-$C_{10}H_7$·OH and (I) in C_5H_5N]; l-*menthoxyacet*-p-*nitroanilide*, m.p. 106; *l*-menthoxyacetamide, m.p. 94—95° (lit. 93°). The *l*-(II) obtained from (III) and (IV) are optically impure. H. B.

Conversion of camphene into *iso*bornyl acetate and formate. V. E. Tischtschenko and G. A. Rudakov (J. Appl. Chem. Russ., 1934, 7, 369—372).—At 15—20° *iso*bornyl acetate (I) is obtained in 98% and formate (II) in 94% yield, when 1·4 mols. of acid are taken per mol. of camphene; the purity of the *iso*borneol obtained from (II) is > that from (I). The reaction is reversible, and the equilibrium point is displaced in the direction of (I) or (II) formation with diminishing temp. The velocity of the reaction of formation of (II) is 10—20 times that of (I), and in both cases varies inversely with the concn. of acids. R. T.

Optical rotation. Rotatory powers of acylbiscamphorquinonehydrazones and camphorylthiocarbamylhydrazides and attempts to prepare compounds possessing abnormal rotation. M. S. Kotnis, B. S. Rao, and P. C. Guha (J. Indian Chem. Soc., 1934, **11**, 579—593).—Condensation of camphorquinone (I) with the dihydrazides of the dibasic acids gives s-*carbonyl*-, m.p. 225°, $[\alpha]_{5780}$ 288·6°, $[\alpha]_{5461}$ 333·4°, s-*oxalyl*-, m.p. 249°, $[\alpha]_{5780}$ 256·1°, $[\alpha]_{5461}$ 298·6°, *malonyl*-, m.p. 185°, $[\alpha]_{5780}$ 251·3°, $[\alpha]_{5461}$ 272·1°, *succinyl*-, m.p. 275°, *glutaryl*-, m.p. 219°, $[\alpha]_{5780}$ 213·7°, $[\alpha]_{5461}$ 261·2°, *adipoyl*-, m.p. 220°, $[\alpha]_{5780}$ 195·4°, $[\alpha]_{5461}$ 260·7°, *terephthaloyl*-, m.p. 279°, and iso*phthaloyl-biscamphorquinonehydrazone*, m.p. 274°. The hydrazides with camphorylthiocarbimide give *carbonyl*-, m.p. 208°, $[\alpha]_{5780}$ 28·2°, $[\alpha]_{5461}$ 32·9°, *oxalyl*-, m.p. 245°, $[\alpha]_{5780}$ 30·4°, $[\alpha]_{5461}$ 50·7°, *malonyl*-, m.p. 185°, $[\alpha]_{5780}$ 29·8°, $[\alpha]_{5461}$ 50·7°, *succinyl*-, m.p. 176°, $[\alpha]_{5780}$ 39·7°, $[\alpha]_{5461}$ 50·5°, *glutaryl*-, m.p. 201°, $[\alpha]_{5780}$ 12·4°, $[\alpha]_{5461}$ 18·6°, and *adipoyl-biscamphorylthiocarbamylhydrazide*, m.p. 207°, $[\alpha]_{5780}$ 33·4°, $[\alpha]_{5461}$ 42·4°. The vals. of [α] and [*M*] and of the dispersions are discussed and compared with the results of Frankland (J.C.S., 1912, **101**, 654) and Hilditch (*ibid.*, 1909, **95**, 1578). Attempts to prepare a series of compounds for which [*M*] might be exalted (cf. this vol., 659) failed. Neither (I) nor its hydrazone (II) condenses with *p*-NH_2·C_6H_4·CHO (III). (II) with *p*-NHAc·C_6H_4·CHO (IV) gives p-*acetamidobenzylidenecamphorquinone-α-hydrazone*, m.p. 232°, $[\alpha]_D$ 95·85° (*oxime*, m.p. 183°, $[\alpha]_D$ 546·3°; *semicarbazone*, m.p. 195°, $[\alpha]_D$ 102·4°; *phenylhydrazone*, m.p. 205°, $[\alpha]_D$ 150·9°), but on hydrolysis (KOH) this gives (IV) (*oxime*, m.p. 207°) and camphor or (dil. acid) azocamphanone and (III). Neither deacetylation of *terephthaloyldi*-p-*acetylphenylenediamine*, m.p. 350° [from *p*-NH_2·C_6H_4·NHAc and *p*-$C_6H_4(COCl)_2$ (V) in AcOH] nor reduction of *terephthaloyldi*-p-*nitroanilide*, m.p. 295° [from (V) and *p*-NO_2·C_6H_4·NH_2] or NN′-*di*-p-*azobenzeneterephthaloyldiamide* [from (V) and *p*-NH_2·C_6H_4·N:NPh] gives the desired diamine. Reduction (Sn–HCl) of 4 : 4′*dinitrodi-α-naphthylcarbamide*, m.p. 275° (from 4-nitro-α-naphthylamine and Ph_2CO_3 at 190—210°), gives the *hydrochloride* (VI) of 4 : 4′-*diaminodi-α-naphthylcarbamide*, which with KCNO affords 4 : 4′-*dicarbamidodi-α-naphthylcarbamide*. (I) does not condense with 4-*p*-aminobenzeneazo-α-naphthylamine or 2 : 7-diamino-9 : 10-phenanthraquinol (modified prep.) and with (VI) it gives tars. (All [α] are + and in EtOH.) F. S. H. H.

Essential oils from East Africa.—See B., 1934, 987, 988.

Essential oil of *Calythrix virgata*.—See B., 1934, 988.

Action of mixed organo-magnesium compounds on *N*-disubstituted amides of β-2-furylacrylic acid. N. Maxim and I. Zugravescu (Bull. Soc. chim., 1934, [v], **1**, 1087—1099).—Grignard reagents react with the above amides to give saturated *N*-disubstituted amides in yields of 70—75% (cf. A., 1906, i, 96). β-2-Furylacryloyl chloride in C_6H_6 with the corresponding *sec.*-amines (2 mols.) gives the N-*diethylamide* (I), b.p. 186°/15 mm., N-*methylanilide* (II), m.p. 117·5°, N-*ethylanilide* (III), b.p. 215°/11 mm., m.p. 60°, and N-*diphenylamide* (IV), m.p. 181·5°, of the acid. (IV) with MgEtBr, $MgPr^{\alpha}Br$, and MgPhBr gives β-(2-*furyl*)-*valeroyl*-, b.p. 253°/15 mm., -*hexoyl*-, b.p. 241°/10 mm., m.p. 47°, and -β-*phenylpropionyl-diphenylamide*, b.p. 291°/12 mm., m.p. 83°, respectively, which on hydrolysis (20% KOH) afford β-2-*furyl-valeric*, b.p. 145°/17 mm. (*Et* ester, b.p. 114°/18 mm.), -*hexoic*, b.p. 148°/11 mm. (*Et* ester, b.p. 126°/16 mm.), and -β-2-*phenylpropionic acid*, m.p. 105° (*chloride*, b.p. 88°/31 mm.; *amide*, m.p. 137·5°; *Et* ester, b.p. 172°/15 mm.). Similarly (I), (II), and (III) with MgEtBr yield the *diethylamide*, b.p. 196°/41 mm., the *methyl*-, b.p. 130°/3 mm., and *ethyl-anilide*, b.p. 211°/27 mm., of β-2-furylvaleric acid and with MgPhBr the *diethylamide*, b.p. 218°/23 mm., and the *methyl*-, b.p. 213°/11 mm., and *ethyl-anilide*, b.p. 236°/14 mm., of β-2-furyl-β-phenylpropionic acid, respectively. These amides cannot be hydrolysed by KOH, and acid hydrolysis gives resinous products. F. S. H. H.

Synthesis of *p*-substituted β-furyl-β-alkyl- and β-furyl-β-aryl-propiophenones. N. Maxim and J.

Angelesco (Bull. Soc. chim., 1934, [v], 1, 1128—1133; cf. A., 1933, 281).—*Furfurylidene*-p-*methoxyacetophenone*, m.p. 75°, with MgEtBr and $MgPr^{a}Br$ affords p-*anisyl* β-2-*furyl*-n-*butyl ketone*, b.p. 218°/14 mm. (*semicarbazone*, m.p. 161°), and p-*anisyl* β-2-*furyl*-n-*amyl ketone*, b.p. 220°/12 mm. (*semicarbazone*, m.p. 149°). p-*Chloro*-, b.p. 200°/10 mm. (*semicarbazone*, m.p. 122°), and p-*bromo-phenyl* β-2-*furyl*-n-*amyl ketone*, b.p. 215°/8 mm. (*semicarbazone*, m.p. 105°), p-*chloro*-, b.p. 242°/15 mm., m.p. 79°, and p-*bromo-phenyl* β-2-*furyl*-β-*phenylethyl ketone*, b.p. 268°/6 mm., m.p. 78°, and the *semicarbazone*, m.p. 125°, of *p*-tolyl β-2-furyl-δ-methyl-*n*-amyl ketone are described. *p*-Substituents in the C_6 ring favour the reaction in the order $Me < Cl < Br < OMe$. F. S. H. H.

Action of phosphorus pentahalides and thionyl chloride on saturated and unsaturated αδ-diketones and 2 : 5-diphenylfurans. R. E. Lutz and F. N. Wilder (J. Amer. Chem. Soc., 1934, 56, 2145—2149).—3 : 4-Dichloro-2 : 5-diphenylfuran (I) is obtained in 35—95% yield from the following compounds and PCl_5 at 100°: 2 : 5-diphenyl- (II), and 3-chloro- (III), 3-acetoxy- (IV), 4-chloro-3-acetoxy- (V), and 3 : 4-diacetoxy-2 : 5-diphenyl-furan; αβ-dibenzoylethylene oxide (VI); *dl*- and *meso*-αβ-dichloro-αβ-dibenzoylethane; αβ-dibenzoylethyl chloride; *trans*-αβ-dibenzoylethylene (VII); *trans*-α-chloro-αβ-dibenzoylethylene. (I) is also obtained from the following compounds and PCl_5 at 25—40°: α-chloro-β-hydroxy-αβ-dibenzoylethane (VIII); COPh·CO·CH:CPh·OR (R=Me or Et); *cis*-α-chloro-αβ-dibenzoylethylene (IX); α-hydroxy-αβ-dibenzoylethylene (X) and its Me ether (XI); *α-chloro-γδ-diketo-αδ-diphenyl-*Δ^{α}*-butene*, m.p. 133—133·5° [prepared from (X) or (XI) and $SOCl_2$]. (IV) and PCl_5 at 25—40° give (V); αβ-dibenzoylethyl alcohol (XII) and its Me ether similarly afford α-chloro-αβ-dibenzoylethane (XIII), whilst *cis*- and *trans*-dibenzoylethylenes give (III). 3 : 4-Dibromo-2 : 5-di-*p*-bromophenylfuran is formed from (II), (IV), (VII), and $(\cdot CH_2Bz)_2$ with PBr_5 at 100° and from (XI) and COPh·CO·CH:CPh·OEt at 25—40°. (I) is also obtained from (VI), (VIII), or (IX) and $SOCl_2$; (VII) and (XII) similarly give (XIII). (I), PCl_5, and $POCl_3$ give *cis*-αβ-dichloro-αβ-dibenzoylethylene. H. B.

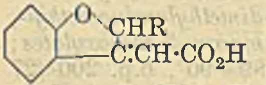
Furan dyes. I. O. Aschan and A. Schwalbe (Finska Kem. Medd., 1934, 43, 48—54, and Ber., 1934, 67, [*B*], 1830—1833).—Furfuraldehyde and NH_2Ph,HCl give the compound, NHPh·CH:CH·CH:C(OH)·CH:NPh,HCl (I), transformed by Ac_2O and NaOAc under defined conditions into *δ-acetanilido-α-acetoxy-*$\Delta^{\alpha\gamma}$*-pentadiene* (II), NPhAc·CH:CH·CH·C(OAc)·CHO, m.p. 184°, and two Ac_1-*aldehydes*, m.p. 132° (III), and m.p. (indef.) 145° (IV), for which the respective structures, NHPh·CH:CH·CH:C(OAc)·CHO and NPhAc·CH:CH·CH:C(OH)·CHO, are available. (II) gives a *semicarbazone*, m.p. 240°, and *phenylhydrazone*, m.p. 206°; with NH_2Ph,HCl in H_2O it affords the *anil hydrochloride*, NPhAc·CH:CH·CH:C(OAc)·CH:NPh,HCl, m.p. 169—170°. (III) and p-$C_6H_4Me\cdot NH_2$,HCl or NH_2Ph,HCl yield, respectively, *dyes*, m.p. 157—160° (decomp.) and about 157° (decomp. after darkening at 140—150°. A *dye* from (IV) and NH_2Ph,HCl is described. Direct acetylation of (I) under modified conditions gives a *product*, $C_{19}H_{19}O_2N_2Cl$, m.p. 154°, unchanged by boiling Ac_2O. H. W.

Carboxylated aminocoumarans. Gomez (J. Pharm. Chim., 1934, [viii], 20, 337—342).—By successive treatments with Br and NaOEt, *Me* 2-*acetoxy*-3-*allylbenzoate*, b.p. 187—190°/30 mm. (from the OH-ester), is converted into *Me* 1-*bromomethylcoumaran*-6-*carboxylate*, b.p. 177°/0·912 mm., which gives *Me* 1-*diethylaminomethylcoumaran*-6-*carboxylate*, b.p. 184°/< 1 mm. [*hydrochloride*, m.p. 182°; *amide*, m.p. 113° (*hydrochloride*, m.p. 207—208°); *acid*], with $NHEt_2$ at 120—130°. Derivatives of the m- and p-*carboxylic acids* are prepared by similar methods, the following new *Me* esters being described: 3-*allyloxybenzoate*, b.p. 167—170°/30 mm.; 3-*hydroxy*-4-*allylbenzoate*, m.p. 61°, b.p. 195°/30 mm. (*acetate*, b.p. 93—95°/30 mm.); 1-*bromomethyl*-, b.p. 167°/0·992 mm., 1-*diethylaminomethyl*-, b.p. 167°/1·312 mm., 1-*dimethylaminomethyl*-, b.p. 175—180°/1·28 mm., -*coumaran 5-carboxylates*; 4-*hydroxy*-3-*allylbenzoate*, m.p. 89—90°, b.p. 200°/27 mm. (*acetate*, b.p. 195—196°/28 mm.), 1-*bromomethyl*-, b.p. 165—169°/0·976 mm., 1-*diethylamino*-, b.p. 158°/0·736 mm. (*hydrochloride*, m.p. 147—148°; free *acid*, m.p. 141°), -*coumaran* 4-*carboxylates*. In their pharmacological behaviour the carboxylated derivatives resemble the parent aminocoumarans, but in addition they show hyperthermic and local anæsthetic properties (cf. A., 1933, 1168). S. C.

Pyrone series. II. Chromones and coumarins derived from 2-hydroxy-4-methoxyaceto- and -propio-phenones. I. M. Heilbron, D. H. Hey, and B. Lythgoe (J.C.S., 1934, 1581—1583).—NaOPr, Pr_2O, and 2-hydroxy-4-methoxyacetophenone (I) give 7-methoxy-3 : 4-dimethylcoumarin and a little of the 7-OH-compound, whilst NaOBu and Bu_2O with (I) form 7-methoxy-4-methyl-3-ethylcoumarin, hydrolysed to 2 : 4-*dimethoxy*-β-*methyl*-α-*ethylcinnamic acid*, m.p. 127·5°, and some 7-methoxy-2-propylchromone. NaOPr, Pr_2O, and 2-hydroxy-4-methoxypropiophenone yield 7-methoxy-3-methyl-2-ethylchromone and some 7-*methoxy*-3-*methyl*-4-*ethylcoumarin*, m.p. 89°, whilst NaOBu and Bu_2O similarly afford 7-*hydroxy*-3-*methyl*-2-*propylchromone*, m.p. 212°, its OMe-derivative (chiefly), and some 7-*methoxy*-3 : 4-*diethylcoumarin* (?), m.p. 63°. The product depends on the ketone, the Me ketone giving chiefly the coumarin and the Et ketone the chromone. F. R. S.

4-Bromomethylcoumarins. Synthesis from phenols and γ-bromoacetoacetic ester. B. B. Dey and Y. Sankaranarayanan (J. Indian Chem. Soc., 1934, 11, 687—689).—Condensation of $CH_2Br\cdot CO\cdot CH_2\cdot CO_2Et$ with *m*-cresol in presence of H_2SO_4 affords 7-methyl-4-bromomethylcoumarin, identical with a specimen prepared by bromination of 7-methylcoumarin-4-acetic acid (see following abstract); similar condensation with α- and β-$C_{10}H_7\cdot OH$ gives, respectively, 4-*bromomethyl*-α- (*loc. cit.*) and -β-*naphthapyrone*, m.p. 197°, hydrolysed by 2*N*-KOH, respectively, to α-, m.p. 162°, and β-3-*naphthodihydrofurylideneacetic acid*, m.p. 172°. J. W. B.

Action of chlorine and bromine on coumarin-4- and coumarin-3-acetic acids: coumarin-3- and -4-halogenoacetic acids and 4-halogenomethylcoumarins. B. B. Dey and (Miss) K. Radhabai (J. Indian Chem. Soc., 1934, **11**, 635—650).—Halogenation of coumarin-4-acetic acids in AcOH at 100° gives the 4-halogenoacetic acids together with 4-halogenomethylcoumarins, which are also obtained on heating the halogeno-acids to the m.p. Less decarboxylation occurs with the chloro- than with the bromo-acids. Addition of halogen to the double linking of the pyrone ring is observed only in the case of (XII). The position of the halogen is determined thus: (*a*) oxidation yields halogen-free salicylic acid derivatives; (*b*) boiling alkali completely removes the halogen and gives 1-carboxy-2-coumaranylidene- (I) and 2-coumaranylidene-acetic acids (II) (isomeric with 2-methylcoumarilic acids derived similarly from the 3-halogeno-4-methylcoumarins), respectively. The acids of type (II) are readily reduced, but could not be oxidised to the corresponding ketones. All attempts to replace halogen in 4-halogenomethylcoumarins by CN, OH, NH_2, or NHPh, or to prepare Grignard compounds failed. 7-Methylcoumarin-4-acetic acid is converted into 7-*methylcoumarin*-4-*bromoacetic acid* (III), m.p. 223° (*Me*, m.p. 162°, and *Et* ester, m.p. 144°), and 7-*methyl*-4-*bromomethylcoumarin* (IV), m.p. 236°. (III) and (IV) give rise to 5-*methyl*-1-*carboxy*- (V), m.p. 231° (Me_2, m.p. 83°, and Et_2 ester, m.p. 118°), and 5-*methylcoumaranylidene*-2-*acetic acid* (VI), m.p. 107° [*anilide*, m.p. 161° (*Ba*, *Cu*, and *Ag* salts; *Me* and *Et* esters)], respectively. (VI) with H_2 and PtO_2 in EtOH gives 5-*methylcoumaran*-2-*acetic acid*, m.p. 130°. (IV) in $COMe_2$ is reduced (Zn–Cu) to 4 : 7-dimethylcoumarin, m.p. 130°, and oxidised ($KMnO_4$) to *m*-hydroxytoluic acid. Similarly 7-*methylcoumarin*-4-*chloroacetic acid*, m.p. 170° (decomp.) (*Me*, m.p. 160°, and *Et* ester, m.p. 158°), gives rise to 7-*methyl*-4-*chloromethylcoumarin*, m.p. 214°, (V), and (VI); 6-*methylcoumarin*-4-*bromoacetic acid*, m.p. 168° (decomp.) (*Me*, m.p. 170°, and *Et* ester, m.p. 146°), gives 6-*methyl*-4-*bromomethylcoumarin* (VII), m.p. 177°, 4-*methyl*-1-*carboxy*- (VIII), m.p. 244° (Me_2, m.p. 102°, and Et_2 ester, m.p. 182°), 4-*methyl*-2-*coumaranylidene-acetic acid* (IX), m.p. 104°, and *p*-hydroxytoluic acid; 6-*methylcoumarin*-4-*chloroacetic acid* (X), m.p. 162° (decomp.) (*Me*, m.p. 156°, and *Et* ester, m.p. 146°), gives 6-*methyl*-4-*chloromethylcoumarin* (XI), m.p. 149°, (VIII) and (IX) [(X), (XI), and (VIII) were incorrectly formulated by Dey, J.C.S., 1915, **107**, 1606]; 7-*methoxycoumarin*-4-*bromoacetic acid*, m.p. 168° (decomp.), gives 7-*methoxy*-5-*bromomethylcoumarin*, m.p. 204°, and 5-*methoxy*-2-*coumaranylideneacetic acid*, m.p. 126°; *coumarin*-4-*bromoacetic acid*, m.p. 135° (decomp.), gives 4-*bromomethylcoumarin*, m.p. 176°, and 2-*coumaranylidene-acetic acid*, m.p. 93°; βα-5 : 6-*naphthapyrone*-4-*bromoacetic acid*, m.p. 190° (decomp.), gives 4-*bromomethyl*-βα-5 : 6-*naphthapyrone*, m.p. 197°, *dihydro*-βα-4 : 5-*naphthafuranylidene*-3-*acetic acid*, m.p. 130° (*Ag* salt), and 1-hydroxy-2-naphthoic acid. Halogenation of αβ-5 : 6-naphthapyrone-4-acetic acid (XII) affords 3-*bromo*- (XIII), m.p. 188° (decomp.) (*Me*, m.p. 172°, and *Et* ester, m.p. 139°), and 3-*chloro*-αβ-5 : 6-*naphthapyrone*-4-*acetic acid* (XIV), m.p. 152° (decomp.) (*Et* ester, m.p. 134°), and decarboxylation of these acids gives 3-bromo-, m.p. 146° (lit. 145°), and 3-chloro-4-methyl-αβ-5 : 6-naphthapyrone (XV) (this vol., 1008). (XIII) and (XIV) with hot alkali give 2-*carboxy*-αβ-4 : 5-*naphthafuran*-3-*acetic acid*, m.p. 252° (decomp.) (Me_2, m.p. 158°, and Et_2 ester, m.p. 104°); (XV) gives 4-methyl-βα-2 : 3-naphthafuran-5-carboxylic acid, m.p. 242° (lit. 240°), and the coumarinic acid. Bromination of coumarin-3-acetic acid gives (probably) the -3-*bromoacetic acid*, m.p. 200° (*Me* ester, m.p. 94°), which could not be decarboxylated; alkali converts it into a substance, m.p. 142°, formulated as *benzopyran*-2-*carboxylic acid* (*Ag* salt). F. S. H. H.



(I) R=CO_2H. (II) R=H.

Xanthen group. E. A. H. Roberts and R. Robinson (J.C.S., 1934, 1650—1651).—1 : 3 : 6 : 8-Tetrahydroxyxanthylium chloride (I) and alkaline $Na_2S_2O_4$ yield 1 : 3 : 6 : 8-*tetrahydroxyxanthen*, converted by Br into a *tribromotetrahydroxyxanthylium bromide*, but oxidised by chloranil to (I). Chloranil is useful as an oxidising agent for leuco-derivatives in the xanthylium salt and similar series. F. R. S.

Syntheses of flavones containing the methylphloroglucinol nucleus. S. Furukawa (Bull. Inst. Phys. Chem. Res. Japan, 1934, **13**, 1098—1107).—Methylphloroglucinol and MeCN (Hoesch) afford *methylphloroacetophenone* (I), m.p. 211—212°, which with Bz_2O and NaOBz followed by hydrolysis gives 6(or 8)-, m.p. 251·5—252° (Ac_2 derivative, m.p. 180·5—181°), and 8(or 6)-*methylchrysin*, m.p. 308—310° (Ac_2 derivative, m.p. 196·5—197·5°). Similarly, (I) with anisic anhydride gives *methylacacetins*, m.p. 190·5—191° [Ac_3 and $(OMe)_3$-derivatives, m.p. 234—235° and 200—201°, respectively], 293° [Ac_3 and $(OMe)_3$-derivatives, m.p. 198—200° and 194—195°, respectively], and 325° (decomp.) [Ac_3 and $(OMe)_3$-derivatives, m.p. 213—215° and 226·5—227·5°, respectively]. J. L. D.

Constitution of tannins. III. Hemlock tannin. Synthesis of bis-(7 : 8 : 3′ : 4′-tetrahydroxy)flavpinacol. A. Russell and J. Todd (J.C.S., 1934, 1506—1508; cf. this vol., 416, 1107).—Gallacetophenone tribenzoate and protocatechualdehyde dibenzoate in dry EtOAc at 0° give with HCl during 60 hr. 2 : 3 : 4 : 3′ : 4′-*pentabenzoyloxychalkone*, m.p. 85° after sintering, hydrolysed by KOH in N_2 to 2 : 3 : 4 : 3′ : 4′-*pentahydroxychalkone*, m.p. 233°, which is reduced (Zn–HCl) in EtOH to amorphous *bis*-(7 : 8 : 3′ : 4′-*tetrahydroxy*)*flavpinacol* (I), which has the same percentage composition and properties as hemlock tannin (II) (prep. described). (II) with alkali affords no *s*-$C_6H_3(OH)_3$, which supports (I) rather than bis-(5 : 7 : 3′ : 4′-tetrahydroxy)flavpinacol with which (I) is very similar qualitatively. J. L. D.

Synthesis of 5-hydroxyflavone. S. Sugasawa (J.C.S., 1934, 1483—1484).—See this vol., 1107.

Attempted flavonol synthesis. E. H. Charlesworth and R. Robinson (J.C.S., 1934, 1651—1652).—*o*-Vanillin and ω-3 : 4-triacetoxyacetophenone condense to 3 : 3′ : 4′-*trihydroxy*-8-*methoxyflavylium chloride* $(+H_2O)$. *o*-Vanillaldoxime with Ac_2O at room temp. gives an *Ac* derivative, m.p. 101° (oximino-group acetylated), whilst with AcCl it forms a Ac_2 derivative, m.p. 100°. The Ac_2 derivative with boiling Ac_2O affords *o-vanillonitrile*, m.p. 61°, which does not condense with ω : 4-dihydroxyacetophenone.

F. R. S.

Derivatives of hydroxyquinol, including a synthesis of pyrylium salts of anthocyanidin type. XXII. (Miss) M. Healey and R. Robinson (J.C.S., 1934, 1625—1631).—2 : 4 : 5-Trihydroxybenzaldehyde (I) gives the Ac_3 derivative, m.p. 115°, and a 4-*OBz*-derivative, m.p. 184°, which condenses with ω : 3 : 4-triacetoxyacetophenone to give a flavylium salt. Hydroxyquinol (II) and methoxyacetonitrile condense ($ZnCl_2$–HCl) to 2 : 4 : *5-trihydroxy-ω-methoxyacetophenone* (+H_2O), m.p. 95°, which with NaOAc–Ac_2O and subsequent hydrolysis yields 6 : 7-*dihydroxy-3-methoxy-2-methylchromone*, m.p. 272° (decomp.) (*diacetate*, m.p. 129—130°; *Me_2 ether*, m.p. 185·5—186°), demethylated (HI) to the 3 : 6 : 7-(*OH*)$_3$-compound. 2 : 4 : 5-*Trihydroxy*-1 : 3-*diacetylbenzene*, m.p. 186° (Ac_3 derivative, m.p. 144°; Bz_3 derivative, m.p. 140·5°), obtained from 2 : 4 : 5-$C_6H_3(OAc)_3$ and $AlCl_3$, and CH_2N_2 yield a mixture containing a *homologue* of *hydroxydimethoxydiacetylbenzene*, m.p. 89·5—90°. (II), HCO_2H, and HCl give 2 : 3 : 6 : 7-*tetrahydroxyxanthylium chloride* (III) (+2·5H_2O), the HCO_2H entering the condensation. (I) and (II) condense (HCO_2H–HCl) to give (III), a xanthylium salt, $C_{13}H_9O_5Cl,H_2O$, and a substance $C_{19}H_{15}O_8Cl$. (I) with ω : 4-diacetoxyacetophenone similarly yields 3 : 6 : 7 : 4′-*tetra*- (+H_2O), with ω : 3 : 4-triacetoxyacetophenone gives 3 : 4′ : 3 : 6 : 7-*penta*- (+3H_2O or +H_2O), and with ω : 3 : 4 : 5-tetra-acetoxyacetophenone forms 3′ : 4′ : 5′ : 3 : 6 : 7-*hexa-hydroxyflavylium chloride* (+0·5H_2O) (*picrate*). The effect of transposition of OH from position 5 to 6 is to make the salts much yellower than the anthocyanins in acid and alkaline solution.

F. R. S.

Synthesis of anthocyanins. XXIII. Glucosides of petunidin chloride. (Miss) J. C. Bell and R. Robinson. **XXIV. Cyanidin 3-biosides and a synthesis of mecocyanin.** (Miss) K. E. Grove, M. Inubuse, and R. Robinson. **XXV. Pelargonidin 3-galactoside.** P. V. Nair and R. Robinson. **XXVI. Resocallistephin and reso-œnin chloride.** (Miss) K. E. Grove, L. F. Levy, P. V. Nair, and R. Robinson (J.C.S., 1934, 1604—1608, 1608—1611, 1611—1614, 1614—1619).—XXIII. ω-Diazo-3-methoxy-4 : 5-diacetoxyacetophenone and HCO_2H give the ω-*OH*-compound (+0·5H_2O), m.p. 86—87°, which with tetra-acetylglucosidyl bromide forms ω-O-*tetra-acetyl-β-glucosidoxy-3-methoxy-4 : 5-diacetoxyacetophenone* (I), m.p. 67—69°. (I) and 2-*O*-benzoylphloroglucinaldehyde (II) condense (EtOAc–HCl) to a benzoylhexa-acetylpetunidin monoglucoside chloride, hydrolysed [$Ba(OH)_2$–MeOH] to 3-*O*-glucosidylpetunidin chloride, isolated as the picrate. (I) and 2-*O*-tetra-acetyl-β-glucosidylphloroglucinaldehyde give 7-*hydroxy*-3 : 5-*di*-(O-*tetra-acetyl-β-glucosidoxy*)-3′-*methoxy*-4′ : 5′-*diacetoxyflavylium chloride*, which with MeOH–HCl in H_2 yields petunidin 3 : 5-diglucoside chloride, which could not be separated from inorg. materials. The colour reactions, distribution no., and absorption spectra of the mono- and di-glucoside have been determined.

XXIV. Hepta-acetylcellobiosidyl bromide and ω-hydroxy-3 : 4-diacetoxyacetophenone yield ω-O-*hepta-acetylcellobiosidoxy*-3 : 4-*diacetoxyacetophenone*, which with (II) in EtOAc–HCl forms 3-*cellobiosidoxy*-7 : 3′ : 4′-*trihydroxy-5-benzoyloxyflavylium chloride* (+4H_2O), hydrolysed to 3-O-*cellobiosidylcyanidin chloride* (+4H_2O). Similarly ω-O-*hepta-acetyl-lactosidyloxy*- (+0·5H_2O), m.p. 78—80°, -*maltosidyloxy*- (+0·5H_2O), m.p. 88°, and -*gentiobiosidyloxy*-3 : 4-*diacetoxyacetophenone* (+0·5H_2O), m.p. 70—72°, yield the corresponding 3-O-*lactosidyl*- (+1·5H_2O), -*maltosidyl*- and -*gentiobiosidyl-cyanidin chloride* (mecocyanidin chloride, identical with the natural compound) (+3·5H_2O).

XXV. ω-*O*-Tetra-acetyl-β-glucosidoxy-4-acetoxyphenone and (II) give 3-β-*glucosidylpelargonidin chloride* (+2H_2O) (callistephin chloride), identical with the anthocyanin of scarlet carnations. ω-Hydroxy-4-acetoxyacetophenone and *O*-tetra-acetylgalactosidyl bromide form ω-O-*tetra-acetylgalactosidoxy-4-acetoxyacetophenone*, which with (II) leads to 7-*hydroxy*-3-O-*tetra-acetylgalactosidoxy-5-benzoyloxy-4′-acetoxyflavylium chloride* (+2H_2O), hydrolysed to 3-*galactosidylpelargonidin chloride* (+4H_2O), isolated as the *picrate*. 2-O-(O-*Triacetylgalloyl*)*phloroglucinaldehyde*, m.p. 148—150°, condenses with ω-3 : 4-trihydroxyacetophenone (III) to 5-O-*galloylcyanidin chloride* (+4H_2O), which with HCl–EtOH gives partly *acetylated* 5-O-*galloylcyanidin chloride* (+3H_2O). Phloroglucinaldehyde and 4-acetoxybenzaldehyde afford 2 : 4-*di*-O-4-*acetoxybenzoylphloroglucinaldehyde* (+0·5H_2O), m.p. 180—182°, which with (III) gives 5 : 7-*di*-O-4-*hydroxybenzoylcyanidin chloride* (+3H_2O).

XXVI. ω-*O*-Tetra-acetyl-β-glucosidoxy-4-acetoxyacetophenone (IV) and β-resorcylaldehyde (V) yield the *penta-acetate* of 7 : 4-*dihydroxy*-3-β-*glucosidoxyflavylium chloride* (+2·5H_2O), which is hydrolysed to *resocallistephin chloride* (+2·5H_2O), isolated as the *picrate*. Similarly the *penta-acetate* (+2·5H_2O) of 7 : 4′-*dihydroxy*-3-*galactosidoxyflavylium chloride* (+2H_2O) and the *picrate* are prepared. The 3-OMe-derivative of (IV) and (V) give a *flavylium salt* (+2·5H_2O), hydrolysed to *reso-oxycoccicyanin chloride* (+0·5H_2O), isolated as the *picrate* (+2H_2O). Condensation of (V) and the required component gives *reso-œnin chloride* (+2H_2O), hydrolysed (HCl) to *reso-œnidin chloride* (+H_2O), also obtained by direct condensation. 2-*O*-Benzoyl-4-*O*-tetra-acetyl-β-glucosidylphloroglucinaldehyde and ω : 4-dihydroxy-3 : 5-dimethoxyacetophenone condense to γ-β-*glucosidylmalvidin chloride*. Distribution properties indicate that probably fisetinin and resocallistephin are not associated in either aq. or *iso*amyl-alcoholic solution.

F. R. S.

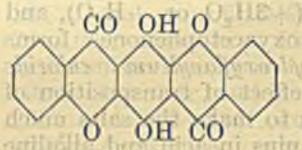
Synthesis of pyrylium salts of anthocyanidin type. XXI. 6-Hydroxy-derivatives of the chief anthocyanidins. E. H. Charlesworth and R. Robinson (J.C.S., 1934, 1619—1624).—Antiarolaldehyde (I) and ω-acetoxyacetophenone (II) condense to 3-*hydroxy*-5 : 6 : 7-*trimethoxyflavylium chloride* (+H_2O), demethylated to the 3 : 5 : 6 : 7-(*OH*)$_4$-compound (+H_2O). 2-*O*-Benzoylphloroglucinaldehyde and (II) give 5-O-*benzoylgalanginidin chloride*, hydrolysed to galanginidin chloride (+H_2O). (I) and ω : 4-diacetoxyacetophenone condense to 3 : 4'-*dihydroxy*-5 : 6 : 7-*trimethoxyflavylium chloride* (+H_2O), hydrolysed to the 3 : 5 : 6 : 7 : 4'-$(OH)_5$-compound (+H_2O), whilst ω:3:4-triacetoxyacetophenone gives 3:3':4'-*trihydroxy*-5:6:7-*trimethoxyflavylium chloride* (+1·5H_2O), demethylated to the 3 : 5 : 6 : 7 : 3' : 4'-$(OH)_6$-compound (quercetagetinidin chloride) (+2H_2O). (I) and ω : 3 : 4 : 5-tetra-acetoxyacetophenone yield 3 : 3' : 4' : 5'-*tetrahydroxy*-5 : 6 : 7-*trimethoxyflavylium chloride* [picrate (+H_2O)], which forms the 3 : 5 : 6 : 7 : 3' : 4' : 5'-$(OH)_7$-derivative (+2H_2O). The colour reactions and absorption spectra of the salts have been examined: they are all redder than the corresponding anthocyanins. F. R. S.

Synthesis of benzopyrylium compounds. I. M. Goswami and A. Chakravarty (J. Indian Chem. Soc., 1934, 11, 713—714).—By condensation of the phenol with coumarin in presence of $POCl_3$ (A., 1933, 281) are prepared 4'-*methoxy*-, m.p. 125°, 3' : 4'-*dimethoxy*-, m.p. 192°, 3' : 4'-*dimethoxy*-4 : 7-*dimethyl*-, m.p. 180°, and 2' : 4'-*dimethoxy*-4 : 7-*dimethyl*-, m.p. 150°, -2-*phenylbenzopyrylium ferrichloride*. J. W. B.

Styrylpyrylium salts. XVI. Conversion of coumarins into *iso*spiropyrans. I. M. Heilbron and G. F. Howard (J.C.S., 1934, 1571—1572; cf. A., 1933, 614, 1169).—7-Methoxy-4-methylcoumarin with MgPhBr in dry Et_2O at room temp., followed by treatment with dry HCl, gives some 7-*methoxy*-2-*phenyl*-4-*methylbenzopyrylium chloride*, but mainly 7-*methoxy*-2 : 2-*diphenyl*-4-*methyl*-Δ^3-*chromone*, m.p. 90—91°. Similarly, 7-methoxy-3 : 4-dimethylcoumarin with excess of MgPhBr in hot Et_2O gives 7-*methoxy*-2 : 2-*diphenyl*-3 : 4-*dimethyl*-Δ^3-*chromene*, m.p. 162—163°. 7-Methoxy-2-phenyl-3 : 4-dimethylbenzopyrylium chloride (A., 1926, 1042) and β-naphthol-1-aldehyde (I) in EtOH containing dry HCl at 0° give 7-*methoxy*-2-*phenyl*-3-*methylbenzo*-β-*naphtha*isospiro*pyran*, m.p. 166—167°, which exhibits the typical colour phenomenon (at a max. in the 7-methoxy-2 : 3-diphenylbenzo-compound below) of the *spiro*pyran series with an unsubstituted 3'-position (cf. A., 1927, 884). 6-*Methoxy*-3 : 4-*dimethylcoumarin*, m.p. 177—178° (from the OH-compound and also obtained from *p*-OMe·C_6H_4·OH and CHMeAc·CO_2Et), with MgPhBr (2 mols.) gives 6-methoxy-2-phenyl-3 : 4-dimethylbenzopyrylium chloride (cf. A., 1931, 1070) [*ferrichloride*, m.p. 80° (decomp.)], which with (I) gives 6-*methoxy*-2-*phenyl*-3-*methylbenzo*-β-*naphtha*isospiro-*pyran*, m.p. 168—169°. 7-Methoxy-3-phenyl-4-methylcoumarin, m.p. 106—107° (lit., 102°) gives, as above, 7-methoxy-2 : 3-diphenyl-4-methylbenzopyrylium chloride, which with (I) gives 7-methoxy-2 : 3-diphenyl-4-(β-2'-hydroxy-1'-naphthavinyl)benzopyrylium chloride (*ferrichloride*), hydrolysed to the isospiro-*pyran*, m.p. 173° (+H_2O, m.p. 126—127°), which in Et_2O gives a deep blue colour with a drop of AcOH. 7-*Methoxy*-3 : 4-*diphenylcoumarin*, m.p. 168° (from the OH-compound and Me_2SO_4), with MgPhBr gives 7-methoxy-2 : 3 : 4-triphenylbenzopyrylium chloride [*ferrichloride*, m.p. 140—142° (decomp.)]. J. L. D.

Pyrylium salts with two fused benzopyran nuclei. E. Keller and R. Robinson (J.C.S., 1934, 1533—1535).—7-Methoxychromanone (I) (prep. described; cf. A., 1926, 732) and β-resorcylaldehyde in EtOAc containing dry HCl afford 7-*hydroxy*-2 : 3-[7'-*methoxychromeno*-(4' : 3')]-*benzopyrylium chloride*; reduction with Pt–H_2 is incomplete, but with Zn–AcOH affords a dimeride (?). Similarly, (I) with *o*-vanillin gives 8-methoxy-2 : 3-[7'-methoxychromeno-(4' : 3')]-benzopyrone [*ferrichloride*, m.p. 202° (not sharp)]. With 2-*O*-benzoylphloroglucinaldehyde and 2-hydroxy-4 : 5-dimethoxybenzaldehyde, (I) gives 7-*hydroxy*-5-*benzoyloxy*- and 6 : 7-dimethoxy-2 : 3-[7'-methoxychromeno-(4' : 3')]-benzopyrylium chloride, the latter of which gives a ferrichloride identical with that of Robinson *et al.* (A., 1926, 732). (I) with 6-aminopiperonal in boiling EtOH containing 20% aq. KOH affords 6 : 7-methylenedioxy-2 : 3-[7'-methoxychromeno-(4' : 3')]-quinoline, isolated as the *picrate*, m.p. about 244°. J. L. D.

Formation and reactions of *meso*-dihydroxychromonoxanthones and reactions of anthraquinone. H. Liebermann [with G. Lewin, A. Gruhn, E. Gottesmann, D. Lisser, and K. Schonda (Annalen, 1934, 513, 156—179).—Et 2 : 5-dichloro- (I) or 2 : 5-dibromo- (II) -*p*-benzoquinone-3 : 6-dicarboxylate, PhOH, and C_5H_5N in $COMe_2$ give *Et* 2 : 5-*diphenoxy*-p-*benzoquinone*-3 : 6-*dicarboxylate*, m.p. 171°, reduced ($Na_2S_2O_4$ in aq. $COMe_2$) to the *Et* ester, m.p. 176° (Ac_2 derivative, m.p. 168°), of 2 : 5-*dihydroxy*-3 : 6-*diphenoxyterephthalic acid* (III), m.p. 268° (darkens > 200°) [$(NH_4)_2$, Ag_2, Ag_4, *Ba*, and Ba_2 salts]. (III) heated with BzCl and a little conc. H_2SO_4 gives the Bz_2 derivative (IV) of ms-*dihydroxychromonoxanthone* (V), m.p. 406° (Ac_2 derivative). (IV) is converted into (V) by hydrolysis (cold conc. H_2SO_4) or by heating with NH_2Ph. KOH-fusion of (V) affords *o*-OH·C_6H_4·CO_2H. *Et* 2 : 5-*di*-β-*naphthoxy*-p-*benzoquinone*-3 : 6-*dicarboxylate*, m.p. 175° [from (I) or (II) and β-$C_{10}H_7$·OH in $COMe_2$–C_5H_5N], is similarly reduced to the *Et* ester, m.p. 220° (Ac_2 derivative, m.p. 196°), of 2 : 5-*dihydroxy*-3 : 6-*di*-β-*naphthoxyterephthalic acid* (VI), m.p. 266° (darkens > 200°) [$(NH_4)_2$ salt], which with BzCl–conc. H_2SO_4 gives 9:10-*dihydroxy*-1:2:5:6-*dibenzchromonoxanthone* (VII), m.p. 438° (Ac_2 derivative), after treatment of the intermediate dibenzoate with NH_2Ph. *Et* 2 : 5-*di*-o-, m.p. 156°, -m-, m.p. 162°, and -p-, m.p. 173°, -*tolyloxy*-, 2 : 5-*di*-s-*xylyloxy*-, m.p. 147°, 2 : 5-*di*-α-*naphthoxy*-, m.p. 180°, 2 : 5-*di*-p-*chlorophenoxy*-, m.p. 197°, 2 : 5-*di*-o-, m.p. 143°, and -p-, m.p. 155°, -*methoxyphenoxy*-, 2 : 5-*di*-p-*diphenylyloxy*-, m.p. 150°, 2 : 5-*di*-(o-o'-*hydroxyphenylphenoxy*)-, m.p. 155°, and 2 : 5-*di*-(p-p'-*hydroxyphenylphenoxy*)-, m.p. 120° (decomp.), -p-*benzoquinone*-3 : 6-*dicarboxylates* are similarly prepared from the appropriate ArOH. These are reduced to the quinol esters, which are then hydrolysed to the acids; the following are prepared: 3 : 6-*di*-o-, m.p. 250°, -m-, m.p. 242°, and -p-, m.p. 265°, -*tolyloxy*- (*Et* esters, m.p. 163°, 156°, and 195°, respectively), 3 : 6-*di*-s-*xylyloxy*-, m.p. > 300° (*Et* ester, m.p. 177°), 3 : 6-*di*-α-*naphthoxy*-, m.p. 262° (*Et* ester, m.p. 192°), 3 : 6-*di*-p-*chlorophenoxy*-, m.p. > 300° (*Et* ester, m.p. 200°), 3 : 6-*di*-o-, m.p. 254°, and -p-, m.p. 275°, -*methoxy*-



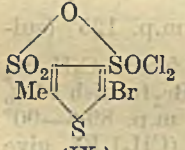
(V.)

phenoxy- (*Et* esters, m.p. 172° and 151°, respectively), 3 : 6-*di*-p-*diphenylyloxy*-, m.p. 290° (*Et* ester, m.p. 218°), 3 : 6-*di*-(o-o′-*hydroxyphenylphenoxy*)-, m.p. 251° (*Et* ester, m.p. 225°), and 3 : 6-*di*-(p-p′-*hydroxyphenylphenoxy*)-, m.p. > 300° (*Et* ester, m.p. 230°), -2 : 5-*dihydroxyterephthalic acids*. These are converted [as (III)] into 4 : 8-, 3 : 7-, and 2 : 6-*dimethyl*-, 1 : 3 : 5 : 7-*tetramethyl*-, 3 : 4 : 7 : 8-*dibenz*-, 2 : 6-*dichloro*-, 4 : 8- and 2 : 6-*dimethoxy*-, 2 : 6-*diphenyl*-, 4 : 8-*di*-o-*hydroxyphenyl*-, and 2 : 6-*di*-p-*hydroxyphenyl*-ms-*dihydroxychromonoxanthone*, respectively; the colours of these compounds in conc. H_2SO_4 are given.

(III) heated with $SOCl_2$ affords [after hydrolysis (aq. K_2CO_3)] a little 5 : 8-*dihydroxy-7-phenoxyxanthone*-6-*carboxylic acid*, m.p. 240° (*K* salt; *Ac* derivative, m.p. 275°), also convertible into (V). (VI) similarly gives (mainly) (VII) and a little 5 : 8-*dihydroxy*-7-β-*naphthoxy*-3 : 4-*benzxanthone*-6-*carboxylic acid*, m.p. > 300°, convertible (BzCl) into (VII). (V) heated with NH_2Ph and H_3BO_3 gives ms-*dianilinochromonoxanthone*, m.p. > 400° (Ac_2 derivative); ms-*di*-o- and -p-*toluidino*- (Ac_2 derivative), ms-*di*-p-*anisidino*-, ms-*di*-p-*toluidino*-4 : 8-*dimethoxy*-, and ms-*dianilino*-3 : 4 : 7 : 8-*dibenzchromonoxanthones* are similarly prepared. Anthraquinone (VIII), H_3BO_3, $SnCl_2$, and NH_2Ph afford 9 : 10-*dianilinoanthracene*, m.p. 306° [Bz_2, m.p. > 320°, Ac_2, m.p. 210° (previous sintering), and *di*(*chloroacetyl*), m.p. 296°, derivatives], also formed (in smaller yield) from 9 : 10-diacetoxyanthracene, m.p. 270°, H_3BO_3, and NH_2Ph. *Anthraquinone*-p-*tolil*, m.p. 165°, is obtained from (VIII), H_3BO_3, and p-$C_6H_4Me\cdot NH_2$.

Et 2 : 5-*diphenylthiol*-p-*benzoquinone*-3 : 6-*dicarboxylate*, m.p. 146° [from (I), PhSH (2 mols.), and C_5H_5N in $COMe_2$], is reduced ($Na_2S_2O_4$) to *Et* 2 : 5-*dihydroxy*-3 : 6-*diphenylthiolterephthalate*, m.p. 155° [Ac_2 derivative, m.p. 162°; corresponding *disulphone*, m.p. 178° (Ac_2 derivative, m.p. 206°)], which is obtained directly (with Ph_2S_2) from (I) and PhSH (4 mols.) in $COMe_2$–C_5H_5N. 2 : 5-*Dihydroxy*-3 : 6-*diphenylthiolterephthalic acid*, becomes turbid at 120° and clears at 218° (*Cd* salt), with BzCl–conc. H_2SO_4 gives the Bz_2 derivative of ms-*dihydroxythiochromonothioxanthone* (V, with >O=>S), m.p. 436° (decomp.) (also obtained directly from the acid and conc. H_2SO_4). (I), the appropriate alcohol, and C_5H_5N give *Et* 2 : 5-*dimethoxy*-, m.p. 118°, 2 : 5-*diethoxy*-, m.p. 67°, and 2 : 5-*dibenzyloxy*-, m.p. 118°, -p-*benzoquinone*-3 : 6-*dicarboxylate*. *Et* 2 : 5-*dihydroxy*-3 : 6-*dimethoxyterephthalate*, m.p. 93°, and 2 : 5-*dihydroxy*-3 : 6-*diethoxyterephthalic acid*, m.p. 196° [Bz_2 derivative, m.p. 233° (decomp.); *Et* ester, m.p. 132° (Ac_2 derivative, m.p. 131°)], are prepared. H. B.

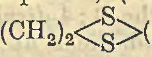
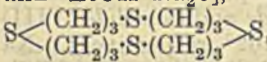
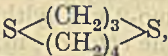
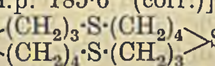
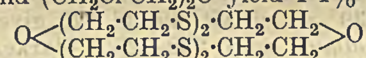
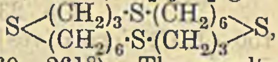
Thiophen series. XXVII. Bromo-derivatives of 2-thiotolene [2-methylthiophen]. W. Steinkopf (Annalen, 1934, **513**, 281—294).—Tribromo-2-methylthiophen (I) and Mg+MgMeBr in Et_2O give [after treatment with the appropriate reagent (see this vol., 1108)] 3 : 4-*dibromo-2-methylthiophen* (II), b.p. 237—237·5°, m.p. 9° [5-NO_2-, m.p. 96—99°, and 5-*ClHg*- (III), m.p. 215°, -derivatives], 3 : 4-*dibromo-2-methylthiophen-5-carboxylic acid*, m.p. 224°, and 3 : 4-*dibromo-5-iodo-2-methylthiophen*, m.p. 66°. (III) and an excess of NaI in $COMe_2$ afford *Hg* 3 : 4 : 3′ : 4′-*tetrabromo*-2 : 2′-*dimethyl*-5 : 5′-*dithienyl*, m.p. 238—240°. *Ph*, m.p. 75°, and *Me*, m.p. 115°, 3 : 4-*dibromo-2-methyl-5-thienyl ketones* are prepared (Friedel–Crafts) from (II). (II) and Mg+MgMeBr give a mixture, b.p. 172—185°, of 3- (IV) and 4-bromo-2-methylthiophens (5-*ClHg*-derivatives, m.p. 237—239° and 165—166°, respectively). Successive treatment of 2 : 5-dibromothiophen with Mg+MgMeBr and p-$C_6H_4Me\cdot SO_3Me$ in Et_2O affords a little 5-*bromo-2-methylthiophen* (V), b.p. 171—175·5°. Contrary to Opolski (A., 1905, i, 367; 1906, i, 33), 2-methylthiophen (VI) and Br (approx. 1·5 mols.) in CS_2 give (after treatment with EtOH–KOH) a mixture of Br_1- (*A*), b.p. 172—183°, and Br_2-, b.p. 220—235°, -derivatives; (*A*) contains (IV) (action of $HgCl_2$) and (V) [since treatment with 33% oleum affords the 3 : 4-*disulphonic anhydride* (VII), decomp. 210° (darkens at 185°)]. (VI) and Br (slightly < 3 mols.) similarly give a mixture from which 3 : 5-*dibromo-2-methylthiophen*, b.p. 227·5—230°, m.p. —13° (no reaction with $HgCl_2$), is isolable; the Br_2-derivative, m.p. 44—45°, of Opolski (*loc. cit.*) was never obtained. (VII), PCl_5, and $POCl_3$ afford 5-*bromo-2-methylthiophen*-3 : 4-*disulphonyl chloride*, m.p. 174°; the *diamide* and *dianilide* (VIII) have decomp. 300° and m.p. 162°, respectively. Na 5-bromo-2-methylthiophen-3 : 4-disulphonate and PCl_5 give the *chloride*, m.p. 189° [as (IX) or with SO_2 and $SOCl_2$ interchanged], which reacts very slowly with C_6H_6–NH_2Ph yielding (VIII). Reduction (Na–Hg, dil. NaOH) of (VII) affords 2-methylthiophen-3 : 4-disulphonic acid [*chloride*, m.p. 138—139°, which with liquid NH_3 gives the *diamide*, m.p. 250—255° (darkens at 240°)]. 3 : 5-Dibromo-2-methylthiophen is converted (Grignard) into 3-*bromo-2-methylthiophen*, b.p. 174—176° [5-NO_2-, m.p. 71—72°, 5-*ClHg*-, m.p. 237°, and 5-SO_3H (*amide*, m.p. 150—151°), derivatives], and 3-*bromo-2-methylthiophen 5-carboxylic acid*, m.p. 197—198°. *Hg* 3 : 3′-*dibromo*-2 : 2′-*dimethyl*-5 : 5′-*dithienyl* has m.p. 266°. 3 : 4 : 5-*Tribromo-2-bromomethyl*- (X), m.p. 86° (quaternary *salt*, m.p. 148°, with $NPhMe_2$), and -2-*dibromomethylthiophen* (XI), m.p. 60—61°, are prepared from (I) and Br. (X) is hydrolysed (aq. Na_2CO_3) to 3:4:5:3′:4′:5′-*hexabromo*-2 : 2′-*dithenyl ether*, m.p. 146—148°. (XI) is hydrolysed ($CaCO_3$, H_2O in CO_2) to 3 : 4 : 5-*tribromothiophen-2-aldehyde*, m.p. 141—142°, converted by conc. KOH into 3 : 4 : 5-*tribromo-2-hydroxymethylthiophen*, m.p. 127—128° (previous sintering), and 3 : 4 : 5-tribromothiophen-2-carboxylic acid (*loc. cit.*).



(IX.)

2-Nitrothiophen forms a 1 : 1-*compound* with KOMe and 1 : 1- and 1 : 2-*compounds* with NaOEt; 2 : 4-dinitrothiophen forms a 1 : 3-*compound* with NaOH and a 1 : 2-*compound* with KOH. H. B.

Ring compounds and polymerides from polymethylene dihalides and dimercaptans. J. R. Meadow and E. E. Reid (J. Amer. Chem. Soc., 1934, **56**, 2177—2180; cf. A., 1933, 398).—The product from s-$C_2H_4Cl_2$ and an excess of NaSH contains 45—55% of $(\cdot CH_2\cdot SH)_2$ (I), 16% of $S(CH_2\cdot CH_2\cdot SH)_2$ (II), b.p. 135—136°/10 mm., m.p. —12·5° (*Ag* salt), about 1·5% of $(\cdot CH_2\cdot S\cdot CH_2\cdot CH_2\cdot SH)_2$, b.p. 168—172°/10 mm., m.p. 15—17° (impure *Ag* salt), 5—6% of 1 : 4-dithian (III), and 10% of polymerides. $(CH_2)_3Br_2$ and EtOH–KSH

(20% excess) at room temp. give 52% of $(CH_2)_3(SH)_2$ (IV), b.p. 66—68°/18 mm., m.p. −79±2°, and 6% of $S([CH_2]_3\cdot SH)_2$, b.p. 138—140°/6 mm., m.p. −9° to −8° (*Ag* salt); $(CH_2Cl\cdot CH_2)_2O$ similarly affords 30% of 1 : 4-thioxan, 12% of $(SH\cdot CH_2\cdot CH_2)_2O$, b.p. 103—104°/18 mm., m.p. −80±2° (*Ag* salt), and 5% of $S(CH_2\cdot CH_2\cdot O\cdot CH_2\cdot CH_2\cdot SH)_2$, b.p. 182—185°/8 mm. (*Ag* salt). (IV) and CH_2Cl_2 (excess) in EtOH–NaOEt give 15% of 1 : 3-dithian (V), b.p. 207—208°, m.p. 53·3° [sulphone, m.p. 307—308° (corr.)], and polymeric material [which when heated in dry HCl affords a further 32% of (V)]. (I) and $CHBrMe\cdot CH_2Br$ similarly yield 2-methyl-1 : 4-dithian (12·5%), b.p. 209—210°, m.p. 20°; (IV) and $C_2H_4Br_2$ furnish the disulphide,  $(CH_2)_2<\begin{matrix}S\\S\end{matrix}>(CH_2)_3$ (8·2%), b.p. 221—222°, m.p. 47° (sulphone, m.p. 287—288°) (cf. *loc. cit.*); (IV) and $(CH_2)_3Br_2$ give *ditrimethylene* 1 : 5-*disulphide* (4%), b.p. 245—246°, m.p. −15° (cf. Autenrieth and Wolff, A., 1899, i, 579) [also obtained (in 2% yield) with trimethylene sulphide, m.p. −64±1°, from $(CH_2)_3Br_2$ and EtOH–Na_2S], and 1% of the *tetrasulphide*,  $S<\begin{matrix}(CH_2)_3\cdot S\cdot(CH_2)_3\\(CH_2)_3\cdot S\cdot(CH_2)_3\end{matrix}>S$, m.p. 46°; (IV) and $(CH_2)_4Br_2$ afford 0·6% of the *disulphide*,  $S<\begin{matrix}(CH_2)_3\\(CH_2)_4\end{matrix}>S$, m.p. 57·5—58° [sulphone, m.p. 185·6° (corr.)], and 1·8% of the *tetrasulphide*,  $S<\begin{matrix}(CH_2)_3\cdot S\cdot(CH_2)_4\\(CH_2)_4\cdot S\cdot(CH_2)_3\end{matrix}>S$, m.p. 61°; (I) and $(CH_2Cl\cdot CH_2)_2O$ yield 1·4% of the *compound* (VI),  $O<\begin{matrix}(CH_2\cdot CH_2\cdot S)_2\cdot CH_2\cdot CH_2\\(CH_2\cdot CH_2\cdot S)_2\cdot CH_2\cdot CH_2\end{matrix}>O$, m.p. 125° (sulphone, m.p. 265—266°), also obtained from *s*-$C_2H_4Br_2$ and $(SH\cdot CH_2\cdot CH_2)_2O$; (II) and *s*-$C_2H_4Br_2$ furnish 1·7% of the *hexasulphide* (VI with O=S), m.p. 89·6—90° (sulphone, m.p. > 330°); (IV) and $(CH_2)_6Br_2$ give 1·1% of the *tetrasulphide*,  $S<\begin{matrix}(CH_2)_3\cdot S\cdot(CH_2)_6\\(CH_2)_6\cdot S\cdot(CH_2)_3\end{matrix}>S$, m.p. 62° (sulphone, m.p. 260—261°). The results show that 9—11-membered rings are rarely obtained. The above cyclic compounds are accompanied by polymerides. Polymerides containing the following structural units give the products quoted in brackets when heated in dry HCl or in a mol. still at 175—200°: $\cdot C_2H_4\cdot S\cdot C_2H_4\cdot S\cdot$ [40—60% of (III)]; $\cdot C_2H_4\cdot S\cdot CH_2\cdot S\cdot$ [30% of 1 : 3-dithiolan]; $\cdot C_2H_4\cdot S\cdot C_3H_6\cdot S\cdot$ [5—10% of (III) and 5—10% of 2-methyl-1 : 4-dithian]; $\cdot C_3H_6\cdot S\cdot C_3H_6\cdot S\cdot$ [indefinite]; $\cdot C_2H_4\cdot SO_2\cdot C_2H_4\cdot S\cdot C_2H_4\cdot S\cdot$ [10—15% of (III) and 20% of the monosulphone of (III)]; $\cdot C_2H_4\cdot S\cdot C_2H_4\cdot S\cdot C_2H_4\cdot O\cdot$ [5—10% of (III) and 15—20% of 1 : 4-thioxan]; $\cdot C_3H_6\cdot S\cdot CH_2\cdot S\cdot$ [30—40% of (V)]; $\cdot C_2H_4\cdot S\cdot C_6H_{12}\cdot S\cdot$ [10% of (III)]; $\cdot C_3H_6\cdot S\cdot C_4H_8\cdot S\cdot$ [10% of $(CH_2)_4>S$]; $\cdot C_3H_6\cdot S\cdot C_5H_{10}\cdot S\cdot$ [15—20% of $(CH_2)_5>S$]. Depolymerisation does not occur unless halogen is present, thus supporting the view of Bennett *et al.* (A., 1927, 958) on inter- and intra-mol. sulphonium addition. The following results further support this view. Heptyl bromide (VII) heated with $Bu^a{}_2S$ gives approx. equal amounts of (VII), BuBr, Bu_2S, and Bu heptyl sulphide: $Bu_2S+C_7H_{15}Br \rightleftharpoons C_7H_{15}\cdot SBu_2Br \rightleftharpoons BuBr+C_7H_{15}\cdot SBu$. $C_2H_4Br_2$ and Bu_2S similarly afford (III) and BuBr, whilst di-*n*-amyl methylene sulphide, $CH_2(S\cdot C_5H_{11})_2$, and $C_2H_4Br_2$ give amyl bromide and 1 : 3-dithiolan.

H. B.

Action of amines on quinolinic acid. A. K. Das and I. B. Sarkar (J. Indian Chem. Soc., 1934, **11**, 707—710).—With NH_2Ph (I) quinolinic acid forms the *NH₂Ph H* salt (II), m.p. 137° with decomp. to the $(NH_2Ph)_2$ salt (III), m.p. 187° (decomp.). When heated with (I) in AcOH at 100°, or by heating (II) or (III) at > 187°, the *dianilide*, m.p. 225°, is obtained, converted by heating at 225—250° into the anil, m.p. 208° (lit., m.p. 248°, 251°, and 228°), which, refluxed with NH_3–MeOH, affords *quinanilic acid*, m.p. 217° (decomp.). Similarly *o*-$C_6H_4(CO_2H)_2$ affords its $NH_2Ph\ H$ salt, m.p. 158° (decomp.) (described by Zincke *et al.*, A., 1890, 784, as the anilic acid), the anil, m.p. 205°, and the anilic acid, m.p. 170° (Meyer *et al.*, A., 1899, i, 755).

J. W. B.

Condensation product of pyridine and keten. O. Wollenberg (Ber., 1934, **67**, [*B*], 1675—1679).—Passage of keten into C_5H_5N followed by immediate treatment of the solution with H_2O yields only a red resin and dehydracetic acid. If, however, the solution of C_5H_5N in anhyd. $COMe_2$, Et_2O, EtOAc, C_6H_6, light petroleum, or dioxan is kept, a violent reaction occurs with formation of a *substance* (I), $C_{13}H_{11}O_3N$, m.p. 204°. (I) is hydrolysed by 0·1*N*-NaOH to an *acid* (II), $C_{13}H_3O_4N$, but does not yield C_5H_5N with conc. HCl or molten alkali. (I) contains *tert.* N which does not unite with MeI. Since also (II) does not unite with MeI, (I) must be a lactone. (I) and (II) contain 2 and 3 active H, respectively (Zerevitinov). (I) is rapidly hydrogenated to the strongly fluorescent *compound*, $C_{13}H_{13}O_3N$, m.p. 242—243° (decomp.), which contains 2 active H and then more slowly to the colourless, non-fluorescent *substance*, $C_{13}H_{15}O_3N$, m.p. 190°; ultimately a non-cryst. *perhydro*-derivative is produced. Oxidation of (I) with $KMnO_4$ or CrO_3 gives $H_2C_2O_4$, AcOH, and NH_2Ac; under milder conditions part of (I) remains unchanged, whereas the rest is completely decomposed.

H. W.

Sulphonation of pyridine in presence of mercuric sulphate as a catalyst. (Miss) A. J. P. Van Gastel and J. P. Wibaut (Rec. trav. chim., 1934, **53**, 1031—1036).—Sulphonation of C_5H_5N with $HgSO_4$ as catalyst at 300—350° yields pyridine-3-, m.p. 357° (*NH₄* salt, m.p. 243°), and about 2% of -2-sulphonic acid, m.p. 247—248° (*NH₄* salt, m.p. 274·2—275·3°). At 225°, only the 3-acid is formed, but sulphonation does not take place below 300° without catalyst.

F. R. S.

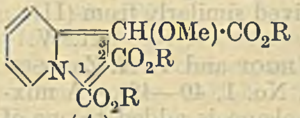
Synthesis of *N*-phenylpiperazine. C. B. Pollard and L. G. MacDowell (J. Amer. Chem. Soc., 1934, 56, 2199—2200).—$NH(CH_2\cdot CH_2\cdot OH)_2$ and NH_2Ph,HCl at 230—240° give about 50% of *N*-phenylpiperazine, b.p. 156—157°/10 mm. (*hydrochloride*), and some $NH(CH_2\cdot CH_2\cdot NHPh)_2$.

H. B.

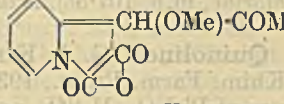
Formation of 2-phenyl-Δ²-tetrahydropyridine by the action of magnesium phenyl bromide on δ-bromovaleronitrile. J. B. Cloke and O. Ayers (J. Amer. Chem. Soc., 1934, **56**, 2144—2145).—Furan is reduced (H_2, Ni, Bu^aOH at 50°) to tetrahydrofuran, converted by red P and Br in H_2O into αδ-dibromobutane, which with aq. EtOH–KCN affords *δ-bromovaleronitrile*, b.p. 110—111°/11 mm. This and MgPhBr give 2-phenyl-Δ²-tetrahydropyridine [platinichloride, decomp. 191—192° (sinters at 190°), re-solidifying with m.p. 210—211° (lit. 202°)]. H. B.

Addition of cyanoacetamide to α-methoxybenzylideneacetophenone. C. F. H. Allen and J. A. Scarrow (Canad. J. Res., 1934, **11**, 395—405).—Addition of $CN\cdot CH_2\cdot CO\cdot NH_2$ to $CHPh\colon CBz\cdot OMe$ (improved prep. of $OMe\cdot CH_2Bz$ described) in dry MeOH–trace NaOMe affords 6-*hydroxy*-2-*keto*-3-*cyano*-5-*methoxy*-4 : 6-*diphenylpyridine* (I), m.p. 241—242°, converted by Me_2SO_4–10% NaOH into 3-*cyano*-2 : 5 : 6-*trimethoxy*-4 : 6-*diphenyl*-1 : 4 : 5 : 6-*tetrahydropyridine*, m.p. 290°, and by PCl_5 in boiling C_6H_6, into 2-*hydroxy*-3-*cyano*-5-*methoxy*-4 : 6-*diphenylpiperidine* (II), m.p. 318—320° (decomp.). Passage of dry HCl into a suspension of (I) in $CHCl_3$ affords (II) and 2-*keto*-3-*cyano*-5-*methoxy*-4 : 6-*diphenyl*-2 : 3 : 4 : 5-*tetrahydropyridine*, m.p. 233—235°, and treatment of (I) with $AlCl_3$ in boiling C_6H_6 and subsequent basification gives (II) and 6-*hydroxy*-2-*keto*-5-*methoxy*-4 : 6-*diphenylpiperidine*, m.p. 155°. Addition of Br–AcOH to (I) in boiling AcOH (+1 drop of $COMe_2$) affords NH_4Br and a *compound*, m.p. 125—130° (decomp.), decomposed by MeOH into a mixture from which (I), (II), 3-*bromo*-6-*hydroxy*-2-*keto*-3-*cyano*-5-*methoxy*-4 : 6-*diphenylpiperidine* (III), m.p. 292—293° (60%), and 6-*hydroxy*-2-*keto*-5-*methoxy*-4 : 6-*diphenyl*-1 : 2 : 5 : 6-*tetrahydropyridine* (IV), m.p. 252—253° (2—5%), were separated. Addition of Br to (I) in MeOH–NaOMe affords unchanged (I), (III), and 6-*hydroxy*-2-*keto*-5-*methoxy*-4 : 6-*diphenyl*-1 : 2 : 5 : 6-*tetrahydropyridine*-3-*carboxylic acid*, m.p. 149—150°, decarboxylated at 180—200° to (IV). When heated with Ac_2O–C_5H_5N (or 2 drops of conc. H_2SO_4) (I) gives 6-*hydroxy*-5-*methoxy*-2-*acetyl*-4 : 6-*diphenyl*-1 : 4 : 5 : 6-*tetrahydropyridine*, m.p. 126°, hydrolysed (H_2SO_4–EtOH) with dehydration to 2-*hydroxy*-5-*methoxy*-4 : 6-*diphenyl*-4 : 5-*dihydropyridine*, m.p. 173—174°. (I) is converted by warm 33% H_2SO_4 into 2-*keto*-5-*benzoyl*-4-*phenylpyrrolidine*, m.p. 172° (isomeric *form*, m.p. 153—154°, by action of HCl–EtOH; *dinitrophenylhydrazone*, m.p. 205°), and a gum (V), from which were separated γ-hydroxy-γ-benzoyl-β-phenylbutyric acid and the corresponding two stereoisomeric lactones, m.p. 130° [*dinitrophenylhydrazone* (VI), m.p. 164°] and m.p. 98° [*dinitrophenylhydrazone* (VII), m.p. 192°] (Kohler, A., 1911, i, 984). Direct treatment of (V) with $NH_2\cdot NH\cdot C_6H_3(NO_2)_2$ gives (VI) and (VII), and a *dinitrophenylhydrazone*, m.p. 182°. With dry NH_3–MeOH the lactone affords only (?) γ-*hydroxy*-γ-*benzoyl*-β-*phenylbutyramide*, m.p. 173°. Mechanisms are discussed. Condensation of α-bromobenzylideneacetophenone with p-$C_6H_4(NO_2)\cdot CH_2\cdot CN$ in presence of NaOMe affords a mixture of 1-*cyano*-2-*benzoyl*-1-p-*nitrophenyl*-3-*phenyl*cyclo*propane*, m.p. 144°, and its *stereoisomeride*, m.p. 151°. J. W. B.

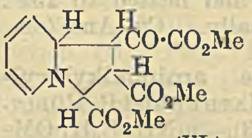
Syntheses in the hydroaromatic series. XXI. Diene syntheses with heterocyclic nitrogen compounds. VIII. Course of the diene synthesis with pyridine in methyl-alcoholic solution. O. Diels and R. Meyer (Annalen, 1934, **513**, 129—145; cf. A., 1932, 1144; 1933, 1058; this vol., 782).—Me acetylenedicarboxylate (I) and C_5H_5N in MeOH at 0° give a colourless *adduct* (II), $C_{16}H_{17}O_7N$, m.p. 142—143°, oxidised (H_2O_2, AcOH) to 2-carboxypyridine 1-oxide (III) and converted by Br in AcOH or MeOH into Me indolizinetricarboxylate [also obtained directly from (I) and MeOH–C_5H_5N in the absence of cooling]. (II) is unaffected by $K_2Cr_2O_7$ in AcOH or Et azodicarboxylate. These results are explained by assigning structure *A* (R=Me) to (II). Hydrolysis (dil. MeOH–KOH) of (II) gives a *salt*, $C_{14}H_{13}O_7N,C_{14}H_{12}O_7NK,H_2O$, decomp. about 200°, whilst hydrolysis with 25% MeOH–KOH affords the *tricarboxylic acid* (+$2H_2O$) (IV) (*A*, R=H), decomp. about 100° [K_3 salt (+$4H_2O$)], which is oxidised [HNO_3 (d 1·4)] to pyridine-2-carboxylic acid and converted by Ac_2O into the *keto-anhydride* (V), decomp. 270°. (II) is reduced (H_2, PtO_2, AcOH) to a *tetrahydro*-derivative, m.p. 103—105°, which is oxidised ($KMnO_4$, $COMe_2$) to the *keto*-ester (+$0{\cdot}5H_2O$) (VI), m.p. 162—164°, and hydrolysed (30% aq. KOH) to the tricarboxylic acid (VII), m.p. 130° (decomp.) [*anhydride*, m.p. 154—155° (loss of H_2O between CO_2H groups marked *), formed by the action of Ac_2O]. The resinous product obtained by similar reduction of (IV) is converted by Ac_2O into the *tetrahydro*-derivative, decomp. 260°, of (V). (II) and dil. HNO_3 in AcOH give *Me* 3-*nitroindolizine*-1 : 2-*dicarboxylate*, m.p. 165°, oxidised (H_2O_2, AcOH) to (III) and reduced (H_2, PtO_2, AcOH) to Me 3-amino-tetrahydroindolizine-1 : 2-dicarboxylate, m.p. 105° (*Ac* derivative, m.p. 167°).



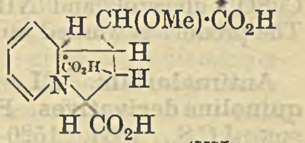
(*A.*)



(V.)



(VI.)



(VII.)

Me fumarate and *Me methoxyfumarate*, b.p. 228—230° [hydrolysed (conc. HCl) to *Me₂ oxaloacetate*, m.p. 73—74°], are isolated from the mother-liquors from the prep. of (II). (II) is probably formed by addition of the residue $\cdot C(CO_2Me)\colon C(CO_2Me)\cdot CH(CO_2Me)\cdot C(OMe)(CO_2Me)\cdot$ to C_5H_5N and subsequent elimination of HCO_2Me. The previously described (A., 1933, 1058) Me quinolizinetricarboxylate is probably *A* with OMe=H and R=Me. H. B.

Catalytic dehydrogenation of cyclic bases. III. Behaviour of the stereoisomeric decahydroquinolines during catalytic dehydrogenation. M. Ehrenstein and W. Bunge (Ber., 1934, **67**, [*B*], 1715—1729; cf. this vol., 534).—*cis*-Decahydroquinoline is dehydrogenated by Pd and more rapidly by Pt, whereas the *trans*-form is resistant towards Pd but dehydrogenated by Pt. The corresponding 1-Me compounds behave analogously to their parents. The two decahydronaphthalenes are readily dehydrogenated, the rate of action being greater with the *cis*- than with the *trans*-compound. Pt is a more active catalyst than Pd.

Quinoline is hydrogenated (colloidal Pt–AcOH–HCl) and the crude product is passed over Pt–asbestos at

310°, thus leading conveniently to 5 : 6 : 7 : 8-tetrahydroquinoline, b.p. 103°/10 mm. [*picrate*, m.p. 158°; *picrolonate*, m.p. 213° (decomp.); *aurichloride*, m.p. 138·5—139°; *platinichloride*, m.p. 212·5—213°]. Hydrogenation of pure quinoline (colloidal Pt–H_2O) yields 1 : 2 : 3 : 4-*tetrahydroquinoline*, b.p. 246—247° (hydrochloride, m.p. 181°; *picrate*, m.p. 145—146°). The *phenylthiocarbamides*, m.p. 143° and m.p. 139°, respectively, and *aurichlorides*, m.p. 200° and m.p. 126°, of *cis*- (I) and *trans*- (II) -decahydroquinoline are described. (I), HCO_2H, and CH_2O at 100° yield cis-1-*methyldecahydroquinoline*, b.p. 208·5—209·5°/1 atm. (*picrate*, m.p. 199—200°; *aurichloride*, m.p. 103°). trans-1-*Methyldecahydroquinoline*, b.p. 204—205° (*picrate*, m.p. 173°; *picrolonate*, m.p. 205·5°; *aurichloride*, m.p. 107·5°), is derived similarly from (II).
H. W.

Quinoline. G. A. Kirkhgof and V. A. Zasosov (Khim. Farm. Prom., 1934, No. 1, 40—42).—A mixture of $PhNO_2$, H_2SO_4, and oleum is added to one of $CuSO_4$, glycerol, and NH_2Ph, and heated to 154°. The product is worked up normally. Ch. Abs. (*e*)

Antimalarials. XI. Some aminoalkylaryl-quinoline derivatives. F. C. Mathur and R. Robinson J.C.S., 1934, 1520—1523).—*p*-$NH_2\cdot C_6H_4\cdot OMe$ (I), *m*-$NO_2\cdot C_6H_4\cdot CHO$, and $AcCO_2H$ in boiling EtOH afford 2-m-*nitrophenyl*-6-*methoxyquinoline*-4-*carboxylic acid*, m.p. 268—269°, which does not lose CO_2 when heated. 2-*m*-Aminophenyl-6-methoxyquinoline (improved prep.) and phthalo-γ-bromopropylimide (II) at 120—130° afford 2-(m-γ-*phthalimidopropylaminophenyl*)-6-*methoxyquinoline*, m.p. 149—150° (*hydrobromide*, m.p. 202—203°), which is converted by N_2H_4,H_2O in boiling EtOH, followed by excess of dil. HCl, into 2-(m-γ-*aminopropylaminophenyl*)-6-*methoxyquinoline hydrochloride* (+1·5H_2O, m.p. 240—241°, which is lost in vac. at 110°). *o*-Nitrocinnamaldehyde with (I) and conc. HCl at 160° affords 2-o-*nitrophenyl*-6-*methoxyquinoline*, m.p. 133—134°, reduced ($SnCl_2$–HCl) to the *amine*, m.p. 158—169°. 6-Methoxyquinaldine, *p*-$NO_2\cdot C_6H_4\cdot CHO$, and Ac_2O at 120—130° afford 2-p-*nitrobenzylidene*-6-*methoxy*-2-*methylquinoline*, m.p. 165—166°, reduced ($SnCl_2$ or Fe–HCl) to the *amine* (III), m.p. about 162—165° (decomp.) with softening from 130° (*hydrochloride*; *stannichloride*). (III) with (II) at 110—120° gives 2-p-γ-*phthalimidopropylaminostyryl*-6-*methoxyquinoline*, m.p. 191—192° (*hydrobromide*, m.p. 241°), converted as above into 2-(p-γ-*aminopropylaminostyryl*)-6-*methoxyquinoline monohydrate*, m.p. 156° (*hydrochloride* +3·5H_2O, m.p. 222—223°; the H_2O is lost in vac. at 110°). 2-*p*-Aminostyrylquinoline with (II) as before gives 2-(p-γ-*phthalimidopropylaminostyryl*)-*quinoline*, m.p. 175—176° (*hydrobromide*, m.p. 248—249°), converted into 2-(p-γ-*aminopropylaminostyryl*)-*quinoline*, m.p. 141—142° [*hydrochloride*, m.p. 269—276° (decomp.)]. Quinaldine, *m*-$NO_2\cdot C_6H_4\cdot CHO$, and Ac_2O at 110—120° afford 2-m-*nitrocinnamylidene*-2-*methylquinoline*, m.p. 158—159° [*methiodide*, m.p. 229—230° (decomp.)], reduced to the *amine*, m.p. 147° [*H sulphate*, m.p. 237° (decomp.)]. Similarly prepared, the corresponding 6-*OMe*-compounds have m.p. 197—198° and 139—140° (+H_2O; *hydrochloride* +1·5H_2O, m.p. 250—251°), respectively. 3-Nitro-*p*-anisidine, $(MeCHO)_3$, and conc. HCl at 100° gives 8-*nitro*-6-*methoxy*-2-*methylquinoline* (IV), m.p. 186—187°, converted into the *amine* (+0·25H_2O, m.p. 102°) by reduction (Pt–H_2) in EtOH–HCl. (IV) with *p*-$NO_2\cdot C_6H_4\cdot CHO$, and Ac_2O at 120° affords 2-p-*nitrobenzylidene*-8-*nitro*-6-*methoxy*-2-*methylquinoline* (+1·5H_2O, m.p. 182—183°). 2-p-*Dimethylaminobenzylidene*- and 2-m-*nitrocinnamylidene*-8-*nitro*-6-*methoxy*-2-*methylquinoline* have m.p. 204—205° and 223—224°, respectively. J. L. D.

Antimalarials. XII. Quinolines with basic side-chains. R. Robinson and (Miss) M. L. Tomlinson (J.C.S., 1934, 1524—1530).—8-Amino-6-methoxyquinoline [*Ac* derivative (I), m.p. 126°] and phthalo-δ-bromobutylimide (II) at 130° afford 8-δ-*phthalimidobutylamino*-6-*methoxyquinoline hydrobromide*, m.p. 196—198° (decomp.); the base is hydrolysed (N_2H_4 in EtOH) to 8-δ-aminobutylamino-6-methoxyquinoline (III) [*dihydrochloride* +0·5H_2O, m.p. 208° (decomp.)]. 8-γ-Aminopropylamino-6-methoxyquinoline with phthalo-γ-bromopropylimide (IV) and with (II), followed by hydrolysis, give 8-γ′-aminopropyl- and 8-δ′-aminobutyl-γ-aminopropylamino-6-methoxyquinoline, respectively. Similarly, (III) gives 8-γ′-aminopropylamino- and 8-δ′-aminobutylamino-δ-butylamino-6-methoxyquinoline, respectively. The above are isolated as extremely deliquescent hydrochlorides, which have a high antimalarial activity. 8-β-Aminoethylamino-6-methoxyquinoline with (IV), followed by hydrolysis and prolonged interaction with *n*-octyl bromide, gives 8-γ′-octylaminopropyl-β-aminoethylamino-6-methoxyquinoline, isolated as a deliquescent hydrochloride. (I) with Cl_2 in AcOH affords 5-*chloro*-8-*acetamido*-6-*methoxyquinoline*, m.p. 169°, hydrolysed to the *amine* (V), m.p. 150—152° [*hydrochloride*, m.p. 264° (decomp.)]. Equimol. quantities of (V) and (IV) at 100° affords 5-*chloro*-8-γ-*phthalimidopropylamino*-6-*methoxyquinoline*, m.p. 153—154°; hydrolysed as above to 5-chloro-8-γ-aminopropylamino-6-methoxyquinoline [*dihydrochloride* +H_2O, m.p. 235° (decomp.)]. (I) (free base) with excess of $CH_2Br\cdot CO_2Et$ at 100° gives Et 6-methoxyquinolyl-8-aminoacetate [*hydrobromide*, m.p. 203° (decomp.)], and with $CH_2Cl\cdot CH_2\cdot OH$, an impure substance, $C_{14}H_{20}O_3N_2Cl_2$. 4-Hydroxy-6-methoxyquinaldine with (IV) and K_2CO_3 at 140° affords 4-γ-*phthalimidopropoxy*-6-*methoxy*-2-*methylquinoline*, m.p. 197°, hydrolysed to 4-γ-*aminopropoxy*-6-*methoxy*-2-*methylquinoline* (VI), m.p. 170° [*dihydrochloride*, m.p. 215° (decomp.)]. (VI) and (IV) at 120° affords 4-γ′-*phthalimidopropyl*-γ-*aminopropoxy*-6-*methoxy*-2-*methylquinoline hydrobromide* +H_2O, m.p. 200—202°, hydrolysed and then converted into 4-γ′-*aminopropyl*-γ-*aminopropoxy*-6-*methoxyquinaldine trihydrochloride* +2H_2O, m.p. 145° (decomp.). Me β-6 : 7-dimethoxyquinaldine-4-propionate (VII) (this vol., 83) with boiling β-diethylaminoethanol (VIII) affords β-diethylaminoethyl β-6 : 7-dimethoxyquinaldine-4-propionate, isolated as the *dihydrochloride* (*picrate*, m.p. 186° after sintering at 175°). The azide of (VII) with warm (VIII) affords β-diethylaminoethyl β-6 : 7-dimethoxyquinaldyl(4)ethylcarbamate (*picrate*, m.p. 187°; very deliquescent hydrochloride). The azide from anishydrazide with (VIII) at 100° gives β-diethylaminoethyl *p*-anisylcarbamate (*picrate*, m.p. 150—152°; hydrochloride). MgEtBr with 6-methoxytetrahydrocarbazole in Et_2O containing BzCl gives 9-*benzoyl*-6-*methoxytetrahydrocarbazole*, m.p. 134°, which is nitrated (HNO_3–AcOH) at room temp. to a 5(or 7)-*mononitro*-derivative, m.p. 150°, which is not hydrolysed (KOH) to δ-5-methoxy-2-aminobenzoylvaleric acid (cf. J.C.S., 1923, **123**, 676). 2-Nitro-4-methoxyaniline (diazonium compound) with $SnCl_2$–HCl gives 2-*nitro*-4-*methoxyphenylhydrazine*, m.p. 127°, which with *cyclo*hexanone at 100° gives a *hydrazone*, m.p. 69°, converted by boiling 18% H_2SO_4 into 8-*nitro*-6-*methoxytetrahydrocarbazole*, m.p. 136°, reduced ($Na_2S_2O_4$) to the NH_2-compound (IX), m.p. 149°. (IX), 6-amino-, 6-amino-9-acetyl-, and 6-amino-9-methyl-tetrahydrocarbazole, and 3 : 6-diaminocarbazole afford no cryst. products with (IV). 6-Nitro-9-acetyltetrahydrocarbazole in boiling EtOH with Fe–HCl gives the *amine*, m.p. 140°, the diazonium compound of which with $m\text{-}C_6H_4(NH_2)_2$ gives an *azo*-derivative, m.p. 195°. Neither 6-chloro-7-nitro- nor 6-chloro-5-nitro-tetrahydrocarbazole condenses with NH_2Me, phthalimide, or $p\text{-}C_6H_4Me{\cdot}NH_2$. 2-Nitro-5-methoxyphenol with (IV) and K_2CO_3 at 145° affords 2-*nitro*-5-*methoxy*-γ-*phthalimidopropoxybenzene*, m.p. 178°, reduced (Fe–HCl) to the NH_2-compound, m.p. 94—96° (with Zn in AcOH it affords a *compound*, $C_{18}H_{20}O_4N_2$, m.p. 162—164°), which cannot be converted into a quinoline or a tetrahydrocarbazole. 4-Iodo-2-nitroanisole, 3-nitro-*p*-anisidine, K_2CO_3, and Cu at 110° give 2 : 2′-*dinitro*-4 : 4′-*dimethoxydiphenylamine* (X), m.p. 218° [*Ac* derivative (XI), m.p. 134—135°] (also a *compound*, $Cu_2I_2,C_5H_5N,3H_2O$, from crystallisation mother-liquors), also obtained from 4 : 4′-dimethoxydiphenylamine with HNO_3 in AcOH. Neither (X) nor (XI) can be converted into an acridine. (X) with CH_2O in conc. H_2SO_4 gives a *compound*, $C_{16}H_{13}O_8N_3$, m.p. 223—224°, converted by boiling Ac_2O into a *substance*, $C_{20}H_{17}O_{10}N_3$, m.p. 219—221°. 2-Bromo-3-nitrobenzophenone with *m*-nitro-*p*-anisidine, K_2CO_3, and Cu at 150° affords 2 : 2′-*dinitro*-4-*methoxy*-6′-*benzoyldiphenylamine*, m.p. 175°, converted by Ac_2O containing $ZnCl_2$ into 1 : 9-*dinitro*-3-*methoxy*-5-*phenylacridine*, m.p. 272°, reduced ($Na_2S_2O_4$) to an amine [Ac_2 derivative, m.p. 258°; *hydrochloride*, m.p. 245° (decomp.)].

J. L. D.

3 : 6-Dialkoxy-10-alkylacridinium derivatives with various kinds of amino-groups attached to the 9-carbon atom. I. Introduction and synthesis of 3 : 6-dialkoxyacridones and 3 : 6-dialkoxy-*N*-alkylacridones. II. Synthesis of 3 : 6-dialkoxy-9-chloro-10-alkylacridinium chlorides. K. Ishihara (J. Chem. Soc. Japan, 1934, 55, 458—470, 557—564).—I. Improvements in the synthesis of 9-amino-3 : 6-methoxyacridinium-methyl chloride are described.

II. The OMe- and OEt-Me and -Et *derivatives* of chloroacridinium chloride have been synthesised (m.p. 221°, 190—191°, 197—204°, 181°, respectively).

Ch. Abs. (*e*)

Preparation of antipyrine. G. M. Nikolaiev (Khim. Farm. Prom., 1934, No. 1, 35—38).—Phenylmethylpyrazolone is methylated with $PhSO_3Me$.

Ch. Abs. (*e*)

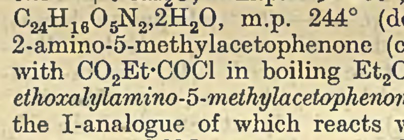
Stereochemistry of diphenyls. XXXVI. Preparation and resolution of dipyrrylbenzenes. C. Chang and R. Adams (J. Amer. Chem. Soc., 1934, **56**, 2089—2092).—4 : 6-Dinitro-*m*-xylene (modified prep.; cf. Errera and Maltese, A., 1904, i, 307) is reduced (H_2, PtO_2, EtOH) to the $(NH_2)_2$-derivative, m.p. 104—105°, which with Et γ-keto-α-acetylvalerate (I) at 110—120° gives [after hydrolysis (EtOH–KOH)] a mixture of cis- (II), m.p. 260—262° (*brucine*, m.p. 172—177°, *strychnine*, m.p. 178—185°, and *cinchonine*, m.p. 154—160°, salts), and trans- (III), m.p. 305° (decomp.), -4 : 6-*di*-(3-*carboxy*-2 : 5-*dimethyl*-1-*pyrryl*)-m-*xylene*. (II) and (III) are meso and racemic forms, respectively. (III) is resolved by brucine into d-, m.p. 275—276°, $[\alpha]_D^{27}$ +172·2° in C_5H_5N (*brucine* salt, m.p. 186—190°), and l-*forms*, m.p. 275—276°, $[\alpha]_D^{27}$ —165·8° in C_5H_5N (impure brucine salt, m.p. 152—159°), which racemise partly in boiling *N*-NaOH but not in boiling C_5H_5N. 2-Acetamido-*p*-xylene and HNO_3 (*d* 1·42) in cold conc. H_2SO_4 give the 5-NO_2-derivative, m.p. 167—169° (lit. 166° and 192°); hydrolysis (EtOH–conc. H_2SO_4) and subsequent reduction (H_2, PtO_2, EtOH) gives 2 : 5-diamino-*p*-xylene. This and (I) afford 2 : 5-di-(3-carbethoxy-2 : 5-dimethyl-1-pyrryl)-*p*-xylene, m.p. 150—157°, separable (with difficulty) by fractional crystallisation (EtOH) into cis-, m.p. 158—160°, and trans-, m.p. 183—185°, -forms. The corresponding cis-, m.p. 419—422°, and trans-, m.p. 455—460° (Maquenne block), -*acids* are racemic and meso forms, respectively; alkaloidal salts could not be prepared. (II) and m-*di*-(3-*carboxy*-2 : 5-*dimethyl*-1-*pyrryl*)*benzene*, m.p. 273—274° [from $m\text{-}C_6H_4(NH_2)_2$ and (I) at 80—100° in N_2, followed by hydrolysis], could not be resolved.

H. B.

Complex salts of 2 : 2′-dipyridyl with bivalent copper.—See this vol., 1317.

Epindoline group. I. Trial of various methods for the synthesis of epindolidiones. A. D. Ainley and R. Robinson (J.C.S., 1934, 1508—1520).—Isatin [Na derivative (I)] with $CH_2X{\cdot}CO_2Et$ (X=Br or Cl) in dry C_6H_6 (room temp.) affords *Et isatin*-N-*acetate*, m.p. 129—130° [different from the product, m.p. 114°, of Putochin (A., 1929, 74)], hydrolysed to an acid, m.p. 206—207° (cf. A., 1928, 771), the *chloride* of which, m.p. 139—140° (previous softening), gives no definite product with $p\text{-}C_6H_4Me{\cdot}NHAc$. (I) with CH_2BzBr in C_6H_6 at room temp. affords a *product*, $C_{16}H_{14}O_2,2C_{16}H_{11}O_3N$, and *isatylideneacetophenone oxide* (II), m.p. 161·5—162° (+*EtOH*, m.p. 161—162°) (cf. A., 1929, 328), which is converted by NaOH into (III) (below) and EtOH, and is reduced (Zn–alkali or Zn–HCl) to COPhMe more readily than (III). (II) when boiled with EtOH–NaOH affords *benzoylformyloxindole* (III), m.p. 178·5—179·5° (*phenylhydrazone*, decomp. at 165° after sintering at 160°, exhibits colour changes in various solvents, and probably has the NHPh·N: residue on the C adjacent to Ph), which is hydrolysed by AcOH–HCl to oxindole, and couples with diazonium chlorides to give sparingly sol. alkali salts (cf. A., 1918, i, 229). (I) with $o\text{-}NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2Br$ in C_6H_6 as above gives *isatylidene*-o-*nitroacetophenone oxide* (IV), m.p. 207—208° (decomp.), converted by boiling

NaOH–EtOH into o-*nitrobenzoylformyloxindole* (V), m.p. 239° (decomp.). Reduction of (IV) by many methods gives indirubin, m.p. 345—347°; the yield is improved by reducing (V). (III) with boiling 10% NaOH affords $BzCO_2H$ and 2-*benzoylindole*-3-*carboxylic acid* (?), m.p. 230—231° (decomp.), converted by fusion with KOH into indole. (III) with boiling NaOH containing Zn gives *mandeloyloxindole* (VI), m.p. 164—165° [also contained by reducing (II)], which is fairly stable to boiling 40% KOH. Diazonium derivatives of (VI) with alkali give PhCHO, as does (VI) with Br followed by NaOH. (II) with o-$C_6H_4(NH_2)_2$ in AcOH–EtOH at 100° affords a *substance*, m.p. 200—201°. Similarly, (III) affords a *quinoxaline* (?), m.p. 255°, the structure assigned to which is in accord with its somewhat anomalous properties. *N*-Benzoyl-4-ketotetrahydroquinoline (cf. A., 1924, i, 1103) with an equimol. amount of o-$NO\cdot C_6H_4\cdot CO_2Et$ at 100° affords a *product*, $C_{22}H_{20}O_5N_2$, m.p. 99·5—100·5°, converted by boiling H_2O into a *product*, m.p. 106—109°. The same reactants in boiling EtOH containing Na_2CO_3 afford a *substance*, m.p. 253·5—254° [probably a compound of (VII) and its Et ester], 3-o-*carboxyanilino*-4-*hydroxyquinoline* (VII), m.p. 255° (decomp.) (*Et* ester, m.p. 274·5—275°), which is not cyclised to an epindolidione. Similarly, α-tetralone gives 2-o-*carbethoxyanilino*-α-*naphthaquinone* $+0{\cdot}5H_2O$, m.p. > 280°, and an *acid*, $C_{24}H_{16}O_5N_2,2H_2O$, m.p. 244° (decomp.). ω-Chloro-2-amino-5-methylacetophenone (cf. A., 1900, i, 663) with $CO_2Et\cdot COCl$ in boiling Et_2O affords ω-*chloro*-2-*ethoxalylamino*-5-*methylacetophenone*, m.p. 144—144·5°, the I-analogue of which reacts with p-$C_6H_4Me\cdot NH_2$ in boiling $COMe_2$ to give ω-p-*tolylamino*-2-*ethoxalylamino*-5-*methylacetophenone* (VIII), m.p. 140·5—141°. The unsubstituted compound is not prepared because ω-bromo-o-nitroacetophenone does not condense with NH_2Ph. Boiling EtOH–NaOH converts (VIII) into 3-p-*tolylamino*-4-*hydroxy*-6-*methylquinoline*-2-*carboxylic acid* (IX), m.p. 237—238° (decomp.) [Ac_2 derivative $+0{\cdot}5H_2O$ (X), m.p. 217° (decomp.)], which with boiling MeOH–H_2SO_4, or with CH_2N_2 in dry Et_2O at 0° affords *Me* 3-p-*tolylamino*-4-*keto*-6-*methyl*-1 : 4-*dihydroquinoline*-2-*carboxylate* (XI), m.p. 227—228° (decomp.). (IX) with CH_2N_2 in MeOH at room temp. affords (XI) and some *Me* 3-p-*tolylamino*-4-*keto*-1 : 6-*dimethyl*-1 : 4-*dihydroquinoline*-2-*carboxylate*, m.p. 246°. (X) with AcCl followed by $AlCl_3$ in $PhNO_2$ at room temp. gives the Ac_2 derivative (infusible) of 4 : 10-dimethylepindolidione; also an *Ac* ($+H_2O$) derivative. Cyclisation is effected better with boiling 60% H_2SO_4 to give 4 : 10-*dimethylepindolidione* (XII) (infusible), which possesses weakly basic and acidic properties, and is not reduced by alkaline $Na_2S_2O_4$ in C_5H_5N or EtOH. J. L. D.



(XII.)

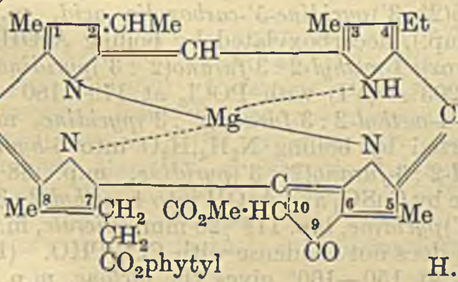
Synthesis of polymethine dyes. T. Ogata (J. Chem. Soc. Japan, 1934, 55, 394—436; cf. this vol., 422).—The prep. and properties of a large no. of cyanine dyes are described. Vals. for the sensitising max. of these dyes are recorded. Ch. Abs. (*r*).

Residual affinity and co-ordination. XXXV. 2 : 2′ : 2″-Tripyridylplatinum salts. G. T. Morgan and F. H. Burstall (J.C.S., 1934, 1498—1500; cf. this vol., 1113).—2 : 2′ : 2″-Tripyridyl (=trpy) with K_2PtCl_4 in H_2O at 90° affords 2 : 2′ : 2″-*tripyridylchloroplatinous platinochloride* (I) $[Pt\ trpyCl]_2PtCl_4$, *bis*-2 : 2′ : 2″-*tripyridyltriplatinous hexachloride* (II), and 2 : 2′ : 2″-*tripyridylplatinous chloride trihydrate* (III), $[Pt\ trpyCl]Cl,3H_2O$ (red), converted by keeping over H_2SO_4, or by EtOH, or by HCl, into the *dihydrate* (IV) [also obtained from the black form of (III) with H_2O or acid]. Prolonged action of tripyridyl on (I) or (II) in H_2O, or Ag_2O followed by HCl on (I), gives (IV). (III) with K_2PtCl_4 in cold H_2O gives (I), whereas with aq. NH_3 it gives 2 : 2′ : 2″-*tripyridylamminoplatinous chloride hydrate* (V), which readily reverts to (III) by loss of NH_3. (III) or (I) with warm Ag_2O–H_2O gives 2 : 2′ : 2″-*tripyridylplatinous hydroxide*, $[Pt\ trpyOH]OH,2H_2O$, which with acids gives the *bromide* and *iodide dihydrates*, also prepared from (III) with the appropriate halides. (III) with Cl_2 affords 2 : 2′ : 2″-*tripyridyltrichloroplatinic chloride dihydrate*, $[Pt\ trpyCl_3]Cl,2H_2O$, desiccated over H_2SO_4 to a *monohydrate*, which is reconverted in air into (III). (I) with hot conc. NH_3 gives the *plato*-salt (VI), $[Pt\ trpyNH_3]PtCl_4$ (black) [converted into (I) with warm HCl], also obtained by interaction of (V) with K_2PtCl_4. Tripyridyl in hot 2*N*-HCl with K_2PtCl_4 affords 2 : 2′ : 2″-*tripyridyl platinochloride*, $trpyH_2PtCl_4$, which is unchanged by boiling H_2O, but when heated at 230—260° for 5 hr. affords some 2 : 2′ : 2″-tripyridyl hydrochloride, the black *form* (VII) (probably a dimeride) of (III) [*plato*-salt converted into (I) with HCl; is converted by hot 2*N*-HCl or boiling H_2O into (III)], and a product of indefinite composition. J. L. D.

Constitution of the purine nucleosides. II. J. M. Gulland, E. R. Holiday, and I. F. Macrae (J.C.S., 1934, 1639—1644).—Methylation of xanthosine (I) with CH_2N_2 gives a mixture of methylated purines and methylriboside, hydrolysed to 1 : 7-dimethylxanthine, 1 : 7 : 9-trimethyluric acid (?), ribose (as furfuraldehyde), and 3-methylxanthine (cf. Levene *et al.*, A., 1925, i, 1463). Comparison of absorption spectra of (I), *iso*caffeine, and caffeine, 9-, 7-, 1-, and 3-methylxanthine, and theophylline-*d*-glucoside (II) and -*l*-arabinoside (III) indicates that (I) is probably xanthine-9-riboside and that (II) and (III) are γ-substituted xanthines. Methylation (MeI) of xanthosine Ag gives 7-methylxanthine and ribose derivatives containing OMe but no N. F. R. S.

Chlorophyll. L. Structure of chlorophyll *a*. H. Fischer and J. Hasenkamp (Annalen, 1934, 513, 107—129).—Chlorin *e* (I) contains the *iso*porphin ring since it undergoes the "oxo-reaction" (this vol., 420) to give a mixture (30% yield) of *oxochloroporphyrin* e_5 (II), $C_{33}H_{32}O_6N_4$, m.p. >305°, and small amounts of oxochloroporphyrins e_4 and e_7. (II) heated with HCO_2H or 60% H_2SO_4 gives oxorhodoporphyrin (III). Short treatment of (II) with Et_2O–CH_2N_2 in C_5H_5N affords a Me_1 ester, decomp. 260°; with MeOH–HCl, (II) affords a Me_2 ester, (?) $C_{35}H_{36}O_7N_4$, m.p. 288° (*oxime*, sinters at 268°). Chlorin e_4 is converted by cold HI–AcOH into 35—40% of *oxochloroporphyrin* e_4

(IV), $C_{33}H_{34}O_5N_4$, m.p. > 300° {*Me*$_2$ ester (V) (CH_2N_2), m.p. 288° [*oxime* (VI), decomp. 260°; *Cu* salt, m.p. 260°]}. Oxophylloporphyrin is formed when (IV) is heated to 309°; (III) is similarly obtained from (V) at 310°. (III) heated to 311° gives oxopyrroporphyrin. Oxophylloerythrin ester dioxime and Ac_2O at 100° (bath) afford a *Ac*$_2$ derivative, decomp. 208°, which when heated at 130° in a high vac. is converted into an isomeric *compound* [hydrolysed (20% HCl) to a new porphyrin]. The *Ac* derivative, decomp. 230°, of (VI) exhibits an analogous behaviour. Oxophylloerythrin (VII) is converted by conc. HCl at 190° and subsequent esterification into (mainly) *de-ethylphylloerythrin* ester, $C_{32(33)}H_{32(34)}O_3N_4$, m.p. 261° (*Cu*, m.p. 266°, and *Fe*, m.p. 320°, salts), which with Br in $CHCl_3$ gives a compound, also obtained from (VII) and Br in HCO_2H. (VII) and conc. HCl at 200° afford de-ethylpyrroporphyrin (8% yield), the *Me* ester, m.p. 215° (*Br*- and *Br*$_2$-, m.p. 268°, -derivatives), of which is identical with 1 : 3 : 5 : 8-tetramethyl-4-ethyl-7-β-carbomethoxyethylporphin (synthesis to be described later). (VII) and AcOH–HBr at 190° give (after esterification) *de-ethyldeoxophylloerythrin Me* ester, m.p. 252°, the constitution of which is established by its synthesis (details to be published later). The above results can be explained satisfactorily only by assuming that chlorophyll derivatives which undergo the "oxo-reaction" contain a CHMe: group. Oxo-derivatives contain an Ac and not a formyl group (cf. *loc. cit.*); their formation involves the following reactions: CHMe:C< $\longrightarrow$ CHIMe·CH< $\longrightarrow$ CHIMe·CI< $\longrightarrow$ OH·CHMe·CI< $\longrightarrow$ OH·CMe:C< $\longrightarrow$ COMe·C≪; C< is C_2 of the porphin structure. Structures are suggested for (I), (II), and methylphæophorbide *a*. Chlorophyll *a* is now assigned the following constitution.



H. B.

Chlorophyll series. XIII. Nuclear isomerism of porphyrins. E. M. Dietz and T. H. Werner. **XIV. Potentiometric titration in acetic acid solution of basic groups in chlorophyll derivatives.** J. B. Conant, B. F. Chow, and E. M. Dietz (J. Amer. Chem. Soc., 1934, **56**, 2180—2184, 2185—2189).—XIII. *iso*Rhodoporphyrin (I) (A., 1933, 403) is converted (to the extent of about 50% in 48 hr.) into rhodoporphyrin (II) by treatment with cold 50% H_2SO_4 in O_2 or N_2; conversion is also effected with conc. or 75% H_2SO_4 (with some decomp.), conc. HCl, and MeOH–, $CHCl_3$–, or AcOH–HCl and –HBr, but in some cases an unidentified porphyrin is also formed. Pyrochloroporphyrin (III) is similarly converted by 50% H_2SO_4 into phylloporphyrin (IV). The changes (I) $\longrightarrow$ (II) and (III) $\longrightarrow$ (IV) are considered to be isomerisations (prototropic) and not reductions. The *Zn* salts of the Me_2 esters of (I) and (II) are not identical (cf. *loc. cit.*) and regenerate the original porphyrins; the *Fe* complexes differ also. Interconversion of (I) and (II) (or their salts) could not be effected by mild dehydrogenating agents, heating in various solvents, or exposure to light (white or ultra-violet) in various solvents. Verdoporphyrin could not be prepared from phæophytin by Treibs and Herrlein's method (A., 1933, 1173); (I) is obtained. The nos. quoted after the following compounds are the no. of mols. of H_2 absorbed on reduction with PtO_2 and Pt-black, respectively, in AcOH (cf. Fischer *et al.*, A., 1930, 932; 1933, 1308): phylloporphyrin Me ester, 4, 3·3; pyrochloroporphyrin Me ester, —, 4·1 [oxidation of the leuco-compound gives (IV)]; pyrroporphyrin Me ester, 3·6—4, — (re-oxidation gives 60—65% of original material); rhodoporphyrin Me_2 ester, 3·7—4·1, 3·1 (re-oxidation affords 60—65% of original material); *iso*rhodoporphyrin Me_2 ester, 4·8—5·4, 4 [re-oxidised to (II) (about 57%)]; chlorin *f* Me_2 ester, 4·4—4·6, 3·2—3·3 [re-oxidised to (II) (about 50%)]; chlorin *e* Me_3 ester, 3·7—4·2, 3·2. These results indicate that *iso*porphyrins are dehydrogenation products of true porphyrins. Little importance is attached to the hydrogenation results and the isomerism of the true and *iso*-porphyrins is maintained.

XIV. Potentiometric titrations of various pyrroles and chlorophyll derivatives with $HClO_4$ in AcOH at const. ionic strength, using a chloranil electrode, are carried out using the procedure previously developed (A., 1931, 40; 1933, 1121). Porphyrins, chlorins, and rhodins all contain 3 basic groups; the titration curves, however, show marked characteristic differences. Revised structures, which are consistent with the data obtained, are assigned to chlorin *f* and rhodin *l*. H. B.

Porphyrins. XXX. Synthesis of 2-(ββ-dicarboxyethyl)-4 : 6 : 8-tri-(β-carboxyethyl)-1 : 3 : 5 : 7-tetramethylporphin (*iso*conchoporphyrin I) and deuteroporphyrin II. H. Fischer and E. von Holt (Z. physiol. Chem., 1934, **227**, 124—144; cf. A., 1932, 285).—2 : 4-Dimethyl-3-β-carboxyethylpyrrole and 4-bromo-5-aldehydo-3-methylpyrrole-2-carboxylic acid in AcOH yield the carbinol base, which with HBr gives *3-bromo-5-carboxy-4 : 3′ : 5′-trimethyl-4′-β-carboxyethylpyrromethene hydrobromide* (I), m.p. ≮ 290°. With Br in CCl_4, (I) affords *3 : 5-dibromo-4 : 3′ : 5′-trimethyl-4′-β-carboxyethylpyrromethene hydrobromide* (II), m.p. ≮ 290°. Fusion of (II) containing perbromide and 5-bromo-4 : 3′ : 5′-trimethyl-3 : 4′-di-(β-carboxyethyl)pyrromethene hydrobromide in citric acid (240°) gives a mixture of porphyrins (15—20% yield), separated by bromination into coproporphyrin I (Me_4 ester, m.p. 246°) and *2-bromo-1 : 3 : 5 : 7-tetramethyl-4 : 6 : 8-tri-(β-carboxyethyl)porphin* (III), m.p. ≮ 290° [*Fe* salt, m.p. ≮ 290°; *Me*$_3$ ester, m.p. 203—204° (*Fe*, m.p. 230—231°, *Cu*, m.p. 316—317°, *Zn*, m.p. 235—236°, salts)]. Debromination of (III) Me_3 ester by Busch's method (A., 1925, ii, 823) gives *1 : 3 : 5 : 7-tetramethyl-4 : 6 : 8-tri-(β-carboxyethyl)porphin* (IV), m.p. ≮ 270° (*Fe* salt, m.p. ≮ 300°), as *Me*$_3$ ester, m.p. 195—196° (*Fe*, m.p. 225—226°, *Cu*, m.p. 189—190°, salts). The Fe salt of (IV) with $CH_2Cl·OMe$ and $SnCl_4$ yields, as *Fe* salt, *1 : 3 : 5 : 7-tetramethyl-4 : 6 : 8-tri-(β-carboxy-*

ethyl)-2-hydroxymethylporphin, which with Et potassiomalonate yields 1 : 3 : 5 : 7-*tetramethyl*-2-(ββ-*dicarboxyethyl*)-4 : 6 : 8-*tri*-(β-*carboxyethyl*)*porphin* (iso*conchoporphyrin* I), isolated as the Me_5 ester, m.p. 172°. Fusion of (II) containing perbromide in succinic and citric acids (205°) affords *deuteroporphyrin II* (V), m.p. $\nless$ 300° [Me_2 ester, m.p. 286° (*Fe*, m.p. 296°, *Cu*, m.p. 302—303°, salts)]. A similar fusion (240°) gives *monobromodeuteroporphyrin II* Me_2 *ester*, m.p. 243—244°. Bromination of (V) Me_2 ester in AcOH yields *dibromodeuteroporphyrin II*, m.p. $\nless$ 270°, as the Me_2 ester, m.p. 303—304° (*Cu*, m.p. 309—310°, *Fe*, m.p. 285—286°, salts). Bromination of 5-formyl-2 : 3-dimethylpyrrole and opsopyrrolecarboxylic acid gives 4 : 5 : 3′-*trimethyl*-4′-β-*carboxyethylpyrromethene hydrobromide*, m.p. 202°, which on bromination and fusion with succinic acid (180—190°) affords (V).

J. H. B.

Crystalline stercobilin and urobilin. See this vol. 1386.

α-*iso*Oxazolehydrazide. M. Freri (Gazzetta, 1934, **64**, 644—649).—*iso*-Oxazole-5-carboxylhydrazide (cf. A., 1932, 1145) (I) with HNO_2 in AcOH gives *di*(iso*oxazole-5-carboxyl*)*hydrazine*, m.p. 212°, which is also formed from (I) and *iso*oxazole-5-carboxyl chloride. Acids hydrolyse it to (I) and N_2H_4. (I) condenses with BzCl, PhCHO, $COPh_2$, and o-$C_6H_4(CO)_2O$ to *benzoyl*iso*oxazole-5-carboxylhydrazine*, m.p. 192—193°, *benzaldehyde-*, m.p. 193—194°, and *benzophenone*-iso*oxazole-5-carboxylhydrazone*, m.p. 190°, and *phthalyl*-iso*oxazole-5-carboxylhydrazine*, m.p. 204—205°, respectively.

R. N. C.

4-Hydroxy-3 : 5-diphenyl*iso*oxazole. A. H. Blatt and W. L. Hawkins (J. Amer. Chem. Soc., 1934, **56**, 2190—2191).—$CHBz_2{\cdot}OAc$ and NH_2OH,HCl in aq. EtOH give 4-*hydroxy*-3 : 5-*diphenyl*iso*oxazole* (I), m.p. 122—123° (decomp.) (*acetate*, m.p. 103°; *benzoate*, m.p. 157—158°; *Me ether*, m.p. 69—70°), oxidised (alkaline $KMnO_4$) to a bimol. *compound*, $C_{30}H_{20}O_5N_2$, m.p. 110—112°, and converted by I in AcOH into an *isomeride* (II), m.p. 151° (decomp.). Acetylation of (II) and subsequent hydrolysis affords (I). (I) heated to 135° gives CO, PhCN, and PhCHO, whilst (I) and Br in $CHCl_3$ at 0° afford [after hydrolysis (H_2O)] PhCN and BzOH.

H. B.

Amine oxides of the novocaine series. J. Lauer (Bull. Soc. chim., 1934, [v], **1**, 857—860).—N-*Oxides* of the following are prepared: novocaine, m.p. 181—182° (*hydrochloride*, m.p. 136—137°; *picrate*, m.p. 165—166°); butelline, m.p. 126—127° [*hydrochloride*, m.p. about 129° (decomp.)]; pantocaine, m.p. 87° (*hydrochloride*, m.p. 146°; *picrate*, m.p. 144—145°); $N(C_2H_4{\cdot}OH)_3$, m.p. 106° (*hydrochloride*, an oil); *N*-β-hydroxyethylmorpholine, cryst., hygroscopic (*hydrochloride*, an oil); β-hydroxyethyldiethylamine and diethyl-δ-hydroxy-ββ-dimethylbutylamine, oils (*hydrochlorides*, oils).

R. S. C.

Derivatives of 3-ethylpyridine and 2 : 3-furano(2′ : 3′)pyridine. R. Robinson and J. S. Watt (J.C.S., 1934, 1536—1543).—ββ′-Dihydroxydiethylaniline with PCl_5 in $CHCl_3$ affords ββ′-*dichlorodiethylaniline*, m.p. 45°, converted by KCN in boiling MeOH into ββ′-*dicyanodiethylaniline*, m.p. 81°, which does not cyclise and is stable to basic catalysts. *Et γ-phenoxy-α-acetylbutyrate* (I), b.p. 195°/30 mm., is hydrolysed to γ-phenoxypropyl Me ketone (cf. A., 1932, 288), which with $Et_2C_2O_4$ gives 5-β-*phenoxyethyl*-cyclo*pentane*-1 : 3 : 4-*trione-2-oxalate*, m.p. 145° (cf. A., 1906, i, 438), hydrolysed to 5-β-*phenoxyethyl*cyclo*pentane*-1 : 3 : 4-*trione*, m.p. 119·5°, the enol form of which is the more stable. (I) or $CH_2Ac{\cdot}CO_2Et$ (Na derivatives) with β-carbomethoxypropionyl chloride in dry Et_2O, followed by hydrolysis, affords no derivatives of succinacetic ester. *Et α-cyano-γ-phenoxybutyrate*, b.p. 190—195°/14—15 mm. (cf. A., 1924, 261) [Na derivative (II)] with Et β-chloroglutarate (cf. J.C.S., 1923, **123**, 2964) gives a product, b.p. about 200°/0·2 mm., but nothing cryst. on hydrolysis. (II) with Et muconate (cf. A., 1931, 1037; 1930, 1163) in boiling EtOH–Et_2O gives *Et α-cyano-α-β-phenoxyethyl-β-carbethoxymethyladip-γδ-enate*, b.p. 212°/0·2 mm., hydrolysed (KOH–MeOH) to an *acid*, $C_{17}H_{17}O_7N$, m.p. 137—138°. (II) with Et β-chloroglutaconate (J.C.S., 1922, **121**, 1642) in hot EtOH gives $OPh{\cdot}C_2H_4{\cdot}CH(CN){\cdot}C(CH_2{\cdot}CO_2Et){:}CH{\cdot}CO_2Et$, b.p. about 210°/0·2 mm., hydrolysed (boiling HCl) to 2 : 6-dihydroxy-3-(β-phenoxyethyl)pyridyl-4-acetic acid (an oil) [*hydrochloride*, m.p. 146° (decomp.)], which with Br gives a mixture of Br_3- and Br_4-compounds, m.p. 187—188° (decomp.). 2 : 6-Dihydroxy-4-methylpyridine (J.C.S., 1905, **87**, 1685) with malic acid in conc. H_2SO_4 at 100° gives the *lactone* (III), m.p. 295—296°, of β-(2 : 6-dihydroxy-4-methyl-3-pyridyl)acrylic acid [*Bz* derivative (IV), m.p. 209°]; this [or (IV)] with Br in AcOH gives an α : 5-Br_2-derivative (V), m.p. 298° (decomp.). (V) with boiling EtOH–KOH rearranges to 5-*bromo*-6-*hydroxy*-4-*methyl*-2 : 3-*furano*-(2′ : 3′)*pyridine-5′-carboxylic acid*, decomp. at 245°, and is reduced (Zn–NaOH) to 6-*hydroxy*-4-*methyl*-2 : 3-*furano*(2′ : 3′)*pyridine-5′-carboxylic acid*, m.p. 278° (decomp.), decarboxylated by boiling AcOH–HCl to 6-*hydroxy*-4-*methyl*-2 : 3-*furano*(2′ : 3′)*pyridine* (VI), m.p. 203°. (VI) with $POCl_3$ at 170—180° gives 6-*chloro*-4-*methyl*-2 : 3-*furano*(2′ : 3′)*pyridine*, m.p. 45°, converted by boiling N_2H_4,H_2O into 6-*hydrazino*-4-*methyl*-2 : 3-*furano*(2′ : 3′)*pyridine*, m.p. 88·5°, and thence by $CuSO_4$ and AcOH into 4-*methyl*-2 : 3-*furano*-(2′ : 3′)*pyridine*, b.p. 118°/20 mm. (*picrate*, m.p. 151°), which does not condense with $CCl_3{\cdot}CHO$. (III) with $POCl_3$ at 150—160° gives the *lactone*, m.p. 175°, of β-(2-hydroxy-6-chloro-4-methyl-3-pyridyl)acrylic acid, reduced (HI–red P) to β-(2-*hydroxy*-4-*methyl*-3-*pyridyl*)*propionic acid*, m.p. 214° [Zn–HCl reduces it to β-(6-*chloro*-2-*hydroxy*-4-*methyl*-3-*pyridyl*)*propionic acid*, m.p. 204—206°], which with $POCl_3$ at 210° gives β-(2-*chloro*-4-*methyl*-3-*pyridyl*)*propionic acid*, m.p. 128°.

J. L. D.

Preparation of 4-phenyl-1 : 4-thiazan. A. Okáč (Chem. Listy, 1934, **28**, 227).—$S(CH_2{\cdot}CH_2Cl)_2$ and NH_2Ph in boiling EtOH containing NaOAc and Na_2CO_3 give 4-*phenyl*-1 : 4-*thiazan*, b.p. 203—204°/13 mm.

R. T.

Syntheses and transformations of natural substances under physiological conditions (biogenesis of natural substances). III. Biogenesis of *iso*quinoline alkaloids. Synthesis of 6 : 7-dihydroxy-1-methyl-1 : 2 : 3 : 4-tetrahydro-

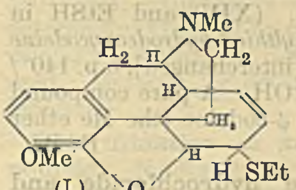
***iso*quinoline under physiological conditions.** C. Schöpf and H. Bayerle (Annalen, 1934, **513**, 190—202; cf. A., 1932, 1046).—β-3 : 4-Dihydroxyphenylethylamine hydrobromide (I) (0·04*M*) and MeCHO (II) (0·08*M*) in aq. solution at p_H 5° and 25° give (after 3 days) a good yield of the *hydrobromide*, m.p. 184—186°, of 6 : 7-dihydroxy-1-methyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline (III) [*picrate* ($+H_2O$), m.p. 205—206° (decomp.) (sinters at 125°), m.p. (anhyd.) 205—206°]. Preliminary experiments with (I) and (II) (leading to the adoption of the above conditions) are described briefly. 6 : 7-Dihydroxy-1 : 2-dimethyl-1 : 2 : 3 : 4-tetrahydro*iso*quinoline [*picrate* ($+H_2O$), m.p. 92°] is similarly obtained from β-3 : 4-*dihydroxyphenylethyl*-N-*methylamine hydrobromide*, m.p. 169—171°, and (II) at p_H 4. These results support the view (cf. *loc. cit.*) that biosynthesis of *iso*quinoline alkaloids occurs in the absence of enzymes.

Acet-β-3 : 4-dimethoxyphenylethylamide is converted (method: Spath and Polgar, A., 1929, 578) into 6 : 7-dimethoxy-1-methyl-3 : 4-dihydro*iso*quinoline, m.p. 101°, reduced (H_2, PtO_2, MeOH) to the 1 : 2 : 3 : 4-tetrahydro-derivative (picrate, m.p. 189°), which is demethylated (HBr) to (III). H. B.

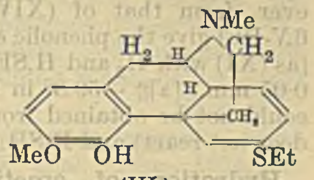
***ind*-*N*-Methylharmine.** V. V. S. Iyer and R. Robinson (J.C.S., 1934, 1635—1637).—Methylharmine and Me_2SO_4 give dimethylharmine methosulphate (I) [*iodide*, m.p. 285° (decomp.)], the corresponding chloride on thermal decomp. giving ind-N-*methylharmine*, m.p. 114—118° ($+2H_2O$) and 124—125° (anhyd.) [*hydrochloride*, m.p. 280° (decomp.); *H nitrate*, m.p. 242—243° (decomp.); *picrate*, m.p. 249—250° (decomp.)]. This combines with Me_2SO_4 and MeI to give (I) and the iodide, respectively. The Me is thus ejected from the N with the cationic charge. F. R. S.

Retamine. H. Wünschendorff and P. Valier (Bull. Sci. pharmacol., 1933, **45**, 601—604; Chem. Zentr., 1934, i, 2452).—Retamine, $C_{15}H_{26}ON_2$, m.p. 168°, prepared from *Retama sphærocarpa*, Boiss., is dextrorotatory in EtOH, gives no colour reaction with Froehde, Mandelin, or Marquis and Lafon reagents, ppts. hydroxides from salts of Fe^{III}, Cu^{II}, Mn^{II}, Ni^{II}, and Co^{II}, liberates NH_3 from NH_4 salts, forms salts with acids, and acts as reducing agent. A. G. P.

Ethylthiocodides. D. E. Morris and L. Small (J. Amer. Chem. Soc., 1934, **56**, 2159—2166).—α-Ethylthiocodide (I), m.p. 77—79° and 86—87° (stable), $[\alpha]_D$ −344·6° in 95% EtOH (*sulphate*, m.p. 185—190°), prepared by Pschorr and Rollet's method (A., 1910, i, 419), is reduced (Na, EtOH) to the same dihydrothebainol (II), m.p. 142°, as is obtained by reduction (Na–Hg) of dihydrothebainone (Kondo and Ochiai, A., 1929, 1088) or dihydrocodeinone. Catalytic reduction of (I) could not be accomplished owing to liberation of EtSH. β-Ethylthiocodide (III), m.p. 144—146°, $[\alpha]_D^{26}$ −49·9° in EtOH (improved prep.; cf. *loc. cit.*), formed by rearrangement of (I) with NaOEt, is also reduced (Na, EtOH) to (II); it is undoubtedly formed in the above reduction of (I). (III) is also reduced (H_2, Pd–$BaSO_4$, EtOH) to *tetrahydro-β-ethylthiocodide*, distils in a high vac., $[\alpha]_D^{26}$ +15·3° in EtOH. (III) is converted by boiling 2*N*-HCl into thebainone (IV) [*hydrochloride*, m.p. 254—256° (decomp.)] (Schöpf and Hirsch, A., 1931, 1313); at 70°, *ethylthiodihydrothebainone* (V), m.p. 181—182°, $[\alpha]_D^{26}$ +55·4° in $COMe_2$ [the "thioketone" of Pschorr (A., 1910, i, 421)], results. The formation of (V) from (III) involves the following reactions: (i) (III) is partly hydrolysed to (IV) and EtSH; (ii) addition of EtSH to (III) gives dihydro-β-diethyldithiocodide (VI) (proved experimentally); (iii) (VI) is hydrolysed to (V). (V) is also hydrolysed (20% NaOH) to (IV). (III) and MeI in 75% EtOH at 100° (sealed tube) give (cf. Pschorr, *loc. cit.*) the methiodide of (IV). (IV) and CH_2N_2 afford a small amount of a *substance*, $C_{19}H_{23}O_3N$, m.p. 142—144° (sinters at 125°). β-Methylthiocodide (VII) (Pschorr, *loc. cit.*) is hydrolysed to *methylthiodihydrothebainone* (VIII) ($+H_2O$), m.p. 95—97° (sinters at 90°), decomp. 110°, m.p. (anhyd.) 138—140° and 164—166°. The formation (Pschorr, *loc. cit.*) of methylthiodihydro-β-ethylthiocodide [from (III) and MeSH or (VIII) and EtSH] and of isomeric ethylthiodihydro-β-methylthiocodide [from (VII) and EtSH], is explained; the former is hydrolysed (2*N*-HCl) to (VIII). The γ-ethylthiocodide of Pschorr (*loc. cit.*) is now shown to be the *sulphoxide* of (III); it is obtained by oxidation (O_2) of (III) in EtOH at 38—40°, and it does not accompany (III) when this is prepared in H_2. δ-Ethylthiocodide (IX), distils in a high vac., $[\alpha]_D^{28}$ +57·7° in EtOH [*perchlorate* (X), m.p. 223—224°; 1 : 1-*compound*, m.p. 176—180° (decomp.), with $AgNO_3$] (improved prep.), is reduced (Na, EtOH) to the phenolic *dihydro-δ-ethylthiocodide*-B (XI), distils at 140°/high vac. (*malonate*, m.p. 170·5—171·5°), and a mixture of the phenolic dihydrodeoxycodeines-*B* and -*C* (this vol., 1117). (X) and EtSH in 6*N*-HCl give the phenolic *dihydro-δ-diethyldithiocodide* (XII), m.p. 125—126°, $[\alpha]_D^{25}$ −100° in EtOAc. Electrolytic reduction of (X) affords the phenolic *dihydro-δ-ethylthiocodide*-A (XIII), m.p. 156—157°, $[\alpha]_D^{25}$ +167·6° in EtOH [*benzoate* ($+H_2O$), m.p. 151—154° (decomp.)], and a *dihydrodeoxycodeine* [*hydrochloride*, m.p. 157—



(I.)



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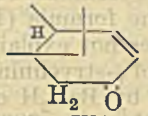

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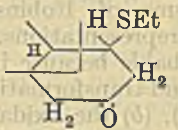

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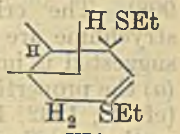

(VI.)

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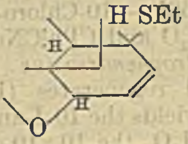

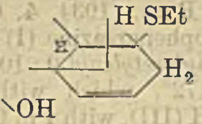

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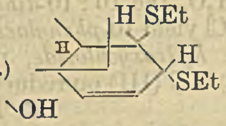

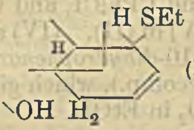

(XIII.)

159° (decomp.)] [which has the properties of deoxycodeine-*C* (XIV); the de-*N*-Me derivative differs, however, from that of (XIV)]. (XIV) and EtSH in 6*N*-HCl give the phenolic *ethylthiodihydrodeoxycodeine* [as (XI) with H_2 and H,SEt interchanged], b.p. 140°/0·05 mm., $[\alpha]_D^{24}$ −59·8° in EtOH. A pure compound could not be obtained from ψ-codeine (the Me ether does not react) and EtSH. H. B.

Hydration of emetine hydrochloride and codeine phosphate. H. WALES (J. Amer. Pharm. Assoc., 1934, **23**, 879—882).—V.-p. curves at 25° give no evidence of a hydrate of emetine hydrochloride; the H_2O present is adsorbed. Codeine phosphate has $1·5H_2O$. C. G. A.

Strychnine and brucine. XXX. Comments on a memoir of M. Kotake and T. Mitsuwa. R. ROBINSON (J.C.S., 1934, 1490—1491; cf. this vol., 908).—The criticisms of Robinson's formula for strychnine are misrepresentations. The formula (I) suggested is improbable because it does not explain (*a*) the properties and transformations of ψ-strychnine (cf. A., 1932, 1147), (*b*) the oxidation by BzO_2H of methoxymethyldihydroneostrychnine (this vol., 789), (*c*) or the fact that (I) requires the ready loss of 2H from the dihydroindole nucleus. Gentle hydrolysis of Tafel's base gives hydroxymethyldihydroneostrychnine (?), m.p. 219° (this vol., 908; A., 1932, 527), which, when heated with H_2O, forms a quaternary NH_4 hydroxide. J. L. D.

Reaction between organo-metallic compounds and certain dihydrophenarsazine derivatives. G. A. RAZUVAIEV (J. Gen. Chem. Russ., 1934, **4**, 629—631).—10-Formyl-9 : 10-dihydrophenarsazine with $HgPh_2$ yields 10-phenyl-9 : 10-dihydrophenarsazine (I), Hg, CO_2, and C_6H_6; with $PbEt_4$ it yields 10-ethyl-9 : 10-dihydrophenarsazine (II) and $(HCO_2)_2Pb$ (III), and with $PbPh_4$ it yields (I) and (III). 10-Chloro-9 : 10-dihydrophenarsazine yields (I) and $PbPh_2Cl_2$ with $PbPh_4$ in C_5H_{11}·OH, (II) and $PbEt_2Cl_2$ with $PbEt_2$, and (I) and HgPhCl with $HgPh_2$. R. T.

10-Phenylacetylenyl-9 : 10-dihydrophenarsazine and its properties. V. SCHPANSKI (J. Gen. Chem. Russ., 1934, **4**, 658—661).—10-Chloro-9 : 10-dihydrophenarsazine (I) in Et_2O and CPh⋮CNa yield 10-*phenylacetylenyl*-9 : 10-*dihydrophenarsazine* (II), m.p. 172°, which with HCl regenerates (I) and CPh⋮CH (III), with I in C_6H_6 yields the 10-*I*-analogue of (I) and CPh⋮CI, and with H_2O_2 the 10 : 10-*dihydroxide* (IV) of (II). (IV) and HCl yield 10-*phenylacetylenyl*-9 : 10-*dihydrophenarsazine hydroxychloride*, m.p. 148° (decomp.), which gives (I) and (III) on reduction with SO_2 in EtOH. R. T.

Organic gold compounds. V. Auration of aromatic nitriles. M. S. KHARASCH and T. M. BECK (J. Amer. Chem. Soc., 1934, **56**, 2057—2060; cf. A., 1931, 1172).—The following are obtained from anhyd. $AuCl_3$ and an excess of the appropriate RCN (alone or, if solid, in presence of $PhNO_2$) and subsequent dilution with Et_2O: *Au cyanophenyl* (I), m.p. 168° (decomp.), 3-*cyano*-4-, m.p. 147—148° (decomp.), and -6-, m.p. 170—171° (decomp.), -*methylphenyl* (converted by Br into 4-bromo-*o*- and 2-bromo-*p*-toluonitrile, respectively), α- and β-*cyanonaphthyl*, m.p. 161—162° (decomp.) and 127° (decomp.), respectively (from α- and β-$C_{10}H_7$·CN, respectively), 6-*bromo*-3-*cyanophenyl*, m.p. 172° (decomp.) (converted by Br into 3 : 4-$C_6H_3Br_2$·CN), m-*nitrocyanophenyl*, m.p. 185—187° (decomp.) (from *m*-NO_2·C_6H_4·CN), *cyanomethylphenyl*, m.p. 127—128° (decomp.) (from CH_2Ph·CN), and p-*nitrocyanomethylphenyl*, m.p. 140—142° (decomp.) (from *p*-NO_2·C_6H_4·CH_2·CN), *dichlorides.* Thermal decomp. of (I) gives Au, HCl, PhCN, and 2 : 5-$C_6H_3Cl_2$·CN. (I) does not react with Br at 25°; at 100°, polybromo-compounds are formed. The rate of formation of the above dichlorides varies with the electronegativity of the aryl group. The relative stability of these compounds suggests that an electron pair is shared by the Au and N atoms. *o*-C_6H_4Me·NO_2 and $AuCl_3$ give *Au* 3-*nitro*-4-*methylphenyl dichloride* (+H_2O), converted by Br into 4-bromo-2-nitrotoluene. EtCN (slight excess) and $AuCl_3$ give a *compound*, EtCN,$AuCl_3$, m.p. 85—89° (decomp.); other aliphatic nitriles generally form additive compounds. H. B.

Simple mercuri-organic derivatives of phenol. A. N. NESMEJANOV and E. M. TOROPOVA (J. Gen. Chem. Russ., 1934, **4**, 664—668).—*m*-OH·C_6H_4·HgCl (I) (*Ac* derivative, m.p. 199—200°) is obtained in 43% yield from *m*-OH·C_6H_4·N_2Cl, $HgCl_2$, and Cu in EtOH at room temp. (I) is converted by $Na_2S_2O_3$ into *Hg*(C_6H_4·*OH*-m)$_2$ (II) (*Ac_2* derivative, m.p. 161°), decomp. at 315°. The *Br*-, sintering at 240°, *I*-, sintering at 200°, *CN*-, m.p. 186—188°, and *CNS*-, m.p. 175—176°, -analogues of (I) are prepared by heating (II) with the corresponding Hg halide. R. T.

Constitution of proteins. A. BONOT (Bull. Soc. chim., 1934, [v], **1**, 1017—1025).—A lecture.

Oxidation of caseinogen. I. S. JAITSCHNIKOV (J. Gen. Chem. Russ., 1934, **4**, 662—663).—Certain of the oxidation ($KMnO_4$) products of caseinogen (I) are acidic, do not give the xanthoproteic, Millon's, and cysteine reactions, and absorb less I than did the original (I). R. T.

Clupein. II. Electrometric titration. K. E. RASMUSSEN and K. LINDERSTRØM-LANG (Z. physiol. Chem., 1934, **227**, 181—212; cf. this vol., 1015).—The titration curves of clupein fractions and unfractionated clupein resemble those of aliphatic $(NH_2)_1$-acids. The logarithms of the acid and basic dissociation consts., P_A and P_B, are 2·9—3·3 and 7·4—8·0, respectively, on the assumption that each clupein prep. is composed of a homogeneous unbranched polypeptide with terminal CO_2H and N groups. The calc. mol. wt. is 4000—4100, corresponding with a content of 19—20 arginine and 7—8 $(NH_2)_1$-acid groupings. J. H. B.

Polysaccharoproteins. III. Compounds of myosin with polysaccharides. S. J. VON PRZYŁECKI and R. MAJMIN (Biochem. Z., 1934, **273**, 262—272; cf. this vol., 961).—Myosin (I) forms well-defined compounds (II), stable at p_H 3—10, with dextrin, glycogen, and starch, each mol. of (I) being united with 1 to > 10 mols. of polysaccharide (III). The proportions in which the constituents unite depend on $[H^{\cdot}]$, purity of (I), nature and amount of (III), and on

the presence of salts in the absence of which practically no combination occurs. The amount of (III) in (II) is the greater the higher is the mol. wt. of (III).
W. McC.

Cysteine from cystine by hydrolysis. P. Holtz (Klin. Woch., 1933, **12**, 1876; Chem. Zentr., 1934, i, 532).—Ultra-violet irradiation of egg-white (I) produces reversibly oxidisable substances. Hydrolytic fission products are probably concerned. On warming (I) with 0·01*N*- or 0·1*N*-NaOH sulphide-S is liberated. Cystine is hydrolysed by heating for 30 min. at 100° with *N*-NaOH; cysteine is formed.
A. G. P.

Partial fission of silk fibroin. T. Uchino (J. Biochem. Japan, 1934, **20**, 65—130).—Hydrolysis of silk fibroin by glycerol (cf. A., 1925, i, 1109) yields a product, extraction of which by EtOAc affords glycylalanine anhydride and tyrosine-containing compounds contaminated with melanins. Hydrolysis at low temp. with 70% glycerol–H_2SO_4 is $>$ that with 70% aq. H_2SO_4, which, in turn, is $>$ that with conc. H_2SO_4. Data from degradation with varying concns. of H_2SO_4 and NaOH are given. With 0·175*N*-H_2SO_4 for 10 hr. at 170° and subsequent fractional extraction with solvents, anhydrides of glycyl-tyrosine and -alanine (but not that of alanyltyrosine) are obtained. Diketopiperazine derivatives yielded by hydrolysis with glycerol are probably not preformed, but are products of the reaction. The results generally support Fischer's acid amide linking theory of protein structure.
F. O. H.

Polypeptide constitution and proteolytic enzymes. J. Matsui (J. Biochem. Japan, 1934, **20**, 141—145).—*Et* αβ-*dichloroacetamidopropionate*, m.p. 88—89° [from abs. EtOH–HCl and the acid (A., 1932, 304)], with EtOH–NH_3 at room temp. and treated with Ag_2SO_4 followed by CO_2 yields *glycyl(glycyldiaminopropionyl) anhydride carbonate* [2 : 5-*diketo*-3-(*glycylaminomethyl*)*piperazine carbonate*], $C_4H_5O_2N_2{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}CH_2{\cdot}NH_2,0{\cdot}5H_2CO_3$ (I), m.p. 144—145°. Trypsin (with and without enterokinase), but not pepsin or erepsin, hydrolyses (I). The action of enzymes on diketopiperazine derivatives is discussed.
F. O. H.

Enzymic hydrolysis of peptides from aspartic and glutamic acids.—See this vol., 1403.

Crystalline progestin.—See this vol., 1268, 1412.

Titration of protein with trichloroacetic acid. R. K. Schofield and L. W. Samuel (Nature, 1934, **134**, 665).—$CCl_3{\cdot}CO_2H$ can be used for the rapid determination of titratable NH_2-groups. Edestin added to 0·1*M*-$CCl_3{\cdot}CO_2H$ gives, after centrifuging, a clear liquid which contains only a trace of the added N, and can be sharply back-titrated.
L. S. T.

Catalytic determination of carbon and hydrogen in organic substances. A. Contardi and C. Ferri (Atti R. Accad. Sci. Torino, Cl. Sci. fisich., 1932—1933, **68**, 181—189; Chem. Zentr., 1934, i, 2165—2166).—Separated layers of PbO_2 (at 160°) and MnO_2 (at 390—400°) are employed for the combustion. Hg, if present, is held in a layer of Ag foil, 3—4 cm. long.
H. J. E.

Semimicro-combustion by the contact process. K. H. Slotta and J. Müller (Chem.-Fabr., 1934, **7**, 380—383).—Apparatus and modified technique for determining C and H by combustion in a stream of O_2, using Pt–asbestos, are described. A 30-mg. sample is used. Methods for determining S and halogens are indicated.
E. S. H.

Determination of sulphur in organic compounds. N. Melnikov (Z. anal. Chem., 1934, **98**, 412—414).—The substance is oxidised destructively, forming SO_4'', by addition of $KMnO_4$ to its H_3PO_4 solution at 70—140°.
J. S. A.

Kuttner–Lichtenstein microcolorimetric method for determining organic phosphorus. D. Glick (J. Lab. Clin. Med., 1934, **19**, 1012—1013).—Excess of H_2O_2 is removed by heating for 3 min. at the b.p. of H_2SO_4.
Ch. Abs. (*p*)

Determination of bromine number of acid products. S. I. Schodtzev (J. Appl. Chem. Russ., 1934, **7**, 605—608).—McIlhiney and Johannsen's method of determining the halogen no. of unsaturated compounds is not applicable to acids. The following universal procedure is proposed. The sample, dissolved in 10 ml. of CCl_4 and treated with excess of 0·2*N*-Br in CCl_4, is left in diffused light for 10—15 min., after which 10—15 ml. of H_2O are added, and 0·5% PhOH drop by drop to almost complete decolorisation of the CCl_4 layer, when 1% aq. PhOH containing Me-orange is added to the appearance of a red coloration in the aq. layer. 10 ml. of conc. HCl and excess of Cl_2–H_2O are now added, followed by 10 ml. of *N*-KCN; air is aspirated through the solution for 5 min., 2 g. of KI are added, and the liberated I is titrated 20 min. later. The Br no. is given by $0{\cdot}7992(v_1-v_2)/w$, where v_1 and v_2 are, respectively, the no. of ml. of 0·1*N*-$Na_2S_2O_3$ equiv. to the Br used, and to the I liberated, and w is the wt. of the sample.
R. T.

Distillation with mercury vapour and the formation of hydrocarbon dross. H. Decker (Ber., 1934, **67**, [*B*], 1636—1640).—The volatilisation of hydrocarbondross during the distillation of bituminous idrialite suggests distillation with Hg vapour as a method of purifying difficultly-volatile hydrocarbons etc. Distillation is carried out in Anschütz flasks of Jena glass which are about 1/4 filled with Hg; 5—10 g. of substance are added and the mixture is heated over a free flame. Bumping is prevented by Cu turnings and the cork stoppers are protected by asbestos or metal foil. The method has been applied successfully to indigotin, chrysene, pyrene, fluoranthene, 2-phenylquinoline, phenanthrene, and anthracene.
H. W.

Determination of formaldehyde by aniline. G. Toussaint, J. Détrie, and M. Vérain (Compt. rend. Soc. Biol., 1934, **117**, 193—194).—Measurement at 15—20° of the optical densities of aq. solutions of NH_2Ph to which CH_2O is added may be used to determine CH_2O.
A. L.

Analysis of mixtures of acetone, acetaldehyde, and acetic acid. M. S. Platonov and V. A. Plakidina (J. Gen. Chem. Russ., 1934, **4**, 472—476).—AcOH is determined by titration with standard $Ba(OH)_2$ (phenolphthalein), $COMe_2$+MeCHO by adding NH_2OH,HCl and titrating the HCl liberated, and

COMe$_2$ iodometrically after oxidising MeCHO with KMnO$_4$, excess of which is removed by adding H$_2$O$_2$. R. T.

3-Nitrobenzhydrazide as reagent for the identification of aldehydes and ketones. K. C. Meng and P. P. T. Sah (Sci. Rep. Nat. Tsing Hua Univ., 1934, **2**, 347—351).—*m*-Nitrobenzhydrazide, from *m*-NO$_2$·C$_6$H$_4$·CO$_2$Et and N$_2$H$_4$,H$_2$O in EtOH, m.p. 151—152°, is recommended as a reagent for CO-compounds. m-*Nitrobenzoylhydrazones* of the following compounds are described: MeCHO, m.p. 160—161°; EtCHO, m.p. 153—154°; Pr$^\alpha$CHO, m.p. 138—139°; Pr$^\beta$CHO, m.p. 141—142°; heptaldehyde, m.p. 118—119°; PhCHO, m.p. 207—208°; *m*-, m.p. 251—252°, and *p*-, m.p. 261°, -NO$_2$·C$_6$H$_4$·CHO; *o*-OH·C$_6$H$_4$·CHO, m.p. 244°; furfuraldehyde, m.p. 197—200°; COMe$_2$, m.p. 151—152°; COMeEt, m.p. 112°; Me hexyl ketone, m.p. 100°; 2-furfurylideneacetone, m.p. 186—187°; COPh$_2$, m.p. 156—157°; pinacolin, m.p. 165—166°; styryl Me ketone, m.p. 168—169°; COPhMe, m.p. 194°; *m*-nitro-, m.p. 248—249°, *p*-methyl-, m.p. 194—195°, *p*-methoxy-, m.p. 199°, and *p*-bromo-acetophenone, m.p. 210°; CH$_2$Ac·CO$_2$Et, m.p. 103—104°; Et lævulate, m.p. 136°, and lævulic acid, m.p. 185—186°. H. N. R.

o-Chlorobenzhydrazide as reagent for the identification of aldehydes and ketones. T. H. Sun and P. P. T. Sah (Sci. Rep. Nat. Tsing Hua Univ., 1934, **2**, 359—363).—*o*-C$_6$H$_4$Cl·CO$_2$Et and N$_2$H$_4$,H$_2$O in EtOH solution yield o-*chlorobenzhydrazide* (I), m.p. 117—118°. The hydrazones formed from (I) and CO-compounds are, in general, more sol. and of lower m.p. than those from the *p*-isomeride. o-*Chlorobenzoylhydrazones* of the following are described: MeCHO, m.p. 145°; EtCHO, m.p. 151—152°; Pr$^\alpha$CHO, m.p. 141°; heptaldehyde, m.p. 129°; COMe$_2$, m.p. 110—111°; COMeEt, m.p. 81—82°; pinacolin, m.p. 125—126°; styryl Me ketone, m.p. 128—129°; COPhMe, m.p. 135—136°; *m*-nitro-, m.p. 212—213°, *p*-methyl-, m.p. 127—129°, and *p*-methoxy-acetophenone, m.p. 125—126°; PhCHO, m.p. 162°; *m*-, m.p. 178—179°, and *p*-, m.p. 219—221°, -NO$_2$·C$_6$H$_4$·CHO, *o*-OH·C$_6$H$_4$·CHO, m.p. 165°; furfuraldehyde, m.p. 162—163°; lævulic acid, m.p. 215°; Et lævulate, m.p. 99—100°, and COPh$_2$, m.p. 142°. H. N. R.

p-Chlorobenzhydrazide as reagent for the identification of aldehydes and ketones. C. Shih and P. P. T. Sah (Sci. Rep. Nat. Tsing Hua Univ., 1934, **2**, 353—357).—*p*-Chlorobenzhydrazide, m.p. 162—163°, prepared from *p*-C$_6$H$_4$Cl·CO$_2$Et and N$_2$H$_4$,H$_2$O in EtOH, is recommended as a reagent for CO-compounds. p-*Chlorobenzoylhydrazones* of the following are described: MeCHO, m.p. 180—181°; EtCHO, m.p. 163—165°; Pr$^\alpha$CHO, m.p. 142—143°; Pr$^\beta$CHO, m.p. 153—154°; PhCHO, m.p. 227—229°; *m*-, m.p. 213—215°, and *p*-, m.p. 246—248°, -NO$_2$·C$_6$H$_4$·CHO; *o*-OH·C$_6$H$_4$·CHO, m.p. 214—217°; furfuraldehyde, m.p. 210—212°; COMe$_2$, m.p. 169—171°; COMeEt, m.p. 161—162°; Me hexyl ketone, m.p. 121—122°; COPhMe, m.p. 175—177°; *m*-nitro-, m.p. 240—242°, *p*-methyl-, m.p. 213—215°, and *p*-methoxy-acetophenone, m.p. 190—192°; COPh$_2$, m.p. 137—139°; styryl Me ketone, m.p. 197—199°; pinacolin, m.p. 197—199°; CH$_2$Ac·CO$_2$Et, m.p. 98—99°; lævulic acid, m.p. 135—137°; Et, m.p. 106—108°, and CH$_2$Ph, m.p. 131—132°, lævulate. H. N. R.

Hydrazines. IV. β-Naphthylhydrazine as reagent for the identification of aldehydes and ketones. H. H. Lei, P. P. T. Sah, and C. H. Kao (Sci. Rep. Nat. Tsing Hua Univ., 1934, **2**, 335—341).—β-Naphthylhydrazine (prep. described; *picrate*, m.p. 176·5°) is recommended as a reagent for CO-compounds. β-*Naphthylhydrazones* of the following compounds are described, some of which may be further characterised by conversion into their picrates and titration with alkali: *o*-OH·C$_6$H$_4$·CHO, m.p. 186—187°; *m*-NO$_2$·C$_6$H$_4$·CHO, m.p. 201—202°; furfuraldehyde, m.p. 134—135° (*picrate*, m.p. 118°); 2-furfurylideneacetone, m.p. 163—164° (*picrate*, m.p. 118—119°); COPh$_2$, m.p. 127—128° (*picrate*, m.p. 157—158°); styryl Me ketone (*picrate*, m.p. 124—125°); *m*-nitroacetophenone, m.p. 143—144° (*picrate*, m.p. 161—162°); CH$_2$Ac·CO$_2$Et, m.p. 107—108° (*picrate*, m.p. 160—161°). The β-naphthylhydrazones of PhCHO, m.p. 194—195°, *p*-NO$_2$·C$_6$H$_4$·CHO, m.p. 233—234°, COPhMe, m.p. 157—158° (*picrate*, m.p. 153—154°), lævulic acid, m.p. 143—144° [*picrate*, m.p. 176° (decomp.)], and Et lævulate, m.p. 138—139° (*picrate*, m.p. 152—153°), were also prepared. H. N. R.

Application of quantitative spectrum analyses to binary mixtures of common carotenoids. E. S. Miller (Plant Physiol., 1934, **9**, 681—684).—Over a limited range of concn. binary mixtures of carotenoids obey Beer's law. Spectrum analysis permits determinations with approx. 1% error. A. G. P.

A. Liebermann–Burchard reaction with compounds containing five-membered monoheterocyclic rings. V. E. Levine and E. Richman. **B. Liebermann–Burchard reaction with carotene.** V. E. Levine and G. E. Bien (Proc. Soc. Exp. Biol. Med., 1934, **31**, 582—584).—A. The Liebermann–Burchard (I) reagent reacts with thiophen, furan, and many of its derivatives, as well as with cholesterol (II).

B. The (I) test for (II) will detect 0·01 mg. of carotene (III) dissolved in CHCl$_3$. The green colour with (III) reaches a max. intensity rapidly and fades in 2 min. to a yellow-brown. The green colour with (II) reaches a max. in 15 min. (III) does not interfere with the determination of (II) in blood. CHCl$_3$ extracts (II) from blood and from plaster of Paris mixture, but does not remove (III). Ch. Abs. (*e*)

Determination of tyrosine by bromination. M. Bonicatti (Boll. uff. R. Staz. sperim. Seta, 1933, **3**, 66—69).—The solution is acidified with HCl, and 5 c.c. of 20% NaBr are added followed by 0·1*N*-NaBrO$_3$ until the solution is deep yellow. After 2 hr. excess of KI is added and the mixture titrated with 0·05*N*-Na$_2$S$_2$O$_3$. A. G. P.

Tryptophan reaction of Adamkiewicz and Hopkins. S. Winkler (Z. physiol. Chem., 1934, **228**, 50—60).—Since small amounts of Cu greatly increase the intensity of the colour, addition of Cu makes the detection of tryptophan in proteins by means of CHO·CO$_2$H much more certain. The Cu addition also facilitates an exact colorimetric determination of tryptophan. J. H. B.

Determination of ecgonine. A. Goris, A. Chalmeta, and C. Chalmeta (Bull. Sci. Pharmacol., 1933, 40, 641—650; Chem. Zentr., 1934, i, 2171).—In de Jong's method (A., 1923, ii, 798) the extraction of ecgonine is not always complete. Hydrolysis with HCl requires at least 3 hr. The use of more conc. acid may cause partial transformation into anhydroecgonine. A. G. P.

Biochemistry.

Changes in the respiratory characteristics following respiration of mixtures with low concentrations of oxygen. R. Margaria and C. Talenti (Atti R. Accad. Sci. Torino, 1933, 68, 483—491).—Inspiration of mixtures containing $< 15\%$ O_2 produced an increase of ventilation and velocity of inspiration; frequency of inspiration increased only slightly. On re-establishment of normal conditions all the respiratory characteristics fell temporarily to vals. < normal. The blood-p_H in hypoventilation (I) from anoxæmia decreased by 0·03—0·10 according to the magnitude of (I); the increase in respiration is therefore attributed to increased [H$^{\cdot}$] of the nerve centres. R. N. C.

Influence of respiration on the oxygen-saturation of arterial blood. K. Matthes (Arch. exp. Path. Pharm., 1934, 176, 683—696).—Spectrophotometric determinations of oxygenated and reduced hæmoglobin indicate that the blood of experimental animals, whether narcotised or not, has an O_2-saturation (I) of 94—98%, the val. falling to 80% with certain types of narcosis; the deficiency disappears on administration of O_2. (I) varies by approx. 0·5—5% when the respiration (II) is fast and slow, respectively. The types of (II) due to injection of adrenaline or pernocton and to vagal stimulation are correlated with the changes in (I). F. O. H.

Spectroscopic comparison of fœtal and maternal blood in the rabbit and goat. F. G. Hall (J. Physiol., 1934, 82, 33—37).—The O_2-dissociation curves for fœtal (I) and maternal hæmoglobin (II) show that in all cases and at all periods of gestation, (I) has a greater affinity for O_2 than (II). The difference in the goat is > in the rabbit, whilst in the latter case at p_H 7·4 it is > at 6·8. Fœtus and mother probably have a sp. difference in their hæmoglobins. R. N. C.

Blood-volume and oxygen-capacity of the fœtal blood of the goat. R. H. Elliot, F. G. Hall, and A. St. G. Huggett (J. Physiol., 1934, 82, 160—171).—The O_2-capacity (I) of the fœtal blood rises during the first half, and is steady during the second half, of pregnancy, at which stage the total (I) of the circulation also becomes const., and the corpuscular carrying-power for O_2 increases and remains high until birth. R. N. C.

Effect of blood transfusion on the condition of the receiver's blood, and of the withdrawal of blood on the donor's gas metabolism. M. Nakanishi (Nagoya J. Med. Sci., 1934, 7, 202—205).—Receiver's blood after transfusion shows temporarily increased sugar and lowered Ca and N contents; that of the donor has increased O_2 consumption. Ch. Abs. (*p*)

Changes in hæmoglobin concentration of blood of growing rats. E. V. Enzmann (Amer. J. Physiol., 1934, 108, 373—376).—Neither Ponder's nor Drastich's suggested formula for relating hæmoglobin (I) to erythrocyte vol. is applicable throughout life. Both are low during the first six weeks of life, *i.e.*, during the period of physiological anæmia, but fairly const. after the adult level of (I) is attained. Nutr. Abs. (*b*)

Hæmoglobin and erythrocyte differences according to sex and season in doves and pigeons. O. Riddle and P. F. Braucher (Amer. J. Physiol., 1934, 108, 554—566).—In both species and all races studied hæmoglobin (I) and erythrocyte count (II) in males were > in females; (I) in winter was >, and in summer <, in the other seasons; (II) was highest in autumn and lowest in summer. (I) and cell count were not necessarily parallel. Both (I) and (II) were slightly higher in adolescent than in adult birds. Nutr. Abs. (*b*)

Rôle of erythrocytes in protein metabolism. I. Exchange of amino-nitrogen between erythrocytes and plasma *in vitro*. B. I. Sbarski and L. Subkova (Biochem. Z., 1934, 273, 279—283).—*In vitro* erythrocytes (I) always have an NH_2-acid (II) content > that of the surrounding plasma (III). (I) take (II) from (III) or give up (II) to (III) according as the (II) content of (III) rises or falls. W. McC.

Microdetermination of protein and protein fractions in serum and plasma without distillation. F. Rappaport and G. Geiger (Klin. Woch., 1934, 13, 563—564).—The NaOBr method for determining non-protein-N is adapted for the determination of fibrinogen, albumin, globulin, and globulin fractions. The fibrinogen-N is determined in the ppt. itself, otherwise Howe's method is followed. 0·2 ml. of serum or plasma is necessary. Nutr. Abs. (*m*)

Serum-albumin and -globulin of new-born, premature, and normal infants. D. C. Darrow and M. K. Cary (J. Pediat. St. Louis, 1933, 3, 573).—Total protein decreases in all infants, the decrease being due chiefly to globulin (I). The decrease in (I) is greatest in premature infants. *Post-mortem* serum of small fœtuses showed essentially the same albumin : (I) ratio as that of full-term infants. Both premature and normal infants may show an increase in (I) during infection. The low (I) in infants may indicate the lack of the usual stimuli that give rise to (I) production in adults. Nutr. Abs. (*b*)

Chemistry and spectroscopy of serum-globulin. J. Gróh and M. Weltner (Biochem. Z., 1934, 273, 389—395).—The chemical (tyrosine and tryptophan contents) and spectroscopic properties of the globulin fractions (I) obtained from dil. blood-serum (II) (horse, man) by pptn. with aq. $(NH_4)_2SO_4$

suggest that there is a relationship between (I) and the kind of hæmagglutinin which (II) contain. Hence there may be also a connexion with the blood-groups.

W. McC.

p_H of serum inactivated by heat. P. L. du Noüy (Nature, 1934, **134**, 628—629).—The p_H of mammalian sera is lowered by heating for 10 min. in sealed tubes. A min. val. occurs at approx. 60°; above this temp. a tendency towards higher vals. is sometimes shown.

L. S. T.

Physical properties of blood-serum. M. Doladilhe (Ann. Inst. Pasteur, 1934, **53**, 379—403; cf. this vol., 912).—When colloids of the gamboge type are treated with increasing concn. of blood-serum (I), two zones of non-flocculation [(II) and (III), respectively] with an intermediate zone of flocculation (IV) occur. With (II) the particles are sensitised, whilst with (III) a protective action occurs. With gum and resin colloids, (I) has a marked dispersive action (V) at (III) to an extent depending on the concn. of electrolyte present, the prior treatment (*e.g.*, heating) of (I), etc. (IV) and (V) are mainly due to the globulin and albumin–lipoprotein constituents of (I), respectively; a mutual action also occurs. The bearing of (V) on complement action in immuno-serology is discussed.

F. O. H.

***Post-partum* changes in blood-urea, -polypeptides, and -chlorine.** E. Estienny, J. Lasserre, and P. Valdiguie (Compt. rend. Soc. Biol., 1934, **115**, 1676).—In the *post-partum* phase, the urea content of the blood was approx. doubled and the polypeptide content multipled 6 times; the Cl content was slightly lowered, this change occurring chiefly in the corpuscles. The kidney appeared to play little part in producing the changes in the N constituents.

Nutr. Abs. (*b*)

A. Changes in urea- and amide-nitrogen of the blood following injection of urease. B. Influence of urea injection on the action of urease. C. Respiratory and chemical changes in exhaled air and in blood reaction following urease injection. A. Aggazzotti, G. Bucciardi, and B. D. Marani (Boll. Soc. ital. Biol. sperim., 6, 597—599, 600—602, 603—605; Chem. Zentr., 1934, ii, 561).—A. The increase in amide-N and lowering of urea-N in blood following injection of urease (I) indicate that the action of (I) is not limited to blood-urea but extends to that of the tissues.

B. Injected urea is partly eliminated through the kidneys and partly stored in tissues. Stored urea is acted on by (I). After heavy administration of urea injection of (I) is fatal.

C. No definite relationships were observed.

A. G. P.

Determination of blood-urea by the urease aëration–titration method. W. W. Kay and H. L. Sheehan (Biochem. J., 1934, **28**, 1784—1794).—The method has been modified to give an accuracy of 0·4 mg. per 100 c.c. of blood, but shows only 96% of the urea, the proportion of the NH_3 removed by the aëration.

H. G. R.

Glutathione content of blood. R. O. Bowman (Proc. Soc. Exp. Biol. Med., 1934, **31**, 616—617).—A modification of the IO_3' titration method of Hess has been applied to the determination of reduced glutathione in the tungstic acid filtrates of blood. An accuracy of 7% is claimed. No relationship was found between glutathione content and clinical condition, exercise, diet, age, sex, or colour.

Nutr. Abs. (*b*)

Tryptophan content of blood-serum. A. T. Brice, jun. (J. Lab. Clin. Med., 1934, **19**, 1113—1115).—Dil. serum (1 : 10) is treated with glyoxylic acid and H_2SO_4. The colour is compared with standard dye tints.

Ch. Abs. (*p*)

Acetylcholine in ox and dogs' blood. G. H. Ettinger and G. E. Hall (J. Physiol., 1934, **82**, 38—40).—Very small quantities of acetylcholine (I) were found in ox and dogs' blood; the yield was greater if the blood was collected in EtOH than MeOH, and was not affected by the presence or absence of $H_2C_2O_4$, or by keeping the blood. (I) was best extracted from blood with EtOH; MeOH gave unsatisfactory results. (I) added to dogs' blood could be recovered quantitatively.

R. N. C.

Alleged occurrence of acetylcholine in normal ox-blood. J. V. Loach (J. Physiol., 1934, **82**, 118—120).—Attempts to extract acetylcholine (I) from normal ox-blood as aurichloride proved unsuccessful, although (I) added before extraction could be recovered as (II). The Au salt obtained when (I) had not been added was identified as choline aurichloride.

R. N. C.

Phosphoric acid compounds in blood after injection of lecithin. Y. Sueyoshi and T. Okonogi (J. Biochem. Japan, 1934, **19**, 489—494).—Ingestion of lecithin by rabbits has little influence on the inorg. (I) and acid-sol. P level (II) of the blood. Intravenous injection increases (I) and (II) [mainly in the corpuscles (III)] and the lipin-P [both in (III) and plasma].

F. O. H.

Lipin-chlorine in serum. J. P. Peters and E. B. Man (J. Biol. Chem., 1934, **107**, 23—34).—Normal sera (I) and those from patients with nephrotic syndrome who have hyperchloræmia and hyperlipæmia (II) are treated with an EtOH–Et_2O mixture (3 : 1), and, after refluxing, the pptd. proteins, the light petroleum extract of the EtOH–Et_2O mixture (III), and the residue from (III) are analysed for Cl. The fatty acids, lipin-P, and cholesterol in (III) are also determined. Amounts of Cl in the lipin fraction of 2—6 and 2—10 m.-equiv. per 100 c.c. were found in (I) and (II), respectively. No Cl was found in the (III), by the same procedure, of bacon, salt butter, or serum-ultrafiltrates. The lipin-Cl of sera is sufficient to account for the observed differences in total base and acids.

H. D.

Cholesterol content of the blood of the hen. Y. Kaishio (Proc. 5th World's Poultry Congr. Rome, 1933).—The total cholesterol (I) of the serum in fasting birds after a normal diet averaged 0·073%, of which 0·044% was free and 0·029% was ester-(I). Figures are also given for the plasma. The content in non-laying hens is similar to that in cocks. When the ovary contained well-developed ova, total (I) was higher than when the ovary was quiescent. The ester-(I) was lower in the former case. There was no correlation between blood-(I) and age or egg production. NUTR. ABS. (*b*)

Determination of plasma-bilirubin. Comparison of the van den Bergh and the Thannhauser and Andersen methods. E. H. BENSLEY (J. Lab. Clin. Med., 1934, **19**, 1122—1125).—In sera from cases of subsiding jaundice van der Bergh's method gave low results. In all other cases the method was satisfactory. CH. ABS. (*p*)

Blood-sugar in monkeys (*Macacus rhesus*). P. V. BOCHKAREV and O. I. NIKOLAEVA (Arch. Sci. Biol. U.S.S.R., 1933, **33**, 235—236).—Fasting venous blood-sugar ranged from 43 to 147 mg. per 100 c.c. CH. ABS. (*p*)

Depression of blood-sugar by egg-yolk fractions. G. HOLLAND, K. HINSBERG, G. KOHLS, and V. NICKEL (Z. ges. exp. Med., 1934, **93**, 62—68; Chem. Zentr., 1934, i, 2444—2445).—Active material isolated from egg-yolk contained highly unsaturated acidic substances, the action of which on blood-sugar was related to the extent of unsaturation. Oxidation destroyed the activity. A. G. P.

Increase in sugar content of blood produced by diastase. J. WEINMANN (Biochem. Z., 1934, **273**, 312—316).—Diastase (I) of animal and vegetable origin and, occasionally, saliva intravenously or subcutaneously injected into rabbits cause an increase, sometimes large, in the blood-sugar. No increase results if (I) is inactivated by heat or acid. W. McC.

Colorimetric determination of fructose in blood and urine. J. H. ROE (J. Biol. Chem., 1934, **107**, 15—22).—The Seliwanoff reaction is modified by using 18% HCl, alcoholic resorcinol, and warming to 80°. Proteins are removed from blood with the Somogyi reagent (A., 1930, 801); urine is decolorised with acid-washed activated charcoal at p_H 3·1. Under these conditions glucose ($<$ 300 mg. per 100 c.c.) does not interfere; furfuraldehyde gives a green colour with the test although xylose ($<$ 1%) does not interfere. Normal human urine secreted under fasting conditions gives a negative fructose test, whilst after a meal containing fruits and sucrose it gives a positive test. H. D.

Diacetyl and acetylmethylcarbinol (or their heat-labile precursors) in blood. H. SCHMALFUSS (Z. physiol. Chem., 1934, **227**, 247—250).—Ac_2 and CHAcMe·OH were detected in fresh ox-blood and in sheep's blood. J. H. B.

Determination of oxalic acid in blood and intermediary oxalic acid metabolism. R. JÜRGENS and E. JUERGENSOHN (Z. ges. exp. Med., 1934, **93**, 441—446).—The method of Merz and Maugeri is used, but 7% aq. $CCl_3 \cdot CO_2H$ is used for deproteinising. Administration of 7·5—40·0 g. of malic, succinic, or tartaric acid causes no increase in the $H_2C_2O_4$ content of the blood. NUTR. ABS. (*m*)

Blood-calcium. A. A. JANSON (Illinois Med. J., 1934, **65**, 91—95).—No const. relationship could be established between total and diffusible Ca or between inorg. P and Ca of blood. Normal vals. for total Ca were associated with high, normal, and low vals. for diffusible Ca, with low vals. predominating. Many cases with low total Ca showed normal diffusible Ca and with high total, low diffusible Ca. The importance of determining diffusible rather than total Ca content of the blood is indicated. NUTR. ABS. (*b*)

Calcium and phosphorus content of the blood-plasma of the fasting laying hen. M. LASKOWSKI (Biochem. Z., 1934, **273**, 284—290).—The P content of the blood-plasma (I) of laying (II) is 3·5 times that of (I) of non-laying (III) hens. No increase in the Ca and P contents of their (I) results from feeding diet rich in Ca and P to fasting hens. 2—4 days' fasting does not interrupt the laying, and the Ca and P contents of (I) remain at the normal val. for (II). 4—6 days' fasting interrupts laying for several days, and the Ca and P contents of (I) fall to the val. characteristic of (III). There is no relation between the Ca and P contents of (I). W. McC.

Escape of potassium from rabbit's red cells into hypotonic solutions. E. PONDER and E. J. ROBINSON (Biochem. J., 1934, **28**, 1940—1943).—When rabbit's red cells are suspended in hypotonic NaCl, K is lost from the cells, probably during the 15 sec. in which swelling to equilibrium takes place, in sufficient quantity to account for the observed vol. changes. A. E. O.

Sulphur content of pancreatic blood and thoracic lymph. II. S. KUMAMI (J. Biochem. Japan, 1934, **19**, 457—467; cf. A., 1933, 965).—The total S levels of the pancreatic venous blood (I) and thoracic lymph (II) of dogs transiently increase after injection of glucose or stimulation of the vagus. The increase is at least partly due to increased secretion of insulin, which is therefore transported by both (I) and (II). Intravenous injection of aq. NaCl diminishes the S content of (II). F. O. H.

Normal bromine cycle in blood. H. FLEISCHHACKER and G. SCHNEIDER (Klin. Woch., 1933, **11**, 1550; Chem. Zentr., 1934, i, 3502).—Roman's method is not applicable to determinations of small amounts of Br′ in blood. A. G. P.

Determination of iodine [in blood]. D. R. McCULLAGH (J. Biol. Chem., 1934, **107**, 35—44).—Blood is heated with saturated aq. KOH in a Ni crucible until foaming ceases, and then heated at 250° for 30 min. H_2O is added, the paste extracted with 95% EtOH, and the extract evaporated to dryness. The residue is heated at 385° for 10 min. in a stream of O_2. The ash is dissolved in H_2O and filtered and 50% H_2SO_4, 10% $Fe_2(SO_4)_3$, and 30% H_2O_2 are added. The solution is distilled into a mixture of aq. H_2SO_4 and 10% $NaHSO_3$ for 30 min. After boiling the distillate for 3 min. KOH is added and the solution is conc. Br is added to the slightly acid solution and after further concn. KI is added and the liberated I is titrated with $Na_2S_2O_3$. H. D.

Water content of the blood of the silk-worm (*Bombyx mori*, L.) during development. K. KURODA (Keijo J. Med., 1934, **5**, 151—164).—The H_2O content of the blood shows complex variations during the life cycle; these are completely different from those obtaining in the mouse, chicken, and salmon, and bear no relation to the H_2O intake. P. G. M.

Mitogenetic spectrum of circulating blood. K. P. Goluisheva (Arch. Sci. Biol. U.S.S.R., 1933, **33**, 107—113).—Spectrographic measurements indicate the spectral regions of glycolysis, oxidation, hydrolysis of hexose phosphate and creatine phosphate, and deamination of peptides. Ch. Abs. (*p*)

Relations between immunity-hæmolysis and diet in the rat. A. Forssberg (Z. Immunität., 1933, 80, 16—27; Chem. Zentr., 1934, i, 2304—2305).—Rats were given a synthetic basal diet of varying composition, immunised against sheep-serum, and the hæmolytic titres (I) estimated. Antibody formation was lowered by vitamin deficiency only for vitamin-*A*. Increase of fat in the diet raised blood-cholesterol, and lowered hæmolysin (II). Substitution of gelatin for caseinogen, ovalbumin, or glutinin in the diet reduced the (I), the fall being considerable if albumin was entirely absent. Addition of lecithin or choline increased the production of (II). R. N. C.

Absorption of simple lysins at cell interfaces. E. Ponder (Proc. Roy. Soc., 1934, B, **116**, 282—295).—The "initial" and "delayed" absorption at red-cell surfaces does not correspond with the adsorption postulated by other investigators (cf. Reiner, this vol., 551). H. G. R.

Hæmostatic possibilities of snake venom. R. G. Macfarlane and B. Barnett (Lancet, 1934, **227**, 985—987).—The venom of *Vipera russellii* contains a coagulant which, in high dilutions *in vitro*, rapidly clots normal and hæmophilic blood. L. S. T.

Effect of snake venom on hapten antibody reaction. W. Schepers (Z. Immunität., 1933, 80, 395—411; Chem. Zentr., 1934, i, 883—884).—Cobra venom (I) inhibits the coagulability of haptens, and even of organ-sp. EtOH brain extracts, group-sp. human blood-*A* extracts, and species-sp. organ extracts. The same inhibition also occurs with lecithin or organ extracts after boiling. There was no indication of the conversion of hapten into hemi-hapten, the production of non-sp. inhibitions by the action of (I) on the lipin vehicle of the hapten function appearing the most probable explanation. Experiments with *Daboia* venom suggested a parallelism between lecithin cleavage and the inhibition of flocculation. The hæmolytic products of snake venoms and lecithin show the same inhibitory action. R. N. C.

Chemistry of immunity. F. Haurowitz (Med. Klin., 1933, 29, 936—939; Chem. Zentr., 1934, i, 3484).—From the use of chemically-known antigens and analysis of their reaction products with antibodies it is concluded that the antigen disturbs globulin (I) formation in the reticulo-endothelial cells, the NH_2-acids, oriented by polar attraction, combining to form the antibody-(I), which does not differ chemically from serum-(I). R. N. C.

Chemo-immunological studies of conjugated carbohydrate proteins. VIII. Influence of the acetyl group on specificity of hexoside–protein antigens. W. F. Goebel, F. H. Babers, and O. T. Avery (J. Exp. Med., 1934, **60**, 85—94).—Introduction of a simple chemical group (*e.g.*, Ac) induces a new specificity in carbohydrates. Ch. Abs. (*p*)

Immunological specificity of the thyroglobulins. M. Adant and P. Spehl (Compt. rend. Soc. Biol., 1934, **117**, 230—231).—Sheep antithyroglobulin immune serum (I) and ox (I), whilst having a high pptn. activity with respect to the corresponding antigens, have very little activity towards the thyroglobulins (II) of the pig and the ox, and (II) of the pig and the sheep, respectively. A. L.

Immunological comparison of iodised protein and thyroglobulins. M. Adant and P. Spehl (Compt. rend. Soc. Biol., 1934, **117**, 232—233).—Thyroglobulin (I) immune sera have a slight pptn. activity towards iodised serum-protein (II) when (I) and (II) are derived from the same species of animal. There is no activity, however, when (I) and (II) are derived from different species. A. L.

Avidity of concentrated and unconcentrated sera. F. Modern (Anal. Asoc. Quím. Argentina, 1934, **22**, 33—40).—The serum ratio (I) of an unconc. diphtheria antitoxin (II) varies with the serum, but is $\not<$ 1. The conc. (II) has (I) approx. 1. The time of flocculation varies considerably with the serum. The L_+ of diphtheria toxin in guinea-pigs usually requires 1·5—1·7 units of (II) for neutralisation. The dilution ratio is slightly higher in unconc. than in conc. (II). Concn. of normal sera lowers the (I) slightly. R. N. C.

Precipitin production in rabbits following intramuscular injection of antigen adsorbed on aluminium hydroxide. L. Hektoen and W. H. Welker (J. Infect. Dis., 1933, **53**, 309—311).—Precipitin production following injection may continue for several months. $Al(OH)_3$ is gradually replaced by connective tissue. Antigens adsorbed on $Al(OH)_3$ retain precipitinogenic properties for at least 1 year. Ch. Abs. (*p*)

Complexes of iron with various biological materials. S. L. Tompsett (Biochem. J., 1934, **28**, 1802—1806).—$Fe^{\cdots}$ but not $Fe^{\cdot\cdot}$ forms complexes with the non-diffusible P of biological materials, such as lecithin, egg-white, and milk, but not with simple proteins. It is liberated on reduction by thiolacetic acid and $Na_2S_2O_4$, and by $Na_4P_2O_7$ with formation of a non-ionised $Fe_2P_2O_7$. In the blood-corpuscles some $Fe^{\cdot\cdot}$ is present. Cu does not form these complexes. H. G. R.

Distribution of vanadium in organisms. A. P. Vinogradov (Compt. rend. Acad. Sci. U.R.S.S., 1934, **3**, 454—458).—Various terrestrial and marine animals and plants contain V in concns. of about 10^{-5}%, but certain species of *Holothuria* and of *Ascidia* contain much higher concns. The ashes of certain species of *Ascidia* contain up to 1·5% of V. W. O. K.

Phosphatic calculi in Silurian polyzoa. K. P. Oakley (Proc. Roy. Soc., 1934, B, **116**, 296—314).—The calculi were probably formed in the cœlomic fluid, due to a rise in p_H during degeneration of polypide structures. H. G. R.

Calcium content of frog nerve. S. R. Tipton (Amer. J. Physiol., 1934, **109**, 457—466).—The Ca content of the sciatic nerves of winter frogs averages 0·735±0·0937 milli-equiv. Ca per 100 g. wet wt. Immersion of the nerve in Ringer's solution of varying

$[Ca^{\bullet\bullet}]$ until equilibrium between Ca inside and outside the nerve has been established produces changes in nerve-Ca, indicating that 55% of the nerve is involved in the diffusion process. If the outside solution (I) contains no Ca, 60% of the nerve-Ca does not diffuse out. As $[Ca^{\bullet\bullet}]$ or $[PO_4''']$ in (I) is increased, at a certain concn. there is a sudden increase in nerve-Ca, the concn. at which this occurs apparently depending on the factors governing $Ca_3(PO_4)_2$ pptn. in (I). At a const. $[Ca^{\bullet\bullet}]$ in (I) the magnitude of the increase depends somewhat on $[PO_4''']$ in (I). The increase occurs even when (I) contains no PO_4'''. Ca diffusion is scarcely affected by varying $[K^{\bullet}]$ or the p_H of (I). Low p_H tends to involve a greater % of the nerve in the diffusion process. R. N. C.

Biochemistry of the brain. A. Palladin (Bull. Soc. Chim. biol., 1934, **16**, 1193—1210).—A lecture.

Citric acid in tissues. C. L. Gemmill (Skand. Arch. Physiol., 1934, **67**, 201—210; Chem. Zentr., 1934, i, 3363).—Citric acid was found in frogs' liver and muscle under anaërobic conditions, and in rabbits' normal resting muscle, liver, brain, and kidneys. It was not present in normal and excited frogs' muscle. R. N. C.

True sugar and glycogen of tissues. Micro-determination. N. Doi (J. Biochem. Japan, 1934, **19**, 469—488).—The importance of parallel determinations of free sugar (I) and glycogen (II) in the study of carbohydrate metabolism of tissues is emphasised. Micro-methods for 0·2—0·5 g. of tissue, based on hydrolyses with acid and alkali and subsequent yeast-fermentation and (I) determination, are given. The action of strong acids or alkalis increases the non-fermentable (I) by 30—50%. The liver and muscle of rabbits vary greatly in their contents of (II), whilst those of (I) (1·068—1·342 and 0·092—0·168%, respectively) are more const. F. O. H.

Coccids produced in Japan. VI. Nitrogen compounds and mineral matter in *Pulvinaria horii*, Kuw. M. Kono and R. Maruyama (J. Agric. Chem. Soc. Japan, 1934, **10**, 360—367).—Analytical data are recorded. Ch. Abs. (*p*)

Human epidermis. I. Amino-acid content of the stratum corneum and its comparison with other human keratins. V. A. Wilkerson (J. Biol. Chem., 1934, **107**, 377—381).—Analysis of the stratum corneum of human epidermis (I) indicates that during the course of specialisation of nail and hair from (I), the mol. ratios of histidine, lysine, and arginine are not significantly altered. A. E. O.

Solubility of the stereoisomerides of cystine with a note on the identity of stone and hair cystine. H. S. Loring and V. du Vigneaud (J. Biol. Chem., 1934, **107**, 267—274).—The solubilities at 25° are *l*-, 0·108; *d*-, 0·108; *dl*- 0·049; *meso*-cystine, 0·056 g. per litre. *dl*-Cystine is a racemic compound and not a mixture. *d*- and *l*-Cystine may form more sol. compounds with *meso*-cystine. Stone- and hair-cystine have the same solubility, which is not increased on mixing, proving their identity. C. G. A.

Creatine, creatinine, iron, and fat contents of fish muscle. S. Namiki (Nagoya J. Med. Sci., 1934, 7, 206—207).—The ratios of creatine, creatinine, and fat in white and in red muscle are 2 : 1, 1 : 1, 1 : 7, respectively. The amounts of Fe are, respectively, 0·67—1·04 and 4·44—7·19 mg. per 100 g. Ch. Abs. (*p*).

Fatty acids of pig liver. II. Octadecenoic acids and the desaturation theory. H. J. Channon, E. Irving, and J. A. B. Smith (Biochem. J., 1934, **28**, 1807—1811).—Oxidation of the octadecenoic acids of pig liver by the method used by Hartley (A., 1909, ii, 597) confirms the original finding (this vol., 913) that the chief constituent is oleic acid and not the Δ^{λ} isomeride. A. E. O.

Occurrence of highly unsaturated fatty acids in oils of common fowls and animal fats. J. B. Brown and C. C. Sheldon (J. Amer. Chem. Soc., 1934, **56**, 2149—2151).—Various oils [goose (I), chicken, duck, turkey] are shown [by conversion (methanolysis) into Me esters and subsequent bromination in cold Et_2O] to contain 0·2—1·16% of (mainly) arachidonic acid (II). Two specimens of (I) contained linolenic acid but no (II). The traces of Me ester polybromides similarly obtained from animal fats (beef, calf, lamb, reindeer) have m.p. $>238°$, indicating the presence of acids either more unsaturated or of higher mol. wt. than (II). H. B.

Highly unsaturated C_{24}-acid in herring, cod-liver-, pilot-whale, and aburazame liver-oils. Y. Toyama and T. Tsuchiya (J. Soc. Chem. Ind. Japan, 1934, **37**, 530—534b).—The fraction, b.p. $< 240°/10$ mm., of the Me esters of the fatty acids of each of these oils is hydrolysed; the $COMe_2$-sol. portion of the Na salts of the resulting acids is converted into Me esters, the portion, b.p. $< 215°/2$ mm., of which by hydrolysis followed by treatment with Br and debromination affords *nisinic acid*, $C_{24}H_{36}O_2$, an oil (*dodecabromide*, decomp. about 240°), affording *n*-tetracosoic acid by hydrogenation. R. S. C.

Gadoleic acid in sei-whale and humpback-whale oils. Y. Toyama and T. Ishikawa (J. Soc. Chem. Ind. Japan, 1934, **37**, 534—536b).—Isolation of the acid is recorded. R. S. C.

New eicosenoic acid from pilot-whale oil. Y. Toyama and T. Ishikawa (J. Soc. Chem. Ind. Japan, 1934, **37**, 536—537b).—The body oil of this whale yields *gondoic acid*, $C_{20}H_{38}O_2$, m.p. 23·5—24°, giving by oxidation a $(OH)_2$-*acid*, m.p. 126·5—127°, and by reduction arachidic acid. R. S. C.

Millipede oil. S. Ueno and R. Yamasaki (J. Soc. Chem. Ind. Japan, 1934, **37**, 507—510b).—1 kg. of *Strongylosoma tambanum*, Attems (I) (235 g., when dried), gave 5·01 g. of oil (n_{D}^{15} 1·6285; acid val. 69·7; sap. val. 175), which yielded 21·4% of unsaponifiable matter (II) and 76·3% of fatty acids (III). (I) contains free $EtCO_2H$ and oleic acid. (III) is mainly palmitic with some myristic acid. (II) contains *yasudesterol*, $C_{24}H_{46}O$, m.p. 134—135° (*digitonide*; *acetate*, m.p. 123—123·5°), and a mono-unsaturated *alcohol*, $C_{18}H_{28}(OH)_2$, an oil, which by hydrogenation (Pd-black), followed by oxidation, gives a *ketone* (*phenylhydrazone*, amorphous). R. S. C.

Cholesterol deposition in the tissues of rats. I. Differences in the liver-lipins of males and

females. R. Okey, H. L. Gillum, and E. Yokela (J. Biol. Chem., 1934, **107**, 207—212).—The fatty acid content of livers from females is slightly > that from males, whilst the total cholesterol (I) is lower, the difference being due to esterified (I), which is almost entirely absent in the case of females on a (I)-free diet. C. G. A.

Pigment content of hen's eggs. T. Radeff (Arch. Geflügelkunde, 1934, 8, 47—51).—The pigment content of Bulgarian market eggs determined colorimetrically by comparison with aq. $K_2Cr_2O_7$ averages 2·25 mg. per yolk, or 13·41 mg. per 100 ml. of yolk. Nutr. Abs. (*m*).

Carotenoid from the scallop, *Pecten maximus*. E. Lederer (Compt. rend. Soc. Biol., 1934, **116**, 150—153).—The chemical and physical consts. of a new carotenoid, *pectenoxanthin* (I), isolated from the genital organ of the scallop, *Pecten maximus*, are described. (I) appears to resemble xanthophyll and phytoxanthin in constitution. Nutr. Abs. (*b*).

Carotenoid content of some invertebrates. H. von Euler, H. Hellström, and E. Klussmann (Z. physiol. Chem., 1934, **228**, 77—89).—The carotenoids of *Calanus finmarchicus*, *Daphnia magna*, *Volsella modiolus* (testes and ovary), ant's eggs, and *Coregonus albula* (eggs) were examined spectroscopically. Acid keto-carotenoids such as astacene are widely distributed in Crustacea and molluscs, and probably in invertebrates. Asteric acid (this vol., 544) recalc. to C_{40} is $C_{40}H_{56}O_6$, *i.e.*, it contains 2 mols. of H_2O >astacene. J. H. B.

Astacene from shells of fresh-water crayfish [*Potamobius* (*Astacus*) *fluviatilis*, L.]. H. Willstaedt (Svensk Kem. Tidskr., 1934, 46, 205—208).—Astacene (I) has been isolated from the shells, and from its chromatic behaviour and that of its reduction products in various solvents it is concluded that (I) is 4 : 5 : 4′ : 5′-tetraketocarotene. Reduction of (I) with Zn is irreversible, and (I) is not recovered when the solution is treated with KOH in EtOH. (I) is changed by $SbCl_3$, the bluish-violet solution in $CHCl_3$ being converted by aq. HCl into a raspberry-red solution not identical with the yellowish-red solution of (I). S. C.

Lipochrome and lyochrome pigments in the skin of the frog and cod. M. van Eekelen (Acta Brev. Néerland., 1934, 4, 65—66).—Spectroscopical investigation of the light petroleum fraction of extracts of the skin of *Rana temporaria* (I) and *R. esculenta* (II) shows that carotene and xanthophyll are present. A yellow-green H_2O-sol. pigment apparently related to the dye-component of Warburg's yellow oxidising enzyme, and a urochrome pigment are obtained from the skin of (I) and in very small amounts from (II). The same carotenoids and fluorescent pigments are found in the skin of the cod. Nutr. Abs. (*m*).

Flavin and a blue-fluorescing substance in the retina of the eyes of fish. H. von Euler and E. Adler (Z. physiol. Chem., 1934, **228**, 1—12).—The flavin content of the pigmented epithelium of the fish's retina varies from < 0·2 to 87 × 10^{-6} g. per eye. Wide variations are shown between species of the same genus. In some species, *e.g.*, *Labrus bergyltra*, a blue-fluorescing substance (I) is present, resembling flavin in its solubility, but differing in its p_H relations. The fluorescence of (I) disappears at p_H 3·0—3·5, but is stable in alkaline medium. Illumination under conditions which produce lumiflavin from lactoflavin converts (I) into a $CHCl_3$-sol. violet-fluorescing substance, very stable to reducing agents. In other organs of fish and marine animals and in plants the flavin content is relatively low. J. H. B.

Free and combined (enzyme-)flavin in animal tissues and fluids and in yeast. H. von Euler and E. Adler (Arkiv Kemi, Min., Geol., 1934, **11**, B, No. 28, 6 pp.).—Extraction and dialysis methods for the free (I) and total flavin (II) contents give the vals. [$\times 10^{-4}$ % for (II)]: dried bottom yeast, 18—21; apozymase prep., 16—20; ox liver, 9—18; ox kidney, 8—16; ox corpus luteum, 4—8; pressed bottom yeast, 7; egg-yolk, 5—6; egg-white, 4—5; cow's milk, 2—3; man's brain, 2; man's urine, 0·3—0·5. Excepting with urine [totally (I)], 70—100% of the flavin of the remainder is combined. F. O. H.

Golgi apparatus of the adrenal gland. G. Bourne (Austral. J. Exp. Biol., 1934, **12**, 123—139).—Histological. In the adrenal cortex probably both the Golgi apparatus and vitamin-*C* are concerned in the formation of the lipoid droplets, which may contain a cortical hormone. W. O. K.

Colour reaction in cocoons treated with formaldehyde. G. Colombo (Boll. uff. R. Staz. sperim. Seta, 1933, 3, 63—64; Chem. Zentr., 1934, ii, 635).—The colour obtained by the action of conc. HCl on cocoons (I) treated with CH_2O is ascribed to the presence of tryptophan. Washing of (I) with warm H_2O prevents the reaction, which is then favoured by presence of oxidising agents. A. G. P.

Cerebrospinal fluid-sugar determinations in experimental hypoglycæmia in dogs. R. Davis and H. Brown (J. Lab. Clin. Med., 1934, **19**, 1049—1053).—The decreased glucose (I) content of cerebrospinal fluid (II) in dogs after administration of insulin is often relatively > that of the blood. Intraspinal injection of (I) during hypoglycæmia causes only a temporary improvement. Intravenous injections of (I) rapidly enter (II). A high concn. of (I) in (II) without correspondingly high concn. in blood will not preserve life. Ch. Abs. (*p*)

Diastase in cerebrospinal fluid. F. Eckardt (Jahrb. Kinderheilk., 1933, **141**, 195—204; Chem. Zentr., 1934, i, 3478).—The presence of diastase is recorded. A. G. P.

Lipins of the thoracic duct lymph in fasting. B. Mortimer and A. O. Tischer (Proc. Soc. Exp. Biol. Med., 1934, **31**, 553—554).—A table shows the range and average vals. for the lipin-P and I, and sap. vals. of the lipins of thoracic duct lymph of dogs after fasting 4—7 days. The I val. and the content of unsaponifiable matter for lymph-fat agree closely with the vals. for fæcal fat. Nutr. Abs. (*m*)

Permeability of blood capillaries to lipins. A. Marble, M. E. Field, C. K. Drinker, and R. M. Smith (Amer. J. Physiol., 1934, **109**, 467—474).—The peripheral lymph of normal fasting dogs on the average contained 56 mg. of cholesterol (I), 239 mg. of fatty acid, and 305 mg. of total lipin (II) per 100 c.c., these being, respectively, 41%, 54%, and 52% of the corresponding vals. for plasma from the same dogs. Intravenous injection of fat-laden chyle or fat emulsion caused a slight rise in lymph (II), but no change in (I), suggesting that the capillary walls are slightly permeable to lipins other than (I), but more so than to (I) itself. R. N. C.

Composition of gastric juice. I, II. G. V. Rudd (Med. J. Austral., 1934, i, 431—436, 455—463).—Methods of analysis for acidity, Na, K, NH_4, Ca, Mg, Cl, PO_4''', HCO_3', urea, and protein are described. The bases of the "neutral chloride" (I) in human gastric juice are Na, K, Ca, Mg, and NH_4. Some of the base is secreted by the parietal cells in the form of (I). The concn. of HCl in the parietal secretion (II) varies. It is doubtful whether the total Cl' of (II) is const. Nutr. Abs. (*m*)

Acidity of the gastric juice and contents of the fasting stomach. W. N. Boldyreff (Acta Med. Scand., 1934, 82, 111—125).—Strongly acid solutions (0·5% HCl) introduced into the isolated stomach of the dog or into gastric pouches are not neutralised, but in the normal stomach are rapidly neutralised by regurgitation of pancreatic juice. Thus neither gastric mucus nor pyloric juice is capable of causing effective neutralisation. The gastric glands always secrete a juice of the same degree of acidity, 0·56—0·59% HCl. Hyperacidity of the gastric juice does not exist; hypersecretion may occur. Secretion of neutral chlorides does not occur. Nutr. Abs. (*m*)

Relation of acidity of gastric juice to the rate of its secretion. M. M. Gorbunova, S. I. Lebedinskaya, and V. V. Savich (Arch. Sci. Biol. U.S.S.R., 1933, 33, 515—521).—The acidity of the juice was largely controlled by its mucin content. Ch. Abs. (*p*)

Secretory work of gastric glands during prolonged effect of sodium chloride. O. F. Sharova-tova-Zavalishina (Arch. Sci. Biol. U.S.S.R., 1933, 33, 471—479).—The effects of NaCl were independent of the nature of the diet and caused an increase in total acids, free HCl, and total Cl' in gastric juice. Ch. Abs. (*p*)

Influence of combinations of basal foodstuffs (chiefly proteins and carbohydrates) on gastric and pancreatic secretions. M. L. Eidlinova (Arch. Sci. Biol. U.S.S.R., 1934, 34, 113—122).—The combination of any two foods may increase or decrease the rate of secretion as compared with each component fed separately. Changes in acidity were paralleled by the vol. secreted, but enzyme activity was not. Ch. Abs. (*p*)

Bile analysis. F. Breusch (Z. physiol. Chem., 1934, 227, 242—246).—Bile (5—10 c.c.) is treated with 50 c.c. of EtOH to remove protein, the filtrate is evaporated, and the residue dissolved in 20 c.c. of H_2O is treated with 2 c.c. of 5% aq. Na_2CO_3. Extraction with $CHCl_3$ removes phosphatides. The aq. portion is heated for 6 hr. after addition of 5 c.c. of 30% KOH to hydrolyse coupled bile acids. Acidification and extraction with Et_2O removes all the acids, leaving the bilirubin. The residue from the Et_2O is subjected to sublimation for 3 hr. in vac. at 150° (bath temp.)/ $\ngtr$ 2 mm., the process being repeated if necessary. The fatty acids sublime, the residue consisting of bile acids. J. H. B.

Separation of principal constituents of bile. R. U. Harwood (J. Lab. Clin. Med., 1934, 19, 1003—1007).—Pigments are absorbed on aq. $Zn(OH)_2$. The supernatant liquid is heated with KOH, acidified, and treated with K_2CO_3 to give a clear solution. Cholesterol is extracted with petroleum, and bile salts with abs. EtOH. Ch. Abs. (*p*)

Micro-determination of cholic acid in bile. K. Lang and B. Lueken (Biochem. Z., 1934, 273, 446—451).—The method (I) is based on the pptn. of cholic acid (II) by I in aq. KI, a compound (III) of 1 mol. of (II) with 2I being produced. (III) is dissolved in AcOH and, after dilution, titrated with $0·005N$-$Na_2S_2O_3$. Other bile acids do not interfere. $\nless$ 0·25 mg. of (I) can be determined. (I) cannot be applied to the determination of (II) in blood and liver. W. McC.

Determination of cholesterol and cholesteryl esters in dog's bile. I. A. Wright (J. Exp. Med., 1934, 59, 407—410).—Elman and Taussig's method for the determination of total cholesterol in dog's bile (I) is accurate. A method of determining cholesteryl esters is described and their absence from normal (I) demonstrated. Nutr. Abs. (*m*)

Toad bile. II. Trihydroxybufosterocholenic acid from winter bile.—See this vol., 1219.

Changes in composition and secretion of bile during the action of certain internal secretions and vegetative poisons. S. M. Leites and R. M. Izabolinskaya (Arch. Sci. Biol. U.S.S.R., 1933, 33, 417—431).—Bile secretion was decreased by subcutaneous injection of adrenaline (I), parathyroid extract (II), thyroxine (III), and atropine (IV), increased by insulin (V) and histamine (VI), and unchanged or irregularly affected by pituitary preps. (VII) and ergotamine. The concn. of bile acids was unchanged or increased by (I), (VII), and (V), unchanged or lowered by (IV) and (VI), and unchanged or variably influenced by (II) and (III). The cholesterol concn. was affected only by (III). In no case were [$Na^{\bullet}$] and [$K^{\bullet}$] changed. Ch. Abs. (*p*)

Effect of thyroid gland on secretion and cholesterol content of bile. V. P. Bezuglov and L. M. Tutkevich (Arch. Sci. Biol. U.S.S.R., 1933, 33, 411—416).—Administration of thyroxine lowers the secretion of bile and the excretion of cholesterol. The effects were intensified by thyroidectomy. Ch. Abs. (*p*)

Bile-stimulating action of *Curcuma domestica* (Temoe Lawak). F. Grabe (Arch. exp. Path. Pharm., 1934, 176, 673—682).—The bile-stimulating action of extracts and of the essential oil and its vac. distillation fractions of rhizomes of *C. domestica* (tumeric) indicates that the principle concerned is α-*p*-tolylethyl alcohol (cf. A., 1932, 1178; 1933, 876). F. O. H.

Influence of bile acids on biliary salt excretion. IV. Ammonium salts. V. Alkali salts. Y. Kawada (J. Biochem. Japan, 1934, 20, 43—50, 51—

57).—IV. The bile-NH_3 in dogs with biliary fistulæ is increased by oral administration of cholic acid (I). Simultaneous administration of yeast-nucleic acid enhances this effect and also increases the vol. of bile secreted.

V. The vol. and K and Na contents of the bile are increased by oral administration of (I), but diminished by subcutaneous injection of atropine. (I) probably has a vago-stimulatory action. F. O. H.

Statistical investigations on milk. B. Rossmann (Z. Unters. Lebensm., 1934, **68**, 279—293).—The seasonal variations in fat content of milk from 7 districts in the Merseburg area are analysed. E. C. S.

Rapid simultaneous refractometric determination of fat and lead acetate serum of milk. W. Leithe (Z. Unters. Lebensm., 1934, **68**, 293—297; cf. B., 1934, 602).—The milk is treated with $Pb(OAc)_2$ and petroleum (b.p. 90—100°), emulsified, and centrifuged. The clear petroleum and aq. layers are together transferred to the refractometer cup, and their *n* successively determined. Fat in milk can be determined to within 0·1%. E. C. S.

Influence of inheritance and environment on milk production and butter-fat percentage in Jersey cattle. J. W. Gowen (J. Agric. Res., 1934, **49**, 433—465).—Approx. 50% of the variation in milk yield and 80% of that in butter-fat are traced to inheritable factors. A. G. P.

Cholesterol content of human milk. O. Mühlbock (Z. Kinderheilk., 1934, **56**, 303—306).—Mixed samples of human milk taken between the 4th and 10th days of lactation have an average total cholesterol (I) content of 26 mg. per 100 ml., most of which is free. The milk-fat contains on an average 1% of (I). Samples taken from one individual show no definite variation between the 12th and 47th day. Cow's milk has an average (I) content of 9·18 mg. per 100 ml., practically all being free. There is no (I) in separated milk. Nutr. Abs. (*m*)

Milk secretion in relation to blood composition. Urea contents of blood and of milk-serum. G. L. Peskett (Biochem. J., 1934, **28**, 1657—1658).—In the cow, whole blood (mammary, venous, or arterial) and the fat-free serum of milk have the same urea contents irrespective of the rate of milk secretion. Urea is not conc. by the mammary gland. A. E. O.

Tryptophan in cow's milk. D. Tiukov and M. Zakomorny (Rocz. Nauk. rol., 1934, **31**, 366—382).—The tryptophan (I) content of milk from different cows is not const., but varies < do other milk constituents. It varies considerably over a lactation (II), being highest in colostrum and at the end of (II). (I) is thought to be produced by a sp. enzyme, the activity or quantity of which is greatest early and late in (II). Nutr. Abs. (*m*)

Maturation of cheese. I. Proteases, diketopiperazine, and proline peptides. E. Parisi and G. De Vito (Atti R. Accad. Lincei, 1934, [vi], **20**, 44—51).—Ripe cheeses contain proline peptides and diketopiperazine, which resist attack by proteases. The extent to which the casein of cheese is broken down appears to be related closely to the % of proline compounds present. T. H. P.

Lane-Eynon volumetric method for determination of lactose in milk. F. T. Adriano, S. B. Oliveros, and L. G. Miranda (Philippine J. Sci., 1934, **54**, 83—89).—The max. difference between results obtained by volumetric and gravimetric methods is 0·1%. The optical method gives variable results. P. G. M.

Vitamin-*A* in milk. W. C. Russell (New Jersey Agric., 1933, **15**, 3).—Of the vitamin-*A* fed as dried lucerne and maize silage < 5% appears in milk. Ch. Abs. (*p*)

Resistance of vitamin-*C* in milk to vacuum pasteurisation. G. Rundberg (Acta paediat., 1934, **15**, 357—373).—The milk from a single cow, maintained on pasture, was pasteurised and freed from air, but failed to protect guinea-pigs from scurvy in the largest dose administered (50 ml. daily), even when raw. Nutr. Abs. (*b*)

Determination of sulphur in pig's milk. F. Lachmann (Bied. Zentr. [Tierernähr.], 1934, **B**, 6, 421—424).—The sample is evaporated in a vac. over P_2O_5 and the product digested with fuming HNO_3 in a sealed tube. S is determined as $BaSO_4$. A. G. P.

Differences in the phosphorus and sulphur content of human and cow's milk. F. Steffen and H. Süllmann (Schweiz. med. Woch., **61**, 114; Chem. Zentr., 1934, i, 2988).—Vals. for S and all fractions of P are considerably higher in cow's milk. A. G. P.

Spectrum analysis of milk ashes. W. F. Drea (J. Nutrition, 1934, **8**, 229—234).—Ag and Mo occurred in milk of cows drinking H_2O containing these elements. Mn and F, although present in H_2O and in lucerne supplied, were not detected. A. G. P.

Mitogenetic radiation. VI. Secondary radiation. L. K. Wolff and G. Ras (Proc. K. Akad. Wetensch. Amsterdam, 1934, **37**, 430—455).—Mitogenetic radiation (Gurwitsch) emitted by milk, pasteurised at 37°, to which rennet has been added, has been passed through a culture contained in a cryst. SiO_2 vessel, and the secondary radiation (*a*) has been studied. (*a*) is transmitted also by the medium of the culture, from which cells have been removed, but not by pure medium, or boiled cultures. (*a*) is more intense than the incident radiation. The effect of (*a*) when the bacterial detector is contained in a SiO_2 vessel is > for glass or paraffin, owing to reflexion at the walls. Similarly, powdered SiO_2 and air bubbles in the detector increase the influence of (*a*). Experiments show that (*a*) polarised by reflexion, or by Iceland spar, is more effective than the unpolarised rays. A plate of amorphous SiO_2 between emitter and detector has no effect, but cryst. SiO_2, topaz, and other minerals accelerate the influence on the detector. The walls of the vessel also influence the induction period for the multiplication of bacteria in a dil. culture (6000—20,000 per c.c.). R. S. B.

Composition and f.p. of cow's colostrum. G. D. Elsdon (Analyst, 1934, **59**, 665—666).—

Analytical data on 9 consecutive samples from each of two cows are given. E. C. S.

Composition of "witch's" milk. R. G. Linton (Vet. J., 1934, **90**, 213—215).—The milk secreted by two foals, 2 and 4 days old, respectively, was lower in total solids, protein, and ash than was the milk of the respective dams. In one case the fat and lactose contents were higher, in the other case they were lower, in the foal's milk than in the dam's. When one foal was 8 days old its milk contained the following percentages: total protein, 3·58, caseinogen, 2·03; globulin, 0·86; albumin, 0·69; ash, 0·58; Cl, 0·230; CaO, 0·041; MgO, 0·014; and P_2O_5, 0·079. Nutr. Abs. (*m*)

Diastase in the urine of infants and children. F. Eckardt (Jahrb. Kinderheilk., 1934, **142**, 319—343).—In infants the urinary diastase (I) is low, but increases with age to reach a more or less steady level in childhood. The excretion of (I) is fairly const. for the individual. No significant differences are observed between the sexes. (I) excretion is increased during starvation and fever, diminished in pylorospasm, in acute digestive disturbances, and in diabetes mellitus, and unaffected in rickets and tuberculosis. Nutr. Abs. (*m*)

Urinary excretion of rennin in infants. J. Suranyi and L. Veszelszky (Le Nourrisson, 1933, **21**, 296—300).—The urine (especially night urine) of artificially fed (I) but not that of breast-fed infants contains the precursor of rennin (II). In (I) there is over-production of (II), the surplus being excreted. Nutr. Abs. (*m*)

Urinary compound of albumin, Bence-Jones protein pseudoglobulin, and an unknown antigen. W. H. Welker and L. Hektoen (J. Infect. Dis., 1933, **53**, 165—168).—The protein could not be separated from the compound by boiling or crystallisation. Precipitins in rabbit serum prepared against the compound were removed by sp. adsorption. Ch. Abs. (*p*)

Trimethylamine oxide in human urine. W. Lintzel (Klin. Woch., 1934, **13**, 304; Chem. Zentr., 1934, i, 2777).—Administered NMe_3 is excreted largely as NMe_3O. A. G. P.

Trimethylammonium bases. III. In human urine. W. Lintzel (Biochem. Z., 1934, **273**, 243—261; cf. A., 1931, 1178).—Urine is made alkaline with $Ba(OH)_2$, Na_2CO_3, or MgO, CH_2O is added, and air is passed through. The only base then expelled is NMe_3, which is determined by trapping in excess of 0·02*N*-HCl and titrating with 0·02*N*-NMe_3. NMe_3O is determined in the same way after reduction with Devarda alloy + HCl [choline (I), betaine (II), γ-butyrobetaine (III), and carnitine (IV) do not interfere]. Total NMe_3 bases (V) are determined as NMe_3 after treating the urine at 120° for 4½ hr. with KOH, Zn dust, and a little H_2O. The N of (V) in 1 day's normal urine is distributed thus: free NMe_3, 1·0; NMe_3O, 12·4; other (V), 22·4 mg. Orally administered NMe_3 is excreted almost quantitatively as NMe_3O, but a small part appears unchanged. NMe_3O given orally is excreted almost quantitatively unchanged and at the same time the excretion (VI) of free NMe_3 is slightly increased. A diet of sea fish results in greatly increased (VI) of NMe_3O and slightly increased (VI) of NMe_3. Administration of (II) leads to no increase of (VI) of (V), that of (I) leads to increase, most of (I) being destroyed in the body, part being unchanged, and part appearing as NMe_3O. (III) appears chiefly unchanged, there being no increased (VI) of NMe_3O. After giving (IV) there is no appreciable increase in (VI) of (V), but after meat extract there is an increase. The production of NMe_3O from (V) results, to some extent, from the action of intestinal bacteria. W. McC.

Determination of urinary ammonia. P. Fleury (J. Pharm. Chim., 1934, [viii], **20**, 319—326).—Mestrezat and Janet's modification of Schlœsing's method (A., 1922, ii, 453) is further modified so that urine-NH_3 is determined in 3 hr. at 20° or in 45 min. at 37°. F. O. H.

Clearance of creatine in dog and man. R. F. Pitts (Amer. J. Physiol., 1934, **109**, 532—541).—Clearance of creatine (I) in the dog is a function of the plasma concn. (II). At low (II), urine is (I)-free, but as (II) rises, clearance rises sharply. At (II) of 15—120 mg. per 100 c.c., the (I) clearance in the dog is intermediate between the xylose (or sucrose) (III) and creatinine (IV) clearances. In man, between 6 and 40 mg. per 100 c.c. of plasma-(I), the clearances of (I) and (III) are equal, but $<$ the (IV) clearance. Administration of Na_2HPO_4 does not affect (I) excretion, but glycine raises (III) clearance relatively more than that of (I). R. N. C.

Clearance of creatine in the phloridzinised dog. R. F. Pitts (Amer. J. Physiol., 1934, **109**, 542—549).—Creatine clearance in phloridzinised dogs is a function of plasma-creatine concn. (I) below 5 mg. per 100 c.c.; between 20 and 130 mg. it is independent of (I). Administration of phloridzin does not affect xylose clearance, but creatine and creatinine clearances fall, and glucose clearance rises, to the xylose level, all four agreeing within an average of $\pm 5\%$. R. N. C.

Diffusion equilibria for isolated frog's kidney. E. J. Conway and F. Kane (Biochem. J., 1934, **28**, 1760—1768).—The concn. of SO_4'' in the blood-plasma of the frog is 6·2 mg. S per 100 ml. The concn. in the urine is approx. 33% of this and of the kidney (I) 40%. SO_4'' passes freely into and out of (I), the equilibrium concn. (II) being attained in 15 min. The (II) for active (I) is 41% of the external SO_4'' and for inactive (I) (CN′), 58%. (II) for muscle (III) is 25%, and for liver (IV) sections 29%, CN′ causing a slight reduction. The rate at which (II) is attained is the same for active or inactive (I), (III), and (IV). C. G. A.

Colorimetric determination of sulphate in serum and urine adaptable to determination of sulphate clearance. T. V. Letonoff and J. G. Reinhold (Amer. J. Med. Sci., 1934, **188**, 142).—The method is based on the colour reaction between benzidine sulphate and Na β-naphthaquinone-4-sulphonate in the presence of $Na_2B_4O_7$–NaOH buffer solution. Addition of $COMe_2$ after the reaction is complete reduces the colour of the reagent. Protein and PO_4''' are removed by U acetate. Ch. Abs. (*p*)

Determination of total and neutral sulphur in urine. A. Friedrich and E. Bauer (Z. physiol. Chem., 1934, **228**, 61—76).—A volumetric micro-method is described, the benzidine method for SO_4'' being employed, since it does not necessitate removal of PO_4'''. Ashing is performed by means of $Br–HNO_3$. The vals. obtained for neutral S are low owing to loss of a volatile S compound on acid hydrolysis, unless the urine is first treated with dil. NaOH. J. H. B.

(*a*) **Excretion of salt by the human kidney.** (*b*) **Thirst and potassium overdosage.** F. Arden (Austral. J. Exp. Biol., 1934, **12**, 111—120, 121—122). —*a*. After oral administration to man of 15 g. of NaCl (10% solution) diuresis took place accompanied by increase of Cl′ in the urine for about 4 hr. up to 0·3—0·4*N*, Cl′ thereafter remaining approx. const., although the vol. of urine decreased. Administration of H_2O caused no extra diuresis, but a second dose of NaCl increased the vol. of urine, but had little effect on [Cl′]. Similar results were obtained with KCl, the diuresis being somewhat greater, whilst the administration of $NaHCO_3$ (30 g.) produced corresponding effects, the max. [HCO_3'] in the urine being 0·318*N*. Urinary Cl′ did not entirely disappear.

b. KCl does not produce thirst as does NaCl in corresponding quantities. Thirst is probably due to the presence in the tissues of an excess of salt and especially of $Na^{\cdot}$. W. O. K.

Organic acids in urine. W. Mecke (Z. ges. exp. Med., 1934, **92**, 688—691; Chem. Zentr., 1934, i, 1666).—The acids fall into two groups, the dissociation consts. of which lie approx. between 10^{-3} and 10^{-4} or 3×10^{-8} and 10^{-8}. L. S. T.

Urinary pigments and their composition. M. Weiss (Klin. Woch., 1933, **11**, 1817—1820; Chem. Zentr., 1934, i, 1516).—Normal urine contains a series of yellow to red pigments, chromogen, and, in certain physiological conditions, coproporphyrin and bilirubin. The existence of Heilmeyer's urochrome-*B* is doubtful. In pathological conditions the pigment content may increase, and new pigments, *e.g.*, urorubin and a melanogen, may occur. A. G. P.

Crystalline urobilin. I. Crystalline stercobilin and its absorption spectrum. II. Crystalline urobilin from urine and its identity with crystalline stercobilin. L. Heilmeyer and W. Krebs (Z. physiol. Chem., 1934, **228**, 33—46, 46—49).—I. Cryst. stercobilin (I), probably $C_{33}H_{42}O_6N_4$, m.p. begins 110°, complete 130° (decomp.), was obtained from fæces. In contrast with Watson's (I) (A., 1932, 296), it gave absorption curves identical with non-cryst. (I) from fæces, urine, and from mesobilirubinogen, but showed const. absorption relations. This prep. is probably "native fæcal (I)."

II. Cryst. urobilin from urine and (I) from fæces agree in solubility, light absorption, and crystallographic behaviour, and are regarded as identical. On keeping, the crystals undergo spontaneous change (pseudomorph formation) making recrystallisation impossible. J. H. B.

Sterol secretion and coprosterol formation. R. Schoenheimer and W. M. Sperry (J. Biol. Chem., 1934, **107**, 1—4).—The fæces of dogs with bile fistulæ fed on a lipin-free diet contain coprosterol (I) and dihydrocholesterol; hence (I) is formed from the cholesterol secreted by the intestinal mucosa. H. D.

Chemical ideas in medicine and biology. H. H. Dale (Science, 1934, **80**, 343—349).—A lecture. L. S. T.

Respiration and glycolysis of red corpuscles in allergic and anaphylactic animals. M. Axsianeff (Z. ges. exp. Med., 1933, **90**, 643—650; Chem. Zentr., 1934, i, 2444).—Mature red corpuscles of the guinea-pig, without nuclei, showed no O_2 consumption. Respiration (I) was slightly raised by horse-serum, fivefold by liver extract (II) from guinea-pigs, and further on addition of anaphylactogen to sensitised erythrocytes (III). (II) had no action on (III) after anaphylactic shock (IV), or on animals killed by (IV), although it raised the (I) of normal guinea-pigs. (I) is increased in (III) of tuberculous animals. "Old tuberculin" (V) has no effect *in vitro* or *in vivo*, but in large quantities reduces (I). Addition of tissue extracts raises the (I) of tuberculous cells. The (I) of liver sections of tuberculous animals treated with (V) is raised 100—150% of the val. for untreated tuberculous animals. R. N. C.

Active allergic substance in the hop. M. J. Gutmann (Heil- u. Gewürz-Pflanzen, 1933, **15**, 89—92; Chem. Zentr., 1934, i, 2159).—The allergic reaction is due to lupulone. Humulone and hop-resin gave weak reactions in isolated cases; the hop essential oils and hop-protein were without effect. R. N. C.

Preparation and standardisation of pollen extracts for the treatment of hay fever. R. A. Cooke (J. Allergy, 1933, **4**, 87—91).—Defatted pollen is extracted with a solution containing 0·5% NaCl, 0·275% $NaHCO_3$, and 0·4% PhOH. The sterilised extract is standardised by determining the protein-N pptd. by phosphotungstic acid. Ch. Abs. (*p*)

Standardisation of pollen extracts proposed by Cooke and Stull. A. F. Coca (J. Allergy, 1934, **4**, 354—362).—The N precipitable by phosphotungstic acid is dialysable and therefore not albumin. There is no parallelism between loss of activity and loss of precipitable N (cf. preceding abstract). Ch. Abs. (*p*)

Allergen content of pollen extracts. Determination and deterioration. A. Stull, R. A. Cooke, and J. Tennant (J. Allergy, 1933, **4**, 455—467).—The activity of pollen (I) extracts as determined by protein-N (II) varied with the condition of (I) and age of extracts. Deterioration was prevented by storing dry (I) in sealed containers. Alkaline salt extracts lost 50% activity in 1 year's storage. Repeated filtration decreased activity and (II) proportionally. Ch. Abs. (*p*)

[Pollen] allergen. H. Weyland and O. Ripke (Med. Chem. Abh. med.-chem. Forsch. I.G. Farbenind., 1934, **2**, 244—252; Chem. Zentr., 1934, i, 3362). —The albuminoid nature of the hay-fever-exciting allergen of grass-pollen is confirmed. R. N. C.

Urinary proteoses in bronchial asthma. A. Trasoff (J. Allergy, 1933, **4**, 136—140).—Urine of asthmatic patients contained a substance resembling

Oriel's "proteose," but showing no sp. skin reactions or therapeutic results. Ch. Abs. (*p*)

Serum-lipins in anæmia. R. Gantenberg Deut. Arch. klin. Med., 1934, **176**, 343—347).—Total cholesterol (I) usually rises in pernicious anæmia during successful stomach or liver treatment from low to markedly increased vals. The behaviour of the serum-(I) has a certain diagnostic val., since variations from the above indicate complications. The (I) rise depends on increased function of the blood-forming apparatus, probably of the reticulo-endothelial system. In secondary anæmias the behaviour of (I) is much less regular. In both forms of anæmia the (I) ester plays a greater part than free (I) in the rise that takes place. The total (I) in the serum moves parallel as a rule to the total fats in the serum, but the phosphatides show no regular relation to the other serum-lipins. Nutr. Abs. (*b*)

Anæmia caused by deaminised caseinogen. A. G. Hogan and W. S. Ritchie (J. Biol. Chem., 1934, **107**, 179—189).—Gelatin and gliadin together were an adequate source of protein for growth, but the addition of deaminised caseinogen was followed by an anæmia. This did not develop if caseinogen was added to the diet, and no effect on the rate of growth was noted. H. G. R.

Effects of various colloidal and crystalloidal metallic compounds in nutritional anæmia in the rat. H. L. Keil and V. E. Nelson (J. Lab. Clin. Med., 1934, **19**, 1083—1088).—The min. requirements of $CuSO_4,5H_2O$ and colloidal $Fe(OH)_3$ necessary to raise the hæmoglobin (I) content in anæmic rats to normal val. were 0·002 and 0·10 mg. per day, respectively. Mn cannot replace Cu in the synthesis of (I). Cu is utilised in the form of Cu_2O, CuS, $Cu(OH)_2$, CuI, and colloidal Cu. Intraperitoneal injection of Fe citrate temporarily increases (I) formation. Zn and Hg salts have no influence. Ch. Abs. (*p*)

Factors influencing the utilisation of the iron and copper of egg-yolk for hæmoglobin formation. W. C. Sherman, C. A. Elvehjem, and E. B. Hart (J. Biol. Chem., 1934, **107**, 289—295).—The incomplete hæmoglobin regeneration in anæmic rats fed with egg-yolk (I) is due not to the unavailability of the Fe in (I), but to a retarded utilisation of Cu, possibly due to formation of insol. CuS in the digestive tract. A. E. O.

Nature of hæmopoietin, the anti-anæmic substance in hog's stomach. II. Production of a thermostable hæmopoietically active substance similar to or identical with the anti-anæmic principle of liver by the action of the thermolabile hæmopoietin on beef. L. Klein and J. F. Wilkinson (Biochem. J., 1934, **28**, 1684—1692; cf. A., 1933, 641).—When concentrates containing the enzyme-like hæmopoietin (I), with or without pepsin, are incubated *in vitro* with beef-muscle at 37°, thermostable hæmopoietically active material is obtained resembling the anti-anæmic principle (II) from liver. It can also be obtained free from protein in a form suitable for intramuscular injection. It is considered that (I) acting, in the stomach of normal individuals, on an unknown substrate in beef yields (II), an end-product ultimately stored in the liver until required by the body for the production of red blood-corpuscles. A. E. O.

Ascorbic acid content in mouse cancer. B. Borghi and R. Deotto (Z. Krebsforsch., 1934, **40**, 293—297; Chem. Zentr., 1934, i, 3488).—Administration of tumour extracts prolongs the life of young scorbutic guinea-pigs only insignificantly, and scarcely hinders loss of wt. Mouse tumours do not require ascorbic acid for their metabolism. R. N. C.

Cathepsin in rats with transplantable cancer. A. Purr (Biochem. J., 1934, **28**, 1907—1910).—Rats into which cancers (I) have successfully become transplanted, and rats which have resisted efforts to transplant (I), both show a high concn. of cathepsin (II) in the liver, and a significant concn. in the muscle, which in normal rats is free from (II). A. E. O.

Effect of heavy water on viability of mouse sarcoma and melanoma. K. Suigiura and L. C. Chesley (Proc. Soc. Exp. Biol. Med., 1934, **31**, 659—661).—Proliferation capacities were unaffected. Ch. Abs. (*p*)

Chromium. I. Determination of chromium in human tumours. A. Dingwall, R. G. Crosen, and H. T. Beans (Amer. J. Cancer, 1934, **21**, 606—611).—The tissue is ashed and the residue fused with Na_2CO_3 and $KClO_3$. The aq. extract of the melt is warmed with HCl to expel CO_2 and treated with a solution of diphenylcarbazide in EtOH–AcOH. The % transmission vals. for λλ 5045 and 5710 Å. are compared with those for standard Cr preps. Results varied from 0·001 to 0·25 mg. Cr. per 100 g. of ash. Ch. Abs. (*p*)

Vitamin-*D* [and dental caries]. E. C. McBeath (Amer. J. Publ. Health, 1934, **24**, 1028—1030).—Avitaminosis-*D* appears to be a factor in the incidence of dental caries in children. F. O. H.

Osteodystrophic diseases of domesticated animals. I. Structure of bone; atrophy; osteoporosis; osteomyelitis. II. Rickets and osteomalacia. A. Theiler (Vet. J., 1934, **90**, 143—158, 159—175).—I. Dietary requirements of Ca and P are examined.

II. With a sufficiency of solar radiation, rickets developed in bovines and ovines under conditions of simple P-deficiency. Ch. Abs. (*p*)

Factors influencing malformation of the leg bones of growing chickens. T. T. Milby (Iowa Agric. Exp. Sta. Res. Bull., 1934, No. 172, 223—252).—With otherwise normal rations excess of P is the primary cause of slipped tendons (I). Leg bones of affected chickens have ash contents substantially the same as those of normal birds. Rice bran and, to a smaller extent, wheat middlings contain a substance counteracting the tendency towards (I). Incorporation of 3% $MgCO_3$ in the ration prevented (I), somewhat reduced the growth rate of chickens, and lowered the ash content of the fat-free femurs. A. G. P.

Crystalline lens. Fate of glutathione in parathyroid cataract. E. I. Evans (Proc. Soc. Exp. Biol. Med., 1934, **31**, 603—605).—The normal glutathione content of the lens (0·385%) in dogs decreased

by 50—70% after parathyroidectomy, and before there was appreciable deposition of Ca in the cataract. Free cystine was absent from the lens filtrates.
CH. ABS. (*p*)

Crystalline elements of stomach lavage of patients with cholelithiasis. H. A. RAFSKY (J. Lab. Clin. Med., 1934, **19**, 959—962).—Appreciable amounts of cholesterol, carbonates, and Ca bilirubate were identified. CH. ABS. (*p*)

Vitamin-*A* and colds. E. L. GARDNER and F. W. GARDNER (Amer. J. Dis. Children, 1934, **47**, 1261—1264).—Administration of vitamin-*A* diminished the incidence and severity of colds. CH. ABS. (*p*)

Changes in the carbohydrate metabolism of the heart following coronary occlusion. H. E. HIMWICH, W. GOLDFARB, and L. H. NAHUM (Amer. J. Physiol., 1934, **109**, 403—408).—Coronary occlusion (I) in dogs was followed by a decrease in the glycogen of the infarcted area, part of the glycogen appearing as increased sol. carbohydrate and lactic acid (II). Before (I), the heart absorbed (II) from the blood-stream, but (I) usually resulted in a release of (II) by the heart, probably due to the diminished O_2 supply to the cardiac tissues. Glucose was absorbed from the blood both before and after (I). R. N. C.

Renal function in diabetes. G. FERRO-LUZZI and A. SALADINO (Arch. Farm. sperim., 1934, **58**, 107—130).—The amount of glomerular filtrate (I) in diabetes is slightly raised by administration of H_2O, and decreased when liquid food is withheld. Variations of (I) and polyuria are not dependent on corresponding oscillations of hydræmia. Hypercreatininæmia and hyperazotæmia, the latter sometimes due to resorption, have been noted. R. N. C.

Clinical experiments with carbohydrate-free meal in diabetics. E. EGEDY (Klin. Woch., 1934, **13**, 334; Chem. Zentr., 1934, i, 3363).—Tresfarin, containing gluten without starch, sugar, or other carbohydrates harmful to diabetics (I), does not raise the blood-sugar when consumed in large quantities at a time, or in small quantities over long periods, either in normal persons or (I). The characteristic sp. dynamic effect for protein (II) is marked, and on account of its high (II) content (61·5%), the meal can be used as a foodstuff. R. N. C.

Use of synthalin in diabetes mellitus. L. K. CAMPBELL (J. Lab. Clin. Med., 1934, **19**, 1067—1073). —After administration of synthalin for 4—6 days, glucose was absent from urine for several days.
CH. ABS. (*p*)

Essential fructosuria. S. SILVER and M. REINER (Arch. Int. Med., 1934, **54**, 412—426).—Fructosuria (I) is thought to be due to an error of metabolism localised in the liver resulting in a loss of ability to fix fructose as glycogen, the metabolism of other carbohydrates being unaffected. Administration of fructose (II) after injection of insulin prevents hypoglycæmia in such cases by the replacement of glucose in the blood by (II), and the increased glycogenolysis caused by adrenaline does not alter the (II) tolerance. Sorbitol administered to a (I) patient caused hyperglycæmia with an increase in blood-(II), and half as much (II) was excreted from a dose of sorbitol as from an equal dose of (II). Formation of 1 mol. of glucose and of (II) may therefore be an intermediate stage in the metabolism of 2 mols. of sorbitol. A. L.

Influencing of diphtheria-immunity in guinea-pigs by vitamin feeding and ultra-violet irradiation. C. K. CHOUN (Z. Immunität., 1934, **81**, 432—444; Chem. Zentr., 1934, i, 2608).—Animals on a vitamin diet (I) showed a stronger resistance to diphtheria toxin than with normal feeding; ultra-violet irradiation (II) with normal feeding gave the same result, but not so strong. The combined (I) and (II) had no effect, as the rays apparently destroyed the vitamins. Animals with normal feeding showed no change when kept in either the light or dark; with (I), resistance to the toxin was increased by exposure to sunlight. R. N. C.

Presence of arsenic in the brain and its relation to pericapillary hæmorrhages or so-called acute hæmorrhagic encephalitis. A. E. OSTERBERG and J. W. KERNOHAN (Amer. J. Clin. Path., 1934, **4**, 362—369).—Following administration of org. As compounds, As is found in the central nervous system (I) and may cause hæmorrhagic encephalitis (II). Ingestion of inorg. As also results in the presence of As in (I), but rarely causes (II). CH. ABS. (*p*)

Calcium treatment of milk-fever. O. STINSON (Vet. Rec., 1934, **14**, 1244).—Milk-fever was cured by subcutaneous injection of a 10% solution of Ca gluconate in a newly-calved cow. R. N. C.

Prolan elimination in essential hypertonia. Ætiology of high pressure. E. KYLIN (Deut. Arch. klin. Med., 1934, **176**, 301—310; Chem. Zentr., 1934, i, 3481).—Prolan elimination in the urine was frequently increased in hypertonics. R. N. C.

Hypoglycæmia hypophysiopriva. W. MAHONEY (Amer. J. Physiol., 1934, **109**, 475—482).—The cachexia hypophysiopriva (I) following hypophysectomy (II) is accompanied by hypoglycæmia (III), administration of glucose resuscitating puppies in an advanced state of (I). In fasting puppies, the physical signs of (III) appear 24—36 hr. after (II) at a blood-sugar level of 50 mg., after which the blood-sugar falls rapidly to zero. Repeated administration of carbohydrates prevents (I) following (II). The low glucose combustion curves indicate a high tolerance. (III) is suggested as an explanation of fatalities following (II). R. N. C.

Infection and the tolerance for glucose. E. G. SCHMIDT, J. S. EASTLAND, and J. H. BURNS (Arch. Int. Med., 1934, **54**, 466—481).—Of 73 cases of infection subjected to the glucose tolerance test, 36 had pyogenic infection (I) and of these 29 gave pathoglycæmic curves, the highest being from cases of cellulitis. Glycosuria, however, was found in only 4 of these. Disappearance of the infection resulted in normal blood-sugar curves. Both *Streptococci* and *Staphylococci* produced disturbances in the carbohydrate mechanism. 9 patients with non-pyogenic febrile conditions (II) also gave abnormally prolonged blood-sugar curves. Of 28 patients with arthritis (III) and rheumatoid conditions, 15 gave diabetic-like blood-sugar curves. After fasting, the curves in (I), (II), and (III) were, in general, normal. A. L.

Radiothorium in leucæmic myelosis. I, II. I. Zadek (Folia hæmatol., 1933, **49**, 287—340; **50**, 369—409; Chem. Zentr., 1934, i, 3227).—I. Cases of leucæmic myelosis (I) have been cured by administration of large quantities of Rd-Th, combined with Th-*X* and *X*-rays.

II. Symptomatological description of the action of Rd-Th. Th-*X* accelerates the release of cells from the bone-marrow into the blood-stream. Rd-Th accumulates in the liver and spleen, Th-*X* in the bone-marrow. Administration of $CaCO_3$ causes an increased excretion of Th-*X* in the urine, suggesting that Th-*X* affects the Ca metabolism. R. N. C.

Chemotherapy in acute pancreatic necrosis. J. Baumann (Sitzungsber. Ges. Beförd. ges. Naturwiss. Marburg, 1933, **68**, 59—74; Chem. Zentr., 1934, i, 2443).—In pancreatic necrosis the organ undergoes autodigestion by trypsin (I), which has been activated in the gland by enterokinase. There is also a considerable excretion in the urine of activated (I) which apparently passes through the blood-stream in the active state. Quinine does not inhibit (I), but activates it still further. (I) is inhibited by rivanol, trypaflavin, and particularly by insulin. R. N. C.

Composition of œdema fluid and lymph in œdema and elephantiasis resulting from lymphatic obstruction. C. K. Drinker, M. E. Field, J. W. Heim, and O. C. Leigh, jun. (Amer. J. Physiol., 1934, **109**, 572—586).—The œdema fluid from dogs with complete lymphatic obstruction in the hind leg was studied over a long period. Proteins reached a concn. of 4—5%; the albumin–globulin ratio was slightly > that in blood. The proteins of lymph and œdema fluid when examined together were fairly similar. R. N. C.

Creatine–creatinine metabolism in infantile paralysis and the effects of glycine. I. W. Gros (Z. klin. Med., 1933, **126**, 152—160; Chem. Zentr., 1934, i, 1517).—Administration of glycine in poliomyelitis increased the excretion of creatine without affecting that of creatinine. A. G. P.

Effect of hyperpyrexia on phosphorus partition of whole blood in paresis. D. Sackett and A. W. Turner (J. Lab. Clin. Med., 1934, **19**, 1045—1049).—Treatment of paresis by hyperpyrexia results in conversion of acid-sol. P of blood into lipin-P. The total P content is unchanged. Ch. Abs. (*p*)

Significance of the inorganic sulphate clearance in renal disease. J. W. Macy (Arch. Int. Med., 1934, **54**, 389—404).—The excretion of inorg. SO_4'' (I) by fasting subjects remains fairly const.; with normal food intake, however, the variations are considerable and > those in the serum-(I) vals. The concn. of (I) in the urine is < that of the urea (II) or creatinine (III), and the clearance vals., whilst being more const. than those for (II) and (III), are scarcely affected by the vol. of the urine. Where renal insufficiency exists, the (I)-clearance val. is reduced in most cases, and in 12% of the subjects examined (I) vals. indicated impaired renal function when other tests gave normal results. A. L.

Treatment of schistosomiasis with acridine compounds. M. Khalil and M. Salah (Lancet, 1934, **227**, 862—863).—Trypaflavine and allied compounds have no curative effect on schistosomiasis due to *Schistosoma hæmatobium* or *S. mansoni.* L. S. T.

Effect of dinitrophenol on metabolism in schizophrenic patients. J. M. Looney and R. G. Hoskins (New Engl. J. Med., 1934, **210**, 1206—1213).—Administration of 2 : 4-dinitrophenol (3—4 mg. daily for 6 weeks) had no harmful effects. Basal metabolic rates were increased. Non-protein-, urea-, and uric acid-N in blood increased gradually, but tended to regain normality as treatment continued. Ch. Abs. (*p*)

Experimental scurvy. XIX. Urine- and blood-lactic acid in scorbutic guinea-pigs. J. Shimada (J. Biochem. Japan, 1934, **20**, 147—159).—The incidence of scurvy in guinea-pigs does not produce an increase in the urine-lactic acid, whilst the blood level varies within normal limits (0·030—0·076%) (cf. A., 1928, 544). An occasional decrease in blood-lactic acid is probably due to inanition. F. O. H.

Relation of avitaminosis-*C* to blood-clotting. A. K. Presnell (J. Nutrition, 1934, **8**, 69—74).—Blood from scorbutic guinea-pigs has a longer clotting-time, smaller no. of platelets and red cells, and less hæmoglobin than that of normal animals. A. G. P.

Resistance of capillaries. I. Decreased resisting power through lack of vitamin-*C*, and through other conditions in hospital patients. P. Schultzer (Acta Med. Scand., 1934, **81**, 113—132; Chem. Zentr., 1934, i, 2611).—Administration of vitamin-*C* generally restored the resisting power of the capillaries in scorbutic patients, but was ineffective when the decreased resistance was due to infection or chronic kidney disease. R. N. C.

Incidental hyperguanidinæmia as a cause of clinical tetany. K. Dodd and A. S. Minot (Amer. J. Dis. Children, 1934, **47**, 948—962).—Tetany associated with alimentary intoxication in infants, and with post-influenzal pneumonia, is caused by the presence of increased amounts of guanidine in the blood. Guanidinæmia may be caused by increased autolysis of tissues, marked dehydration, or a disturbed Ca : P balance. Blood-Ca remains normal. Chem. Abs. (*p*)

Iodine content of blood and of urine and the basal metabolic rate; their value in the diagnosis of the function of the thyroid gland. A. W. Elmer and M. Scheps (Acta Med. Scand., 1934, **82**, 126—136).—In cases of different diseases with normal thyroids and normal or low basal metabolic rate and in cases of non-toxic goitre, vals. for blood-I of $8—19\times10^{-6}$ g. per 100 ml. were found. The urinary I excretion for 24 hr. in these cases varied from 16 to 32×10^{-6} g. In cases of exophthalmic goitre, blood-I was $20—112\times10^{-6}$ g. per 100 ml. Urinary I excretion was greatly increased in severe cases, $96—136\times10^{-6}$ g. per 24 hr. Typical cases of myxœdema had blood-I of $4—6\times10^{-6}$ g. Excretion was within normal limits except in one case, in which it was low. Nutr. Abs. (*b*)

Calcium and phosphorus metabolism in diseases of the thyroparathyroid apparatus. I. Calcium, phosphorus, and total metabolism in hyperthyroidism. Rôle of the parathyroid glands. F. S. HANSMAN and F. H. WILSON (Med. J. Austral., 1934, i, 37—66).—Hyperthyroidism alone has no effect on Ca and P metabolism. If there is disturbance of the latter there will be some degree of associated hyperparathyroidism.

NUTR. ABS. (*m*)

Effect of toxæmia on the tolerance for glucose and on the action of insulin. II. J. S. SWEENEY, N. BARSHOP, L. C. LOBELLO, and R. A. ROSENTHAL (Arch. Int. Med., 1934, **54**, 381—388).—Previous findings (this vol., 799) are confirmed, viz., the amounts of insulin (I) necessary to dispose of quantities of glucose injected with (I) into normal rabbits are inadequate in the case of animals injected with diphtheria toxin. A. L.

Vitamin therapy in pulmonary tuberculosis. VI. Effect of viosterol on the carbon dioxide content, hydrogen-ion concentration, chlorides, glucose, and urea-nitrogen of the blood, and protein, calcium, and phosphorus of the serum. Effect of physiological saline on these constituents during hypercalcæmia. P. D. CRIMM and J. W. STRAYER (J. Lab. Clin. Med., 1934, **19**, 966—971).—Administration of viosterol sufficient to produce hypercalcæmia in tubercular patients causes an increase in the P, total protein, and albumin contents of serum, and in the urea-N of the blood, and a decrease in serum-globulin and blood-Cl′. Intravenous injection of physiological saline reduces the concns. of Ca, P, and total protein. CH. ABS. (*p*)

Gastric ulcer. Rôle of cathepsin in ulcer formation. H. TAMESUE (Z. Chirurg., 1934, **242**, 706—713).—Autolysis of gastric mucosa (I) is most marked in rabbits at p_H 4·0—5·0, in man [(I) obtained at operation] at 4·0 and 8·0. The presence of excess of O_2 in the environment inhibits, and of excess of N_2 promotes, autolysis. KCN, reduced glutathione, and hexose phosphate accelerate autolysis and activate the cathepsin in (I). The production of gastric ulcer is attributed to circulatory disturbance leading to increased glycolysis in (I), formation of lactic acid, increase in acidity, and O_2 deficiency.

NUTR. ABS. (*m*)

Gaseous metabolism of tissues *in vitro*. VI. Determination of tissue respiration and glycolysis by evolved ammonia. Y. OGATA (J. Biochem. Japan, 1934, **19**, 377—390).—The evolution of NH_3 by tissues necessitates a correction to the Warburg formulæ. The solubility of NH_3 in Ringer's solution, and the max. tension and vol. which can be neglected in metabolic experiments, are determined. The application of the findings to data of the respiration of rabbit's kidney medullary tissue is given.

F. O. H.

Tissue metabolism of warm-blooded animals at normal and at febrile temperatures. M. E. MARSH (Amer. J. Physiol., 1934, **109**, 502—514).—The average increase in O_2 consumption per 1° rise in temp. of liver and kidney tissues of the rat, rabbit, cat, and dog was fairly uniform in all the series under the same conditions. In Ringer's PO_4'''–glucose solution, equilibrated with O_2, the Q_{10} vals. averaged 1·7 for the first hr., but the accelerated decline in metabolism at the higher temp. made them of little significance. With serum and air, the metabolism at febrile temp. was maintained for several hr. at a rate parallel to the normal rate and slightly higher, the average Q_{10} being 2·0, which compared more favourably with that found in intact animals. R. N. C.

Oxygen consumption of large-mouth black bass (*Huro floridiana*) fingerlings. A. H. WIEBE and A. C. FULLER (Trans. Amer. Fish. Soc., 1933, **63**, 208—214).—The O_2 consumption is not related to the O_2 tension or p_H of the H_2O. CH. ABS. (*p*)

Metabolism of the frog's egg in course of development. I. Respiration and glycolysis from segmentation to hatching. J. BRACHET (Arch. Biol., 1934, **45**, 611—728).—Anaërobic conditions have no effect on segmentation (I) of developing frogs' eggs, but gastrulation (II) is impeded and neurulation (III) inhibited entirely. Reduced methylene-blue is oxidised in certain parts of the egg in anaërobiosis (IV), max. oxidation occurring in the sub-equatorial regions with $rH > 14$. O_2 consumption in (I), (II), and (III) is inhibited by 0·001*M*-KCN in the order of 85—100%, the inhibition falling to approx. 50% as growth proceeds. $NHPh{\cdot}CO_2Et$ in 0·001—0·002*M* concn. inhibits (I) and (III) and arrests (II). $CH_2I{\cdot}CO_2H$ has no action in presence of air; in (IV) it inhibits (III). The R.Q. of the eggs rises steadily through (I) and (II) to a max. at (III), when it falls slightly, then remaining const. until hatching occurs. Lactic acid, absent from the new-laid eggs, appears at the beginning of (I) and rises to a max. after (III), afterwards falling. (IV) is accompanied by the formation of considerable quantities of acid at the commencement of development. In more or less complete (IV) the eggs continue to produce CO_2, which in complete (IV) is still approx. 50% of its aërobic val. Pulped eggs contain indophenol-oxidase (V), and also reducing substances (VI). Pulping is followed by a momentary increase of O_2 consumption that may reach 800%; it is inhibited by KCN, but not by *p*-$C_6H_4(NH_2)_2$ or $CH_2I{\cdot}CO_2H$. The cause of this is probably connected with (V). R.Q. of tadpoles falls on pulping. (VI) decolorise methylene-blue in absence of air; one or more of them are thermolabile at 52°, and all at 100°; they are inhibited to a small extent by $NHPh{\cdot}CO_2Et$. They probably consist partly of dehydrogenases. The pulped eggs show no trace of either cytochrome or hæmatin spectra, although both are to be found in frogs' spermatozoa. Iodometric determinations indicate the possible presence of traces of glutathione, which, however, certainly plays no part in the respiration of the eggs. The reducing action of extracts of the pulped eggs suggests the possibility of ascorbic acid being one of the (VI). R. N. C.

Synthesis of thymonucleic acid in the development of the trout's egg. M. VAN DER GHINST (Arch. Biol., 1934, **45**, 729—734).—Thymonucleic acid is absent from the new-laid egg, but is synthesised progressively in the cellular portion of the egg as it develops. R. N. C.

Fish metabolism under increasing temperature. R. C. CLAUSEN (Trans. Amer. Fish. Soc., 1933, 63, 215—219).—The daily rhythm of O_2 consumption (I) corresponds with the activities of the fish. (I) varies irregularly with rising temp., showing peak vals. at 12° and 20°. CH. ABS. (*p*)

Basal metabolism of old people. Y. KISÉ and T. OCHI (J. Lab. Clin. Med., 1934, 19, 1073—1079).—Between the ages of 50 and 93 years the metabolic rate declines 3—5% for each 10-year period. CH. ABS. (*p*)

Growth and basal metabolism. I. Basal metabolism of pre-school children. I. NAKAGAWA (Amer. J. Dis. Child., 1934, 47, 963—969).—The basal metabolic rate for Japanese children is $>$ the Benedict–Talbot standards. CH. ABS. (*p*)

Blood-pigment and the living cell. I. Hæmoglobin decomposition in tissue cultures. II. Bilirubin formation *in vitro*. III. Formation of a yellow pigment in tissue cultures. L. DOLJANSKI and O. KOCH (Virchow's Arch., 1933, 291, 379—389, 390—396, 397—400; Chem. Zentr., 1934, i, 882).—I. Tissue cultures, especially from connective tissue (fibroblasts), liver, and spleen, transform added hæmoglobin (I) more rapidly and markedly than do the tissue extract controls. Addition of embryonic extracts to a blood-pigment (II) solution results in a decomp. of (I). In presence of the living cell the fission of the Fe-containing group from (I) does not occur.

II. Tissue cultures from spleen, fibroblasts, and liver formed no bilirubin (III) from added blood-pigment, whilst in the controls, which contained no living tissue and only tissue extract, (III) was detected.

III. Tissue cultures treated with (II) contained, besides methæmoglobin, another pigment which must be related to the decomp. of (I). Solubility and spectrum data indicate that the pigment is xanthorubin. L. S. T.

Site of bilirubin formation from experiments on angiostomised dogs. I. E. S. LONDON and L. J. KRYZANOVSKAYA (Z. physiol. Chem., 1934, 227, 229—232).—Blood samples were drawn from the venae lienalis and hepatica and the femoral vein and/or artery after production of hæmolysis by injection of H_2O into the jugular vein. The samples were analysed for bilirubin (I). The formation of (I) from hæmoglobin occurs chiefly but not entirely in the spleen. After splenectomy the femoral and hepatic veins showed a very small (I) content, indicating that the reticulo-endothelial system is not involved in (I) production. J. H. B.

Nutritional requirements of brook trout. A. V. TUNISON and C. M. MCCAY (Trans. Amer. Fish. Soc., 1933, 63, 167—177).—Milks dried by various processes had equal food vals. Peanut and cotton-seed meal were equally well utilised. The thermolabile factor *H* can be preserved by drying meat in a vac. in inert gas. The difficult digestion of fat by trout is not entirely due to the physical state of the fat at H_2O temp. Hg_2Cl_2, $C_{10}H_7{\cdot}OH$, and CCl_4 were effective in freeing trout from *Octomitus salmonis*. CH. ABS. (*p*)

Nutritive value of whale-liver. T. OSEKI (Bull. Inst. Phys. Chem. Res. Japan, 1934, 13, 1160—1165).—Liver-proteins of finback- (I) and sei-whale have a high nutritive val. and contain vitamin-*A*, but no -*B*. (I) contains some -*E*. J. L. D.

Alimentary value of soya beans. M. LIGORI (Arch. Farm. sperim., 1934, 58, 142—148).—Rats on a diet of soya beans show limited rates of growth, due to deficiencies of salts and vitamin-*A* and -*D*. Addition of 2% of cod-liver oil or butter resulted in the death of most of the animals, but the survivors showed a considerable improvement in growth and general condition. R. N. C.

Nutritive value of canavanine. I. M. OGAWA (J. Agric. Chem. Soc. Japan, 1934, 10, 225—231).—Canavanine is non-toxic; 0·01—0·1 g. per kg. per day promotes the growth of mice. CH. ABS.

Digestion and nutrition of heated cow's milk. J. OKADA and T. SANO (Jap. J. Exp. Med., 1934, 12, 169—198).—Heated milk has a lower nutritional val. and digestibility than raw milk. Effects of additions of gelatin, peptone, $Na_4P_2O_7$, and $CaCl_2$ are recorded. CH. ABS. (*p*)

Fish-meat powder as a substitute for horse-meat protein in synthetic diets used for feeding experiments. M. MATSUOKA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, 24, 335—340).—The nutritive val. of the proteins of fish-meat (I) is nearly the same as that of horse-meat powder. Albino rats died within 98 days on a vitamin-*A*-free diet containing (I), many exhibiting xerophthalmia. J. L. D.

Nitrogen balance of laying hens. J. S. WILLCOX (J. Agric. Sci., 1934, 24, 636—648).—Variations in the N retention of hens are not related to the output of egg-N or with the no. of eggs laid. The N required for egg production can be obtained mainly, if not entirely, from the food supply during the laying period. A. G. P.

Factors determining renal weight. XVI. Nature of the protein intake. E. M. MACKAY and L. L. MACKAY (J. Nutrition, 1934, 8, 187—195).—The influence of increased protein (I) intake by rats on the renal wt. varied with the nature of (I) in the order gelatin>ovalbumin>caseinogen. A. G. P.

Experiments on nutrition. XIII. Relative values of proteins. R. H. A. PLIMMER, J. L. ROSEDALE, W. H. RAYMOND, and J. LOWNDES (Biochem. J., 1934, 28, 1863—1886).—The proteins (I) in common foodstuffs were fed to chicks in conjunction with the carbohydrates of various cereals (II), the biological val. of (I) being given by (increase in wt.)^2/time × (I)-consumption. Animal (I), such as egg-white, egg-yolk, caseinogen, and fish-meal, are far superior to vegetable (I) in pulses (III), grass, and lentils. When chicks were fed on (II) or (III) alone, the best results were obtained with buckwheat, barley, oatmeal, and wheat or maize in that order. The inferior val. of (III) is due to their low cystine content. A. E. O.

Feeding experiments with mixtures of highly purified amino-acids. IV. Supplementing effect of caseinogen fractions obtained by carbamate procedure. V. Additional pro-

perties of unknown growth-factor present in proteins. C. T. Caldwell and W. C. Rose (J. Biol. Chem., 1934, **107**, 45—55, 57—72; cf. A., 1932, 83).—IV. Caseinogen (I) was refluxed with aq. H_2SO_4 and neutralised with $Ba(OH)_2$; the filtrate was conc. in vac. Addition of $Ba(OH)_2$ pptd. Ba aspartate, which was discarded. After further concn. 95% EtOH was added and the Ba salts of the dicarboxylic acids were converted into their acids. The filtrate was fractionated by the Ba carbamate procedure of Kingston and Schryver (A., 1925, i, 89). Rats fed on a diet containing purified NH_2-acids as sole source of N showed greatest growth recovery when fed with the NH_2-acids pptd. by EtOH. Several of the other fractions were also effective to a smaller degree. Glycine may be removed from the growth-stimulating factor (II) by the relative insolubility of its carbamate in ice-cold H_2O.

V. The hydrolysed (I) was fractionated by the Cu salt procedure (Town, A., 1928, 1148). From growth curves of rats (II) is absent from the H_2O-insol. Cu salt fraction, and is very slowly extracted with MeOH from the H_2O-sol. salts. None of several synthetic products similar to proline, valine, and *iso*leucine had growth-promoting powers. H. D.

Tryptophan deficiency. R. S. Alcock (Biochem. J., 1934, **28**, 1721—1728).—Partial replacement of hydrolysed caseinogen by zein affords an improved tryptophan (I)-deficient diet on which rats lose but little wt. Rats on this diet, injected with (I), failed to grow, but showed increased growth when injected with anterior pituitary hormone. The rat can synthesise sufficient (I) for maintaining wt. C. G. A.

Utilisation of energy-producing nutriment and protein as affected by individual nutrient deficiencies. I. Effects of cystine deficiency. R. W. Swift, O. J. Kahlenberg, L. Voris, and E. B. Forbes (J. Nutrition, 1934, **8**, 197—219).—Deficiency of cystine (I) in the diet of rats had an adverse effect on appetite, but no definite influence on the digestibility of dietary protein. Supplementary feeding with (I) improved growth and increased the storage of N and of energy. The C : N ratio of the urine (2·0) was not significantly affected.

A. G. P.

Metabolism of *l*- and *dl*-cystine in adult dogs maintained on a protein-free diet. J. A. Stekol (J. Biol. Chem., 1934, **107**, 225—228).—*dl*-Cystine, in contrast to *l*-cystine, is only partly retained by animals, 40% of the S being excreted in the urine as inorg. SO_4'' and neutral S. The S of *d*-cystine is not used by dogs to replace tissue waste. C. G. A.

Site of deamination of amino-acids from experiments on angiostomised dogs. I. E. S. London, A. M. Dubinsky, N. L. Vassilevskaya, and M. J. Prochorova (Z. physiol. Chem., 1934, **227**, 223—228).—Blood samples from the portal and kidney veins and the femoral artery of fasting dogs were examined for NH_3, O_2, CO_2, and $AcCO_2H$ (I), before and after injection of *d*-alanine (II) or *l*-aspartic acid into the femoral vein. Deamination of NH_2-acids under physiological conditions occurs principally in the intestinal wall. The deamination of (II) is accompanied by increased O_2 uptake, (I) being formed. Deamination also occurs in the kidney; the increased O_2 uptake again indicates (I) production. No increase of (I) (but often a decrease) is, however, observed in the kidney vein, presumably owing to its removal by the kidney. J. H. B.

Oxidation of tyrosine and phenylalanine by the livers and kidneys of certain animals. F. Bernheim and M. L. C. Bernheim (J. Biol. Chem., 1934, **107**, 275—282).—Tyrosine (I) is oxidised by broken cell suspensions of the livers (II) of the rat, guinea-pig, rabbit, cat, and dog; phenylalanine (III) is also oxidised by these preps., but in some cases very slowly. Preps. of the kidneys (IV) oxidise (III) but not (I). Oxidation of 1 mol. of (I) requires $2O_2$ and of (III), $0·5O_2$. (I) is not deaminated, but tyramine and (III) are. $0·005M$-KCN inhibits oxidation of (I) but not (III). (III) but not (I) reduces methylene-blue. C. G. A.

Influence of temperature on protein metabolism. III. Hexone bases of toad's liver during winter. H. Makino (J. Biochem. Japan, 1934, **20**, 1—3).—The hexone base fraction from toad's liver during winter contained 0·0439% of cadaverine and 0·0934% of choline, but no lysine, arginine, or histidine (cf. this vol., 321). F. O. H.

Perfusion of the stomach. IV. Perfusion with urea. S. Sumida (J. Biochem. Japan, 1934, **19**, 449—456; cf. A., 1933, 745).—Blood containing added urea perfused through the isolated dog's stomach (I) experiences an increase in NH_3-N which, however, is only approx. 1/6 of the decrease in urea-N. The NH_3-N levels of the contents and muscular and mucosa layers of (I) are increased, whilst the corresponding urea-N levels are practically unchanged. The catabolism of urea in (I) is discussed. F. O. H.

Participation of ornithine, citrulline, and arginine in the normal process of urea formation in the liver, using angiostomy. I. E. S. London, A. K. Alexandry, and S. V. Nedsvedski (Z. physiol. Chem., 1934, **227**, 233—241).—Ornithine (I) injected into the portal vein together with NH_4Cl gives a greater increase in the urea in the liver vein than NH_4Cl alone. (I) alone gives a considerable increase. (I) injected with NH_4Cl into the peripheral veins does not cause an increase in the urea in the arterial blood over that produced by NH_4Cl alone. Citrulline and arginine disappear from the blood much more slowly than NH_4Cl; the production of urea is also slower. No support is found for Krebs' proposed scheme for urea production in the liver based on *in-vitro* experiments (A., 1932, 1059). J. H. B.

Non-enzymic uricolysis in animal tissue. D. Michlin and A. Ryžova (Biochem. Z., 1934, **273**, 354—358).—In the presence or absence of O_2 added uric acid is partly or wholly destroyed by fresh or dried, boiled or unboiled extracts of the mammary glands of cows or of rat or rabbit kidney. Hæmoglobin has no effect (cf. Gomolinska, A., 1928, 1269) on the process, which is accompanied by production of urea but not of allantoin. No glycine is produced.

W. McC.

Fate of carotene introduced into the circulation. J. C. Drummond, H. P. Gilding, and R. J. Macwalter (J. Physiol., 1934, 82, 75—78).—Carotene introduced into the blood-stream as a colloidal suspension in aq. solution was taken up very rapidly, principally in the liver, which, however, could absorb only a limited amount, excess being retained by the lungs. The liver showed carotene granules in the Kupffer cells, suggesting that it was absorbed from the circulation by the reticulo-endothelial system.
R. N. C.

Is cholesterol absorbed by the mucous membrane of the gall-bladder ? B. Varela, J. Vilar, and A. Terra (Compt. rend. Soc. Biol., 1934, **115**, 1652—1656).—Results of previous workers were confirmed. The ratio of cholesterol to bilirubin in bile secreted by the gall-bladder was $<$ in duodenal juice or hepatic bile, collected simultaneously. The differences observed are not attributed to any special function of the mucous membrane of the gall-bladder.
Nutr. Abs. (*b*)

Spleen and cholesterol metabolism. F. Goebel (Compt. rend. Soc. Biol., 1934, **116**, 233—236; J. Physiol. Path. gén., 1934, **32**, 59—61).—In normal dogs, subcutaneous injection of cholesterol (I) produced hypercholesterolæmia of about 30 min. duration, often followed by slight hypocholesterolæmia. After removal of the spleen (II) the rise in blood-(I) lasts at least 24 hr. (II) probably produces (I), removes excess of it from the blood, and stores it.
Nutr. Abs. (*m*)

Diagnostic value of blood-cholesterol determination after peroral loading with cholesterol. P. Barreda (Klin. Woch., 1934, **13**, 290—292; Chem. Zentr., 1934, i, 3081).—Attempts to confirm Bürger's observations of the regular appearance of alimentary hyperglycæmia in metabolic recovery after peroral loading with cholesterol (I) lead to a reverse result. The results are not considered sufficient evidence from which to deduce any far-reaching conclusions on (I) metabolism.
R. N. C.

Physiology of phospholipins. R. G. Sinclair (Physiol. Rev., 1934, **14**, 351—403).—A review.
Ch. Abs. (*p*)

Action of phosphoaminolipins in fat assimilation. I. Injection of iodised fats. C. Artom (Boll. Soc. ital. Biol. sperim., 7, 126—129; Chem. Zentr., 1934, i, 2449).—Shortly after injection fat constituents appear in the liver in the form of COMe$_2$-sol. compounds. Blood also contains a part of the iodised fat.
A. G. P.

Significance of the liver in metabolism of lipins. III. Changes in lipins in blood and bile when various kinds of bile acids are administered. Y. Asoda (Jap. J. Gastroenterol., 1934, 6, 1—6).—Feeding of Na salts of bile acids to rabbits caused a temporary increase of blood-lipins and a decrease in bile-lipins.
Ch. Abs. (*p*)

Liver-lipins during the intake of neutral fat. C. Artom (Boll. Soc. ital. Biol. sperim., 7, 133—136; Chem. Zentr., 1934, i, 2449).—After administration of fats to fasting dogs, the fatty acids and P of phosphoaminolipins, the CHCl$_3$-sol. P, and the P pptd. by COMe$_2$ increase proportionally. Total and non-phosphatide fatty acids also increase. The dry matter and unsaponifiable fraction vary irregularly.
A. G. P.

Fatty acids produced by the metabolism of nematodes. J. Waechter (Z. Biol., 1934, **95**, 497—501).—The Et$_2$O-sol. material from 1% aq. NaCl (saturated with CO$_2$) in which *Ascarides* have been kept at 37° for 72 hr. yields on fractional distillation *n*- but not *iso*-valeric acid (cf. A., 1902, ii, 155).
F. O. H.

Fat metabolism. IV. Bi-lateral β-oxidation of the dicarboxylic acids arising by ω-oxidation of saturated fatty acids. P. E. Verkade and J. van der Lee (Z. physiol. Chem., 1934, **227**, 213—222).—After administration of triundecoin to man, undecanedicarboxylic, pimelic, and azelaic acids are excreted in the urine, and after tridecoin, sebacic, adipic, and suberic acids. Thus both β- and ω-oxidation occur.
J. H. B.

Relation between surface tension of solutions and solubility of physiologically important fatty acids.—See this vol., 1304.

Good growth of albino rats fed on a polished rice diet. M. Matsuoka (Bull. Inst. Phys. Chem. Res. Japan, 1934, **13**, 1139—1154).—Growth is rapid when polished rice is the source of carbohydrates if the other necessary dietary constituents are present in adequate amount.
J. L. D.

Stereochemical constitution and selective [animal] resorption of carbohydrates. G. Malyoth (Klin. Woch., 1933, **12**, 1930—1933; Chem. Zentr., 1934, i, 2308).—A dextrin–maltose mixture partly fermented (50%) by *Aspergillus* to produce a preponderance of *α*-compounds increased the live wt. of piglings to an extent $>$ that produced by the untreated mixture.
A. G. P.

Rate of absorption of glucose from the intestine of the dog. H. C. Trimble and S. J. Maddock (J. Biol. Chem., 1934, **107**, 133—142).—The max. rate of absorption is 0·92 g. per kg. per hr. The optimal concn. for absorption of 13·5% was not confirmed.
H. G. R.

Metabolism of galactose. P. de Lucia and M. Torelli (Boll. Soc. ital. Biol. sperim., 7, 250—251; Chem. Zentr., 1934, i, 2449).—Administration of 1 g. of galactose (I) per kg. live wt. to fasting dogs was followed by 70% utilisation of (I) within 72 hr. The balance appeared in the urine.
A. G. P.

Metabolism of fructose. IV. Hepatic influence on utilisation of galactose and fructose. A. W. Rowe, M. A. McManus, and A. J. Plummer (New. Engl. J. Med., 1934, **210**, 1163—1169).—Utilisation of fructose (I) and galactose (II) is influenced by hepatic disturbance, which lowered the tolerance for (I) and (II) in most cases.
Ch. Abs. (*p*)

Fate of dulcitol and dulcitan in the animal body. C. J. Carr and J. C. Krantz, jun. (J. Biol. Chem., 1934, **107**, 371—376).—Dulcitol (I), but not its anhydride dulcitan (II), can be stored as glycogen (III) in the liver of white rats. Each tends to reduce tissue storage of (III). Neither (I) nor (II) affects the R.Q., or is effective in relieving insulin shock or in raising the blood-sugar of rabbits when administered orally. A. E. O.

Utilisation of blood-sugar and formation of lactic acid by the lungs. C. L. Evans, F. Y. Hsu, and T. Kosaka (J. Physiol., 1934, 82, 41—61).—Perfusion of blood through exsected dog's lungs causes conversion of the blood-sugar into lactic acid (I). The rate for the first hr. is about 100 mg. of glucose (II) per 100 g. of lung, forming 50 mg. of (I), and slows down as perfusion proceeds. After all the (II) has been removed, (I) shows a slight fall. Ventilation of the lungs with CO_2 reduces the rate of glycolysis, which rapidly becomes normal on resumption of air supply. Perfusion with serum alone shows the same results. Blood-(I) of heart–lung preps. (III) is formed partly by glycolysis in the blood-stream and partly by the lungs, as is the (I) consumed by the beating heart in (III). R. N. C.

Metabolism of lactic and pyruvic acids in normal and tumour tissue. I. Methods and results with kidney cortex. K. A. C. Elliott and E. F. Schroeder (Biochem. J., 1934, 28, 1920—1939).—Lactate is slowly metabolised by slices of rabbit-kidney cortex (I), but less rapidly than pyruvate, which in turn is oxidised less rapidly than succinate, fumarate, malate, and oxaloacetate, none of which is converted into glycogen by (I). Acetate is also fairly rapidly metabolised, but β-hydroxybutyrate does not appreciably affect the respiration of (I). β-Carboxylase, but not α-, is present in (I). After mincing the tissue, only succinic dehydrogenase, fumarase, and (to a slight extent) β-carboxylase remain active. Formate is not oxidised by (I). A. E. O.

Intermediate metabolism of endocrine organs. II. Glycolysis in adrenals and corpus luteum. III. Glycolysis and proteolysis in adrenals during increased production of hormone. A. Utevski, S. Epstein, V. Ossinskaja, and E. Mima (Biochem. Z., 1934, 273, 359—361, 362—364).—II. The medullary and cortical regions of the adrenal glands (I) and the corpus luteum (II) of the cow are rich in preformed lactic acid (III), the amount of which increases on autolysis. Addition of glycogen (IV) or $AcCO_2H$ does not stimulate production of (III) in (I) or (II). Alanine slightly stimulates production of (III) in (II) but not in (I), and glucose stimulates it slightly in (I) but not in (II). 100 g. of (I) contain 40 mg. and of (II) 150 mg. of (IV)

III. In dogs electrical stimulation (V) of the splanchnic nerve leads to increase in the sugar and (III) contents of the blood and in the (IV) content of (I). The (III) content of (I) decreases. (V) has no effect on the N content of (I) (cf. this vol., 102). W. McC.

Chemistry of anaërobic recovery in muscle. J. K. Parnas and P. Ostern (Nature, 1934, 134, 627).—Three intermediate reactions in the conversion of glycogen into lactic acid are proposed. L. S. T.

Disappearance of hexose monophosphate from muscle under aërobic and anaërobic conditions. G. T. Cori and C. F. Cori (J. Biol. Chem., 1934, 107, 5—14).—The leg muscles of frogs are analysed for hexose phosphate (I) and lactic acid (II) during recovery from tetanic stimulation (III) and adrenaline treatment (IV) under aërobic (V) and anaërobic (VI) conditions. The rate of disappearance of (I) under (V) after (III) is uninfluenced by the presence of (II) and ∝ the concn. of (I); in 30 min. of recovery 77 mg. per 100 g. disappear, reaching the basal val. in 2 hr. Under (VI) decreases of 49, 63, and 78 mg. per 100 g. occurred in 60, 90, and 120 min., respectively. After (IV) the rate of disappearance of (I) under (V) is uninfluenced by changed p_H or addition of $MgCl_2$, (II), PO_4''', and KCl, and it occurs thrice as rapidly as under (VI). After (III) and (IV) the disappearance of (I) under (VI) was accompanied by equiv. (II) and inorg. P formation. H. D.

Phosphagen in plain muscle. M. G. Eggleton (J. Physiol., 1934, 82, 79—87).—The ratio (I) of phosphagen (II) to the sum of (II) and inorg. PO_4''' in the resting aërated muscle of *Mytilus edulis* is 0·8; fatigue induced by intermittent contractions reduces it to 0·45, and that from a tetanus to 0·6. The muscle at rest recovers its original (II) content under aërobic, but not under anaërobic, conditions; thus (II) plays the same part in plain as in skeletal and cardiac muscles. The hydrolysis const. of the *Mytilus* (II) in 0·01*N*-HCl at 28° is similar to that of argininephosphoric acid (III); the effect of MoO_4'' on the rate of hydrolysis is also the same for both substances. (III) can be determined rapidly by separating it from P_2O_7'''' and PO_4''' as sol. Ba salt and then hydrolysing. Both $Na_4P_2O_7$ and muscle "P_2O_7''''" are slightly hydrolysed in 0·05*N*-acid at 28°, the latter twice as fast as the former. R. N. C.

Transparency and action-metabolism of muscle. E. von Baeyer (Klin. Woch., 1933, 12, 1278—1279; Chem. Zentr., 1934, i, 2783—2784).—The intensity of the transmitted light through frogs' sartorii was measured under varied conditions. The course of the colour curve was not essentially altered in any case, but there was a parallel shifting of the intensity. In the breakdown of creatinephosphoric acid the extinction (I) by the muscle decreased; in lactic acid formation it increased in presence of Ringer's solution, a swelling generally taking place. It has not been definitely proved that the changes in (I) are dependent on p_H, and the nature of the optical changes is still unknown. R. N. C.

Effect of prolonged hard muscular work on sulphur and nitrogen metabolism. H. E. C. Wilson (J. Physiol., 1934, 82, 184—188).—The excess N excretion during and after the riding of a bicycle-ergometer for a prolonged period increases with the protein intake during the work period; S excretion runs on similar lines. The excess S tends to precede the N in excretion, the S output returning to its basal val. before the N. The S : N ratio of the total excess of each experiment does not show that the excess is derived from any one tissue-protein. R. N. C.

Efficiency and performance of a vegetarian racing cyclist under different dietary conditions. G. M. Wishart (J. Physiol., 1934, 82, 189—199).—The best performance is obtained on a high-cal. diet rich in animal proteins (I). The gross efficiency (II)

is > that on (I)-poor diets; the lower (II) is not explained by the higher sp. dynamic action of the (I).
R. N. C.

Chemico-physiological basis of muscular fatigue. H. Rigler (Med. chem. Abh. med.-chem. Forsch. I.G. Farbenind., 1933, 198—206; Chem. Zentr., 1934, i, 2444).—Theoretical. R. N. C.

Effect of varying sugar intake on nitrogen, calcium, and phosphorus retention of children. R. B. Hubbell and M. Koehne (Amer. J. Dis. Children, 1934, 47, 988—992).—Addition to diets of girls (7—11 years) of sugar sufficient to raise the calorific val. (I) by 6% did not affect the retention of N, Ca, or P. An increase of 16—18% in (I) caused an increase in the N and P, and a decrease in Ca, retained.
Ch. Abs. (*p*)

Influence of various additions to the ration, of potassium, calcium, magnesium, and iron on the mineral status of these elements in the blood of cattle during stall feeding and pasturage. E. Berndt and H. Bethmann (Bied. Zentr. [Tierernähr.], 1934, B, 6, 292—350).—The relative effects of electrolyte ions on blood functions are in accordance with the Hofmeister series, especially in relation to antagonism. The K content of blood in old cows was > that in younger animals. Vals. fluctuated between 27·7 and 78·6 mg. per 100 c.c., and were increased during pasture feeding. Blood-Ca (I) in all animals showed approx. const. mean vals. These were lower during pasturing than during stall feeding and were influenced by the Ca content of the ration. Feeding of sugar-beet leaves caused a marked increase in (I). Blood-Mg was not affected by the Mg content of the food during either indoor feeding or pasturing. Blood-Fe was higher in animals at grass, but otherwise was unrelated to the Fe content of the food. A. G. P.

Influence of the addition to rations of chlorine, sodium, phosphorus, and protein on the mineral status of these elements in blood of cattle during stall feeding and pasturage. E. Berndt and G. F. Baumgarten (Bied. Zentr. [Tierernähr.], 1934, B, 6, 351—397).—Blood-Cl′ was higher in old than in young cows, was not affected by the amounts fed, but was higher during stall feeding (I) than in pasturage (II). Variations in blood-Na were small. The Na : K ratio widened with increasing age and also increased in spring at the transition period from (I) to (II). Blood-PO_4''' varied considerably and was directly affected by the PO_4''' content of the ration. During (I) blood-protein (III) increased with age, but the digestible protein of the food bore no relationship to (III). A. G. P.

Mobilisation of calcium during development. O. Glaser and E. Piehler (Biol. Bull., 1934, 66, 351—356).—The % of Ca in hen egg-shell during incubation was const., but the total Ca declined by approx. 150 mg. in 21 days. Ch. Abs. (*p*)

Effect of carbon dioxide on calcium and phosphorus retention. J. C. Forbes (J. Biol. Chem., 1934, 107, 283—287).—CO_2 in concn. up to 12% of the air breathed has no significant effect on the retention of either Ca or P by young rats. C. G. A.

Nitrogen and salt metabolism in monkeys. P. V. Bochkarev and N. P. Korotkova (Arch. Sci. Biol. U.S.S.R., 1933, 33, 255—261).—N and mineral balances are examined. Ch. Abs. (*p*)

Salt requirements of *Ligia* in Bermuda. T. C. Barnes (Biol. Bull., 1934, 66, 124—132).—Longevity of *L. baudiniana* in air, sea-H_2O, and NaCl solutions is examined. Ch. Abs. (*p*)

Relation between the spleen and sulphur metabolism, especially the effect of various endocrine glands thereon. I. Effect of removal of spleen on sulphur metabolism. II. Effect of thyroid glands on sulphur metabolism of splenectomised dogs. III. Effect of insulin and glucose on sulphur metabolism of splenectomised dogs. IV. Effect of adrenaline on sulphur metabolism of splenectomised dogs. S. Nishikori (Folio Endocrinol. Japan, 1933, 9, 5—6, 6—7, 17—18, 18—19).—I. During 7—35 days after splenectomy the total N and S excreted decreased considerably, although the N : S ratio increased. The % of SO_4'' fell, but the proportion of total S appearing as SO_4'' increased. The proportion of alkylsulphuric acid was unchanged. Neutral S decreased.

II. Feeding of thyroid gland to splenectomised dogs (I) produced the same effect on N and S metabolism as on normal animals.

III. Administration of insulin to (I) increased the total N and S excreted without affecting the N : S ratio; inorg. S decreased and neutral S increased. Simultaneous injection of glucose accentuated these effects.

IV. Injection of adrenaline into (I) increased the excretion of total N and S, inorg. S, and neutral S.
Ch. Abs. (*p*)

Bromine metabolism in the human organism. P. Serbescu and G. A. Buttu (Bull. Acad. Méd., 1934, 111, 232—238; Chem. Zentr., 1934, i, 3489).—Human blood contains $\not>$ 0·1 mg. of Br per 100 c.c. The pituitary does not control Br metabolism, since no Br can be detected in it. The thyroid (I) always contains Br, and possibly controls both I and Br metabolism. Br introduced into the blood is taken up by the tissues, since it is eliminated only very slowly. (I)-Br appears to decrease with age. R. N. C.

Effect of water drinking, mineral starvation, and salt administration on the total osmotic pressure of the blood in man, chiefly in relation to the problems of water absorption and water diuresis. E. J. Baldes and F. H. Smirk (J. Physiol., 1934, 82, 62—74).—H_2O drinking lowers the blood-osmotic pressure (I), but any changes in the urine flow that follow are not dependent on the lowering of (I). The time of absorption of H_2O can be determined by observation of (I). A diet deficient in salts lowers (I) to a new level, without causing diuresis (II). Administration of salt to normal subjects raises (I); subsequent administration of H_2O causes (II), even if (I) has not been lowered to its normal val., showing that the onset of (II) is not dependent on the initial level of (I). R. N. C.

Physiological importance of nickel and cobalt. G. Bertrand and H. Nakamura (Ann. Inst. Pasteur, 1934, **53**, 371—378).—The addition of small amounts of $NiCl_2$ and $CoSO_4$ to a diet of starch, lactose, caseinogen, and mineral salts (containing only traces of Ni and Co) increases the max. wt. attained and the survival period (the latter by approx. 17%) of mice. F. O. H.

Iron metabolism of the growing organism. F. Thoenes and R. Aschaffenburg (Abh. Kinderheilk. Grenzgeb. No. 35, 1—103 ; Beih. Jahrb. Kinderheilk., 1934, **141** ; Chem. Zentr., 1934, i, 1668—1669). —A monograph on the Fe economy and the intermediate Fe metabolism in children, together with fresh investigations concerning normal and pathological vals. of serum-Fe, the effect of exogenous and endogenous Fe on serum-Fe, and the influence of bacterio-toxins. L. S. T.

Iron and copper retention in young children. A. L. Daniels and O. E. Wright (J. Nutrition, 1934, **8**, 125—138).—The Fe retention (I) ranged from 0·12 to 0·25 mg. per kg. and was met by rations containing 0·6% of Fe. Larger amounts of dietary Fe did not increase (I). Cu retention averaged 0·026 mg. per kg. Suitable diets should contain $\nless$ 0·1 mg. Cu per kg. body-wt. A. G. P.

Iron and copper metabolism in the developing chick embryo. W. D. McFarlane and H. I. Milne (J. Biol. Chem., 1934, **107**, 309—319).—Determinations of the daily changes in Fe and Cu contents of the livers (I) and of the body-tissue (II) of chick embryos indicate that although the abs. amount of Fe in the liver increases steadily up to hatching time, the % Fe and % Cu per unit dry tissue decreases in inverse ratio to the dry wt., although remaining const. in (II). 50—60% of the Fe in (I) before hatching is non-hæmatin-Fe. A. E. O.

Analysis of oxidation and reduction of indicators in living cells. R. Chambers (Cold Spring Harbor Sympos. Quant. Biol., 1933, **1**, 205—213).—Aërobic reducing intensities, which express an average of the relative velocities of the reducing and oxidising reactions within the cell, have been measured. Ch. Abs.

Reactions of oxidation–reduction indicators in biological material, and their interpretation. B. Cohen (Cold Spring Harbor Sympos. Quant. Biol., 1933, **1**, 214—223).—The reducing intensity of sol. indicators injected into various plant and animal cells under aërobic and anaërobic conditions was approx. the same for the same indicators. Ch. Abs.

Determination of ethyl alcohol in brain. R. J. Abernethy, E. R. Russell, and C. H. Thienes (J. Lab. Clin. Med., 1934, **19**, 1014—1018).—Brain-tissue is distilled in steam, and the distillate oxidised with $K_2Cr_2O_7$–H_2SO_4. AcOH produced is separated by distillation and determined volumetrically. In very small samples the product of oxidation is treated with $Ca(OH)_2$ and distilled in steam a second time to prevent volatilisation of org. acids. Ch. Abs. (*p*)

[Effect of] nembutal (pentobarbital sodium). M. W. Hemingway, J. van de Erve, and J. D. Booth (J. Lab. Clin. Med., 1934, **19**, 738—742).—In nembutal anæsthesia (dogs) blood-sugar is slightly raised, but -urea-N, -non-protein-N, and serum-protein are unaffected. Ch. Abs.

Diazo-reaction for detection of certain local anæsthetics in urine and tissues. W. E. Gibb and W. M. Dean (J. Lab. Clin. Med., 1934, **19**, 1018—1019).—Riegel and Williams' technique is applied to detect procaine and aminobenzoic acid derivatives. Ch. Abs. (*p*)

Effect of anæsthetics on the surface precipitation reaction. L. V. Heilbrunn (Biol. Bull., 1934, **66**, 264—275).—Anæsthetics, including Mg, inhibit the formation of a ppt. on the surface of extruded protoplasm of *Stentor* and *Arbacia* eggs. Ch. Abs. (*p*)

Retention of caffeine in the animal organism. A. Krupski, A. Kunz, and F. Almasy (Biochem. Z., 1934, **273**, 317—320).—The caffeine (I) content of guinea-pigs (II) which have received a single oral dose of (I) decreases in about 47 hr. to 0·1 of the amount administered, about 20% being excreted in urine and fæces and 70% degraded. After about 130 hr. (II) contain no more (I). In a goat, (I) orally administered became regularly distributed throughout the whole organism within 2 hr. W. McC.

Pilocarpine and gastric anacidity in monkeys. J. H. Ferguson, J. McGavran, and E. R. B. Smith (J. Physiol., 1934, **82**, 1—10).—Pilocarpine on injection into monkeys produces complete disappearance of free acid and a fall in total acidity of the gastric contents, without affecting total Cl′. R. N. C.

Effect of morphine on secretory processes of the intestinal tract. M. M. Gorbunova-Nikolaeva (Arch. Sci. Biol. U.S.S.R., 1933, **33**, 509—513). —Morphine abolished the stimulatory effects of Hg_2Cl_2 and HCl. Ch. Abs. (*p*)

Physiological action of *l*- and *d*-derivatives of morphine alkaloids. T. Takebe (Kitasato Arch. Exp. Med., 1934, **11**, 48—63).—The action of various morphine derivatives depended on their configuration. Ch. Abs. (*p*)

Relation between liver-glycogen and liver function. T. Ikushima (Japan. J. Gastroenterol., 1934, **6**, 349—356).—Rabbit liver-glycogen (I) is reduced by strychnine, by phloridzin, or by hunger. Lowered (I) is probably unfavourable to excretion of dyes. Ch. Abs. (*p*)

Bile acids and carbohydrate metabolism. XXIX. Influence of cholic acid and spleen on the sugar excretion threshold. C. Tateishi (J. Biochem. Japan, 1934, **19**, 409—423).—Subcutaneous or oral administration of Na cholate to rabbits lowers the sugar excretion threshold to an extent $\propto$ the dose. Splenectomy has a similar effect, subsequent administration of spleen extract or Na cholate causing a return to normal vals. F. O. H.

Bile acids and carbohydrate metabolism. XXX. Influence of bile acids on glycogenesis from liver-fatty acids. I. Okii. **XXXI. Liver-glycogenesis on administration of pituitary extracts and cholic acid.** K. Ohashi (J. Biochem. Japan,. 1934, **20**, 37—42, 59—63).—XXX. Liver-glycogenesis (I) in rabbits due to oral administration of stearic, palmitic, or oleic acid is enhanced by simultaneous administration of Na cholate (II).

XXXI. (I) due to intravenous injection of glucose is enhanced by subcutaneous injection of pituitrin and, to a greater extent, by that of pituitrin+(II). F. O. H.

Influence of bile acids on the digestion of nucleins. II. Hydrogen-ion and phosphate concentrations of intestinal juice. III. Sodium, potassium, calcium, and magnesium levels of intestinal juice. T. Kuramoto (J. Biochem. Japan, 1934, **19**, 425—436, 437—448; cf. A., 1932, 1287).—I. In dogs with duodenal fistulæ, parenteral or, more especially, oral administration of Na cholate (I) increases the vol., sp. gr., p_H, and total and inorg. PO_4 levels of the intestinal secretion.

III. (I) increases the $Na^{\cdot}$, $K^{\cdot}$, and $Mg^{\cdot\cdot}$ levels of the intestinal juice; that of $Ca^{\cdot\cdot}$ is lowered. The action of (I) on the secretion of Na, K, Mg, and Ca into the intestine occurs after their absorption. The bearing of the data on nuclein catabolism is discussed. F. O. H.

Influence of bile acids on urinary and gastric acidity. I. Urinary excretion of sodium chloride, sodium, and potassium. T. Hasegawa (J. Biochem. Japan, 1934, **19**, 403—407).—Intravenous injection of Na cholate into dogs diminishes the urinary excretion of NaCl and $K^{\cdot}$ and increases that of $Na^{\cdot}$. F. O. H.

Influence of bile acids on the synthesis of phenylsulphuric acid in the animal organism. I. Okii (J. Biochem. Japan, 1934, **20**, 31—35).—Subcutaneous injection of PhOH into rabbits increases the urinary excretion of ethereal SO_4, an effect enhanced by subcutaneous or oral administration of Na cholate. Hence bile acids increase the detoxifying action of the liver by increasing the glycogenesis. F. O. H.

Pharmacology of tannic acid. I. Coagulant action on proteins of egg-albumin. U. Sammartino (Arch. Farm. sperim., 1934, **58**, 131—141).—The proteins are pptd. fractionally. Viscosimetry is recommended for demonstrating the physico-chemical modifications preceding and following the pptn. of natural proteins by drugs. R. N. C.

Significance of phenol–indole metabolism. VI. Latent phenol–indole intoxication and adrenal hypertrophy. M. Biebl (Z. ges. exp. Med., 1933, **91**, 622—637; Chem. Zentr., 1934, i, 2941).—Rabbits fed for long periods with doses of PhOH or cresol developed a latent intoxication which was often followed by hypertrophy of the adrenal cortex, suggesting that this tissue acts as a detoxicator of phenol and indole derivatives. R. N. C.

Action of dinitro-compounds on sea-urchin eggs. G. H. A. Clowes and M. E. Krahl (Science, 1934, **80**, 384—385).—At 21°, optimum concns. of 4 : 6-dinitro-*o*-cresol stimulate O_2 consumption by 400% in fertilised, and by 600% in unfertilised, eggs of *Arbacia punctulata*. Cell division (I) is simultaneously suppressed. KCN antagonises the stimulation of respiration (II), but supplements suppression of (I). The NO_2-substituted mol. is responsible for suppression of (I), and the optimum concn. for (II) is a crit. concn. for (I). In the case of NO_2-compounds (I) and (II) decrease with a decrease in ability to penetrate the cell. L. S. T.

Pharmacodynamic action of nitrophenols. An agent accelerating cell oxidation : 2 : 4-dinitrophenol (Thermol). I. General effect of 2 : 4-dinitrophenol poisoning. II. Effects of 2 : 4-dinitrophenol poisoning on the principal processes of nutrition. Effect on carbohydrate status. III. The non-lethal dose, chronic poisoning and tolerance. H. Magne, A. Mayer, and L. Plantefol. **IV. Analytical data of dinitrophenol and derivatives. Detection of these substances in urine, organs, and blood.** M. Guerbet. **V. Presence of dinitrophenol and derivatives in organs and body fluids during poisoning. Elimination in urine.** M. Guerbet and A. Mayer. **VI. Glycuronic acid content of urine after injection of 2 : 4-dinitrophenol.** J. Georgescu. **VII. Action of 2 : 4-dinitrophenol on cell respiration and plant tissues.** L. Plantefol. **VIII. Pharmacological action of various nitrophenols. Comparison of 2 : 4-nitrophenol with other nitrophenols.** H. Magne, A. Mayer, and L. Plantefol. **IX. Action of nitrophenols on hæmoglobin.** A. Mayer and F. Vles (Ann. Physiol. Physicochim. Biol., 1932, **8**, 1—50, 51—69, 70—91, 92—116, 117—121, 122—126, 127—156, 157—175, 176—194; Chem. Zentr., 1934, i, 2614—2615).—I. In all conditions examined poisoning was accompanied by rise in temp. and a marked increase in O_2 consumption.

II. Glycogen in liver and muscle is increased and changes in N elimination indicate protein decomp.

III. Solubility data, reactions, and analysis of 2:4-dinitro- (I), 4-nitro-2-amino- (II), 2-nitro-4-amino- (III), 2 : 4-diamino-phenol, picric (IV) and picramic acid (V) are given.

V. (I) and (IV) are reduced within the organism. Products include (II), (III), and (V) probably combined with glycuronic acid (VI) or as nitro-uramidophenols.

VI. Urinary (VI) increases.

VII. (I) is more toxic to *Aspergillus niger* than are tri- or mono-nitrophenols. Toxicity of the latter is in the order *o*-<*m*-<*p*-.

VIII. Toxicity to higher animals is in the order *p*->*m*->*o*-nitrophenol and among dinitrophenols, 2 : 4-, 2 : 5-, and 2 : 6->3 : 5-, 3 : 4-, and 3 : 2-.

IX. Effects of mono-, di-, and amino-nitrophenols are compared. A. G. P.

Effect of histamine on jejunal secretion. A. L. Berndt and I. S. Ravdin (Amer. J. Physiol., 1934, **109**, 587—591).—Injection of histamine diphosphate produced a temporary increase in the rate of secretion of juice from an isolated jejunal loop. There was no apparent effect on the production of enzymes by the loop. R. N. C.

Protein therapy and glycæmia. R. V. Ulloa and C. M. Domingo (Kitasato Arch. Exp. Med., 1934, **11**, 78—86).—Injection of caseinogen caused, in nearly all cases, an immediate hyperglycæmia, followed by hypoglycæmia within 30 min. Ch. Abs. (*p*)

Physiological effect of the active principles of *Solanum tuberosum* on the larvæ of *Leptinotarsa decemlineata*. B. Trouvelot, M. Raucourt, and J. Castets (Compt. rend., 1934, **199**, 684—686).—When the active extract is offered simultaneously with other nutriments, the extent to which each is attacked by the larvæ is a function not only of its concn. and intrinsic activity, but also of the activities of the other nutriments. A. E. O.

Yew poisoning in domestic animals. J. A. Nicholson (Rep. Cambridge Inst. Animal Path., 1932—1933, 169—199).—Taxine (I) contents of fresh female leaves are : *T. baccata* var. *fructu luteo* 0·24, *T. canadensis* 0·12, *T. cuspidata* 0·22, *T. baccata* var. *barroni* (young) 0·29, (old) 0·33%. The prep. of (I) is described, and m.l.d. recorded. Aq. (I) hydrochloride is rendered non-toxic by heating for 1 hr. at 60° or 10 min. at 100°. (I) (1 : 100) does not affect the digestion of fibrin by pepsin. Ch. Abs.

Histological changes in the bone marrow of the dog following amidopyrine administration. D. K. Miller (Science, 1934, **80**, 320).—Oral administration of amidopyrine to dogs exerts a toxic effect on bone marrow, with little or no evidence of the effect in the circulating granular elements of the blood. L. S. T.

Ascaricidal action of sodium santoninate in oral and subcutaneous administrations. R. E. S. Schultz and K. I. Abuladze (Khim. Farm. Prom., 1934, No. 2, 21—26).—Na santoninate is no less efficient than santonin. Ch. Abs. (*p*)

Irritant constituent of anti-leprotic oils. H. Paget, J. W. Trevan, and A. M. P. Attwood (Int. J. Leprosy, 1934, **2**, 149—158).—Fractionation of the acids of sapucainha oil yields chaulmoogric (I), hydnocarpic (II), and palmitic acids, two fractions containing unsaturated and keto-acids, respectively, and a fraction (III) of tarry acids giving Cu salts insol. in $COMe_2$ and Et_2O. (III) is highly irritating, and may be identical with the irritating substance derived from (I) and (II) on exposure to light and air. W. O. K.

Lipæmia caused by absorption of products of intestinal putrefaction of proteins and effects thereon of hormones. I. Influence of thyroid gland. II. Effect of adrenaline. M. Mitani (Folia Endocrinol. Japan, 1932, **8**, 47—48).—I. Administration of tyramine (III), indole, PhOH, NaOBz, or histamine results in increased fat (II) and lipin (I) (notably cholesterol) contents of blood. If thyroid powder is also given, these changes are restricted. In thyroidectomised animals administration of the above increases total fatty acids, but not (I).

II. Injection of adrenaline (IV) causes a temporary increase in (I) and (II). Lipæmia caused by (III) is increased by (IV). Prolonged administration of (IV) reduces blood-(I) and -(II) and also checks (III)-lipæmia. Ch. Abs. (*p*)

Influence of monobromoacetic and hydrocyanic acids on ciliary and vibratory motion. E. Wertheimer (Pflüger's Archiv, 1933, **231**, 155—168).—$CH_2Br\cdot CO_2H$ (I) inhibits the motion of muscle, heart-auricle, -ventricle, vibratory epithelium of tracheal mucosa, and also the isolated spermatozoa (II) of guinea-pigs. Halogen derivatives of homologues of AcOH are without effect. The effect of (I) is inhibited by lactic (III) and pyruvic acid (IV), but not by AcCHO (V), dihydroxyacetone (VI), or the Robison (VII) and Neuberg hexose monophosphoric ester (VIII). The motion of (II) is inhibited irreversibly by 0·001*N*-NaCN. *Paramecia* are not affected by (I) or NaCN, or the two together. Glucose in concn. 0·00025% is antagonistic to NaCN in its action on (II), fructose in higher concns., galactose still higher, whilst (III), (IV), (V), (VI), (VII), (VIII), arabinose, and glucosamine are practically without effect. R. N. C.

Physiological and thermal investigations on taste-affectors. S. Michael and G. Limmer (Pflüger's Archiv, 1933, **233**, 645—651).—An apparatus is described which imitates and measures the thermal effects of taste-affectors (I) on the tongue, and can be used to correlate these with their thermal data. The gradation of their temp. effects on the tongue is the same as that of their effects in solution in the apparatus. The temp. effects of all (I) $\propto$ their heats of dissolution in the same vol. of H_2O. R. N. C.

Diffusion rates of anions and urea through tissues. E. J. Conway and F. Kane (Biochem. J., 1934, **28**, 1769—1783).—The diffusion coeff. (I) of SO_4'', Cl', PO_4''', and lactate through frog's sartorius is $6{\cdot}0\pm1{\cdot}5\times10^{-5}$ sq. cm. per min. The vals. for muscle, liver, and kidney for SO_4'' are the same. The ratios of the equilibrium concn. in isolated muscle to the external concn. are 0·30, 0·25, and 0·29 for Cl', SO_4'', and PO_4''', respectively. (I) for urea through muscle or kidney is $1{\cdot}1\times10^{-5}$. Urea in freshly excised kidney, blood, and sartorius is 85, 45, and 41 mg. per 100 g., respectively. H. G. R.

Ion effects on ion permeability of *Fundulus* chorion. M. Sumwalt (Biol. Bull., 1933, **64**, 114—123). Ch. Abs.

Biological significance of certain ions. VII. Production of ammonia in nerve tissue with various stimulations as a general law. V. V. Pravdich-Neminskiĭ (Arch. Sci. Biol. U.S.S.R., 1933, **33**, 121—144).—Changes in NH_3 content following stimulation by electric currents, osmotic effects, chemicals, and temp. are examined. Ch. Abs. (*p*)

Effect of hypertonic solutions on tissue respiration. II. Sodium salts of univalent anions. B. Kisch (Biochem. Z., 1934, **273**, 324—337 ; cf. this vol., 918).—The restriction of respiration of tissues (I) at p_H 7·4 by 0·2*M* solutions of NaF, NaCl, NaBr, NaI, $NaNO_3$, and NaCNS varies in a manner similar to that described for the cations, the effect of NaF being particularly strong. The extent to which (I) are supplied with nutrient material also affects the results. W. McC.

Effect of calcium lack on tissue respiration. B. Kisch (Biochem. Z., 1934, **273**, 338—344).—Lack of Ca causes restriction of respiration in some tissues, but increase in others, and results also vary according to the kind of nourishment supplied. W. McC.

Effect of fluoride on tissue respiration. B. Kisch (Biochem. Z., 1934, **273**, 345—348).—The powerful inhibitory effect of 0·2*N*-NaF on tissue (rat kidney) respiration (I) is counteracted by addition of Ca salts (II) or by removal of NaF even in absence of (II). At least part of the Ca compounds (III) of tissue cannot be pptd. as CaF_2. Very dil. (0·002—0·00143*N*) aq. NaF stimulates (I). (I), which is increased by addition of lactate (IV), is inhibited by NaF despite simultaneous addition of (IV). The action of NaF is partly due to its action on (III) and partly sp. W. McC.

Influence of neutral sodium salt solutions on chemical stimulation. I. Chao (Amer. J. Physiol., 1934, **109**, 550—560).—The relative effectiveness of isotonic solutions of Na salts in sensitising curarised frogs' sartorii to chemical stimulation follows the order of the Hofmeister series for anions. The increased sensitivity is a direct function of the concn. of the salt, the min. concn. necessary to produce a given increase depending on its position in the series. The change of irritability increases rapidly with the duration of immersion in the solution, the rapidity in reaching the max. response depending also on the position of the salt in the series. The effect of any given Na salt is antagonised by HCl and alkaline-earth chlorides, the antagonising effects increasing in the order $SrCl_2 < MgCl_2$, $CaCl_2 < HCl$. The min. concn. of any of the salts required depends also on the position of the Na salt in the series. Skeletal muscle is more susceptible to chemical stimulation at low temp., and the sensitising action of every Na salt except NaCl shows a negative temp. coeff. The stimulating solution (0·005*N*-KCl in isotonic NaCl solution) exerts a double stimulation—a primary stimulation followed by inhibition due to $K^{\cdot}$, and a secondary stimulation due to exchange of anions. R. N. C.

Cold stimulation and influence of neutral sodium salts on cold stimulation. I. Chao (Amer. J. Physiol., 1934, **109**, 561—568).—Frogs' muscles sensitised in isotonic solutions of Na salts are stimulated by sudden exposure to lower temp. The contraction depends on the fall in temp., the initial temp., the concn. of the Na salt, and the duration of immersion in the sensitising solution. The relative effectiveness of Na salts on cold stimulation increases in the order of the Hofmeister series. $CaCl_2$ antagonises their action, but produces contraction if used as the cold solution. R. N. C.

Physiological effects of high altitudes. K. M. Buikov and E. E. Martinson (Arch. Sci. Biol. U.S.S.R., 1933, **33**, 147—187).—Hyperventilation lowers the CO_2 tension and alkali reserve in the blood, and is followed by an increase of urinary Cl', and, to a smaller extent, of bases. The org. acids excreted are unchanged. Ch. Abs.

Action of poisonous gases on the liver and kidney function. M. Yagata (Japan. J. Gastro-enterol., 1934, **6**, 280—314).—Excretion through kidneys (I) and liver (II) of rabbits of phenolsulphonephthalein, azocochineal, azorubin-S, and eosin-A is decreased by inhalation of CO. HCN and Cl_2 act more strongly on (I) than on (II). $COCl_2$ destroys (I) function in dye excretion. Ch. Abs. (*p*)

Lead poisoning. Detection in the ash of the corpse. H. Jesser (Süddeut. Apoth.-Ztg., 1934, **74**, 65—66; Chem. Zentr., 1934, i, 2628).—The ash is treated with dil. HCl, 30 c.c. of 0·5% aq. $CuSO_4$ are added, and H_2S is passed to ppt. Pb and Cu. Pb is then determined as $PbSO_4$ or by electroanalysis as PbO_2. H. J. E.

Rôle of lead poisoning in the etiology of gastric ulcer. Effect of lead poisoning on the external secretion of the pancreas. S. D. Reiselman (Arch. Sci. Biol. U.S.S.R., 1933, **33**, 221—234).—Administration of $Pb(OAc)_2$ to dogs with a pancreatic fistula disturbed the parallelism of amylase, lipase, and trypsin. Ch. Abs. (*p*).

Effect on the iodine content of the thyroid glands and blood of wethers and ewes when dosed with potassium iodide. M. C. Franklin (Rep. Cambridge Inst. Animal Path., 1931, 134—142).—Weekly administration of KI (40 mg. per day) increased blood-I from 0·0008—0·0040 to 0·0480—0·0800 mg. per 100 c.c.; thyroid-I increased from 0·144—0·224 to 0·212—0·355%. Ch. Abs.

[Physiological] action of alkali iodides. J. J. Westra (Amer. J. Physiol., 1934, **109**, 450—456). R. N. C.

Effect of potassium cyanide poisoning on the respiration of tissues, especially the influence of different hormones on the action of potassium cyanide. I. Effect of insulin, thyroid substance, and adrenaline. II. Effect of genital glands. III. Effect of extract of adrenal cortex and of thyroidectomy. K. Mitzutani (Folia Endocrinol. Japan, 1932, **8**, 33—3, 636—37, 42—43).—Injection of KCN in rats increased the O_2 consumption of heart muscle and decreased this in liver (I), kidney, and skeletal muscle, thyroid (II), and spleen (III). The respiratory disturbance was reduced by simultaneous injection of insulin or of extracts of adrenal cortex [except in (II)] or corpus luteum and was increased by thyroidectomy [except in (III)] and by simultaneous injection of adrenaline or of extracts of testicles or of thyroid [except in (I)]. Ch. Abs. (*p*).

Effect of injection of potassium cyanide on the oxygen dissociation curve of blood, especially with respect to the effect of the cyanide on the activity of various hormones. I. Effect of injection of small doses of insulin and of insulin and glucose. II. In relation to the thyroid gland. III. Effect of genital glands on the action of potassium cyanide. IV. Effect of adrenal cortex and adrenaline on the action of potassium cyanide. V. Effect of castration. VI. Effect of extirpation of spleen. T. Fukui (Folio Endocrinol. Japan, 1933, **8**, 94—96).—I. The lowering of the O_2-dissociation curve (*D*) following injection of aq. KCN is checked by previous injection of glucose and still more by insulin.

II, III. Large doses of thyroid gland or of extracts of genital glands increased, and smaller doses decreased, the fall in *D* following KCN injection.

IV. Single administrations of extract of adrenal cortex with aq. KCN reduced the decline in *D* produced by the latter. Repeated injection or oral administration had the reverse effect. The action of adrenaline was similar.

V. The action of KCN is increased.

VI. The decline in *D* is $<$ normal. CH. ABS. (*p*)

Methæmoglobin and methylene-blue as cyanide antagonists. O. M. SOLANDT, D. V. SOLANDT, E. ROSS, and R. W. GERARD (Proc. Soc. Exp. Biol. Med., 1934, **31**, 539—541).—For *Venus mercenaria* methylene-blue acts as substitute for a cyanide-poisoned respiratory catalyst. Addition of sufficient methæmoglobin reverses CN′ inhibition. CH. ABS.

Mechanism of the antidotal action of methylene-blue in cyanide poisoning. W. B. WENDEL (Science, 1934, **80**, 381—382).—Mainly critical (cf. this vol., 912). It is probable that the binding of cyanide by methæmoglobin accounts for most of the action of the dye. L. S. T.

Pharmacology of the rare earths. I. Anti-emetic effect. II. Hæmolytic action and simultaneous protective action of some members of the group. III. Preparation of rare-earth calcium gluconates. P. M. NICCOLINI (Boll. Soc. ital. Biol. sperim., 1931, **6**, 202—204, 204—206; 1932, **7**, 14—17).—I. Subcutaneous injection of $SmCl_3$ in the dog produced protection against the emetic action of *apo*morphine. Oral administration of $SmCl_3$ retarded the vomiting and rendered it incomplete, but did not prevent it. Injection of $Nd_2(SO_4)_3$ also retarded vomiting.

II. Red corpuscles were suspended for variable periods in isotonic solutions of $PrCl_3$, $NdCl_3$, and $SmCl_3$, and then transferred to solutions of concns. 0·1—0·9%. Partial hæmolysis occurred in all solutions, but it was not complete even in distilled H_2O.

III. Nd and Sm form double gluconates with Ca, which are prepared by treating a solution containing 3·1738% Ba gluconate and 0·742% Ca gluconate with a saturated solution of $Nd_2(SO_4)_3$ and $Sm_2(SO_4)_3$, respectively, until the Ba is pptd. The resultant solutions contain 2% of the rare-earth gluconate and 1·53% of Ca gluconate, and have p_H and mol. concns. similar to those of plasma. The presence of Ca has no effect on the physiological action. R. N. C.

Chemical changes accompanying the re-absorption of irradiated tissue. J. LOISELEUR (Compt. rend., 1934, **199**, 686—688).—During the reabsorption of irradiated thymus (I), PO_4''' is liberated (from tissue-nucleins) and the Cl′ content of the cellular residues from (I) increases. In the blood, the akaline reserve and p_H both increase, and the urea content of erythrocytes diminishes while their Cl′ content increases. The PO_4''' and Cl′ contents of the urine show a considerable increase and decrease, respectively. A. E. O.

Ultra-violet light and blood-iodine. Bioclimatology. C. BENNHOLDT-THOMSEN and M. WELLMANN (Klin. Woch., 1934, **13**, 800—803).—One group of male white rats, kept in complete darkness for 4 months on a diet of bread and skim milk, was irradiated with a quartz lamp for 15 min. and another group was given 0·05 ml. of vigantol daily. The thyroids of untreated rats contained less colloid and were more active than those of the treated groups and the average I content was 211×10^{-6} g. per 100 mg. of dry substance as compared with 167 for the vigantol and 112 for the irradiated rats. Blood-I varied inversely with thyroid-I, the vals. being 40·5, 31·0, and $25{\cdot}2\times10^{-6}$ g. per 100 ml. NUTR. ABS. (*b*)

Concentration of eosin and the photodynamic effect on tentacles of a terebellid worm. J. H. WELSH (Biol. Bull., 1934, **66**, 346—350).—Stimulation of tentacles of *Terebella magnifica* in sea-H_2O by light was increased by the presence of eosin. The survival period was shortened. CH. ABS. (*p*)

Influence of α-, β-, and γ-rays of radium on the aërobic respiration of animal organisms. J. STOKLASA (Strahlenther., 43, 685—700; Chem. Zentr., 1934, i, 2305).—The intensity of respiration of both fish and guinea-pigs is raised considerably by α-rays (I), slightly by γ-rays (II); it is lowered by β-rays (III) and (II) together, as is also that of plants. (II) lower CO_2-production in plants, but raise it in animals. (I), (II), and (III) over long periods depress anaërobic respiration and lactic acid increases in the lungs, and inhibit the other respiratory enzymes. R. N. C.

Reversible dehydrogenase systems. III. Carrier-linked reactions between isolated dehydrogenases. D. E. GREEN, L. H. STICKLAND, and H. L. A. TARR (Biochem. J., 1934, **28**, 1812—1824).—Purified dehydrogenases isolated from cells together with the appropriate substrate (*e.g.*, formic dehydrogenase+formate) do not react with positive enzyme systems (I) (*e.g.*, nitratase+nitrate) except in the presence of an added indicator (II) of suitable potential. (II) functions even at dilutions at which its colour cannot be detected, is continuously reduced by the negative and re-oxidised by the positive (I), and is most efficient as a catalyst in (I) in which it is reduced and re-oxidised at comparable rates. The reaction between formate and nitrate, linked by Nile-blue, proceeds linearly. An acidic (II), being reduced much more slowly than a basic (II), is a less efficient H carrier. The kinetics of such linked reactions is discussed. None of the known natural hydrogen carriers, *e.g.*, glutathione, ascorbic acid, cytochrome, lactoflavin, with the single exception of pyocyanine, is effective as a link in any of the (I) studied, and attempts to extract natural carriers from cells failed. Considerations of potential show that intact cells of *B. coli* must contain at least two such carriers, since they catalyse the reaction succinate–nitrate as well as H_2–pyruvate. A. E. O.

Biological reduction. V. Specificity of lactic acid dehydrogenase. I. YAMAMOTO (J. Biochem. Japan, 1934, **20**, 23—30).—The lactic acid (I) dehydrogenase system of washed pig's heart muscle and co-enzyme (A., 1932, 537) rapidly oxidises (dehydrogenates) α-OH-acids, *e.g.*, malic (II), tartaric (III), hydroxyglutaric, fumaric (IV), maleic (V), citric, etc. With (I), the *d*- but not the *l*-isomeride is oxidised, the reverse being true for (III); both forms of (II) are oxidised. (IV) and (V) are equally good H_2-donators, the presence of co-enzyme being dispensable only with the latter. Et lactate is unaffected. F. O. H.

Cozymase and the dehydrogenating enzyme system in milk. B. Andersson (Arkiv Kemi, Min., Geol., 1934, **11**, A, No. 17, 9 pp.).—Cozymase (I) does not promote the dehydrogenation of xanthine, and it inhibits the dehydrogenation of MeCHO. Decomp. products of (I), such as adenyl pyrophosphate, muscle-adenylic acid, and adenosine, do not act as inhibitors. Heat and alkali [which deactivate the promoting power of (I) for fermentation] increase its inhibiting power for dehydrogenation. R. P. B.

Relation of iron and copper to cytochrome and oxidase content of animal tissues. E. Cohen and C. A. Elvehjem (J. Biol. Chem., 1934, **107**, 97—105).—Cytochrome (I) is determined spectroscopically after reduction of the tissue with $NaHSO_3$; hæmoglobin (II) is converted into methæmoglobin by treatment with $K_3Fe(CN)_6$ after poisoning the oxidase (III) with KCN. CO or KCN intensifies the band of the *A* component (IV) of (I). The heart, brain, and liver of rats contained all four bands of (I), whilst in the medulla of the adrenals the *C* component was in high concn. and *A* and *B* were absent. (IV) is absent from the hearts of severely anæmic rats (V). (V), fed with Fe and Cu for 6 weeks, have normal (I) spectra. In (V) given Cu alone the (IV)-band appeared earlier, but *B* and *C* were reduced. (III) tests by the "Nadi" reagent (Keilin, A., 1929, 470) were feeble in the livers of rats fed on milk alone or milk supplemented with Fe. With Cu and Cu+Fe good (III) tests were obtained. The (III) test is independent of the (II) response, but directly dependent on the level of Cu intake; a close relationship exists between (III) and (IV). A very active reducing system is present in the livers of (V) fed on milk alone or milk and Fe. H. D.

Spectroscopic examination of cytochrome preparations. Absorption bands in the red. E. J. Bigwood, J. Thomas, and D. Wolfers (Compt. rend. Soc. Biol., 1934, **117**, 220—222).—The two absorption bands, given by yeast cytochrome (I) preps. in alkaline solution, and situated at 675 and 640—645 mμ, are unaffected by oxidation and reduction of (I). The red fluorescence of (I) preps. is not due to a free porphyrin, either orginally present in the yeast, or formed during the concn. of (I). A. L.

Oxidation of cytochrome-*c*. E. J. Bigwood, J. Thomas, and D. Wolfers (Compt. rend. Soc. Biol., 1934, **117**, 222—224).—KCN has no action on the rate of reoxidation by O_2 of aq. solutions of cytochrome reduced by evacuation, although the presence of indophenol-oxidase increases the rate. A. L.

Distribution of peroxidase in animal tissues. G. Bancroft and K. A. C. Elliott (Biochem. J., 1934, **28**, 1911—1919).—Neither alkaline phosphate nor 50% glycerol solution removes peroxidase (I) completely from tissue, and attempts to remove catalase (II) without affecting (I) failed. The method of Willstätter and Stoll (A., 1918, i, 555) for the determination of (I) was modified so that (I) and (II) could be determined separately. Spleen and lung tissues show true (I)-activity; liver and kidney show slight (I)-activity probably due to hæmoglobin (III) and removable by perfusion; most other tissues contain no (I). Among hæmatin derivatives, only the C_5H_5N- and nicotine-hæmochromogen have (I)-activities > those of (III) derivatives. A. E. O.

Catalase determination in fæces, urine, and gastric juice. J. Kretz and A. F. Pellegrini (Wien. klin. Woch., 1934, **47**, 388—391; Chem. Zentr., 1934, i, 3093).—The catalase reaction (I) does not give the same indications as the guaiacum or the benzidine reaction. The latter is invariably positive where blood-pigment or Fe-containing derivatives occur (cooked meat, absorbed blood, etc.) in which cases (I) is negative. A. G. P.

Influence of reductone and thiol compounds on catalase. H. von Euler and H. Larsson (Arkiv Kemi, Min., Geol., 1934, **11**, A, No. 13, 7 pp.).—Glutathione increases the reaction coeff. of barley catalase (I)–H_2O_2 systems, probably due to combination with the small amount of destructive metals in the enzyme prep. Ascorbic acid and reductone (A., 1933, 937) destroy (I), whilst cysteine activates or protects (I) from inactivation. Liver-(I) resembles barley-(I). F. O. H.

Immunological action of tyrosinase from mealworms. W. L. Dulière and M. C. Adant (Biochem. J., 1934, **28**, 1659—1664).—Injection of an active tyrosinase prep. (I) into rabbits yields a serum which inhibits an active (I), but reactivates a feebly active (I). A serum prepared against the latter has no effect on an active (I), but reactivates a feebly active (I). It is suggested that two antibodies are formed, sp. to the enzyme and to an antagonistic factor in (I), respectively. A. E. O.

Inhibition of the "dopa reaction" by vitamin-*C*. H. Schroeder (Klin. Woch., 1934, **13**, 553—554; Chem. Zentr., 1934, i, 3488).—Frozen sections of human skin or that of guinea-pig's ear were treated with a 1% solution of "dopa" (3 : 4-dihydroxyphenylalanine) (I). The development of the brown coloration in the cells was hindered by addition of 1 pt. of ascorbic acid (II) per 100 pts. of (I). Inhibition of oxidation of adrenaline by (II) was also observed. R. N. C.

Carboxylase. II. W. Langenbeck, H. Wrede, and W. Schlockermann (Z. physiol. Chem., 1934, **227**, 263—276; cf. this vol., 110).—Acetoin was determined in presence of MeCHO as Ni dimethylglyoxime by evaporating the oxime–dioxime mixture in presence of $NiSO_4$, since acetaldoxime, which interferes, is readily volatile. The "carboligase quotient," C.Q. (mols. of acetoin/mols. of CO_2), increases with increasing MeCHO and decreases with increasing $AcCO_2H$. The enzymic nature of acyloin formation is confirmed. The identity of carboligase and carboxylase is probable, since in a no. of purified enzyme preps. the two effects could not be separated. J. H. B.

Emulsin in certain marine invertebrates and micro-organisms. D. L. Fox (Biochem. J., 1934, **28**, 1674—1677).—The California mussel (*Mytilus californianus*) (I) excretes an emulsin (II) independently of the presence of micro-organisms (III).

PhMe-preserved extracts of the viscera or cryst. style of (I) also contain (II). Many marine moulds, yeasts, actinomyces, and bacteria produce HCN from nutritive media containing amygdalin (IV), usually after a long period of incubation, but cultures killed by PhMe or $CHCl_3$ are inactive. No (IV) has so far been detected in any marine plant, including (III).
A. E. O.

Action of emulsin. II. S. Veibel (Biochem. J., 1934, 28, 1733—1745).—For *d*- and *l*-α-methylamyl-β-*d*-glucoside, $k_d=1{\cdot}75\times10^{-2}$ and $k_l=0{\cdot}51\times10^{-2}$, respectively. The equilibrium is at approx. 95% hydrolysis. For the γ-methylamyl-β-*d*-glucosides the vals. are $0{\cdot}16\times10^{-2}$, $0{\cdot}15\times10^{-2}$, and 96%, respectively.
C. G. A.

Emulsin. XVI. Fission of β-*d*-xylosides by almond emulsin. B. Helferich and U. Lampert (Ber., 1934, **67**, [*B*], 1667—1669).—o-*Cresol*-β-d-*xyloside*, m.p. 161—162·5° after softening at 159°, $[\alpha]_D^{18}$ −51·7° in H_2O (obtained by the action of NaOMe in MeOH on o-*cresol*-β-d-*xyloside triacetate*, m.p. 116·5° (corr.), $[\alpha]_D^{19}$ −52·3° in $CHCl_3$, prep. from β-*d*-xylose-tetra-acetate, *o*-$C_6H_4Me{\cdot}OH$ and *p*-$C_6H_4Me{\cdot}SO_3H$ at 100°), is readily hydrolysed by emulsin from sweet almonds. The increased ease of fission, in comparison with phenol-β-*d*-xyloside, is the same as for the glucosides within the experimental limits. Parallelism exists between ease of hydrolysis and purity of enzyme prep. in the case of β-*d*-xylosides and β-*d*-glucosides. Hence there is no reason to assume that different enzymes are involved in the respective hydrolyses.
H. W.

Diastase in blood. G. Katsch (Münch. med. Woch., 1934, 81, 505—507; Chem. Zentr., 1934, i, 3092—3093).—Diastatic activity of blood as determined by hydrolysis of glycogen (Otterstein) is either abnormally high or very much depressed in pathological cases.
A. G. P.

Chemistry of enzymes of cereals. I. Starch-liquefying enzyme in rice. II. Starch-liquefying enzyme in polished rice. G. Yamagishi (J. Agric. Chem. Soc. Japan, 1934, **10**, 496—501, 502—509).—I. The enzyme in aq. extracts of unhulled and unpolished rice showed optimum activity at p_H 4·1—4·3 and 36—42°. It was absent from polished rice (*P*).

II. The aq. extract of a mixture of *P* and papain liquefies starch. Zymogen may occur in *P*.
Ch. Abs. (*p*)

Effect of temperature on the digestion of starch by amylase. S. Trautmann and L. Ambard (Ann. Physiol. Physicochim. Biol., 1933, 9, 707—712; Chem. Zentr., 1934, i, 3353).—The increase in the rate of starch hydrolysis with rising temp. is related to changes in the concn. of co-enzyme (I) ($H^{\cdot}$ or Cl'). The increased rate per 10° (Q_{10}) is small (1·02) for the transition of (I), considerable (2·2) for the amylolytic action.
A. G. P.

Influence of temperature on amylases of cold- and warm-blooded animals. L. C. Chesley (Biol. Bull., 1934, **66**, 330—338).—The time of inactivation (I) with rising temp. was in the order fish > terrapin > human amylases. (I) probably results from protein coagulation.
Ch. Abs. (*p*)

Content of amylase in the organs of fed and starving animals. W. Seyfarth (Arch. exp. Path. Pharm., 1934, **176**, 745—750).—Of the liver (I), kidney (II), and heart (III) of normal rats, (II) has the highest content (per g.) of amylase (IV). Starvation diminishes the (IV) content of (II) and (III), whilst an exclusively fat diet does not influence that of (I), (II), or (III). Phloridzin poisoning lowers the (IV) level of (II) and, when the fat content is high, of (I) and (III). (I), (II), and (III) in the same rat have a parallel content (*i.e.*, high or low) of (IV).
F. O. H.

Preparation of highly active yeast invertase. J. G. Lutz and J. M. Nelson (J. Biol. Chem., 1934, **107**, 169—177).—A highly active prep. (time val. 0·102 min.), sol. in saturated $(NH_4)_2SO_4$, was obtained by adsorption on kaolin and $Al(OH)_3$.
H. G. R.

Determination of the activity of commercial invertase. C. E. Prélat (Anal. Asoc. Quím. Argentina, 1934, 22, 73—75).—The method of Gore is recommended.
R. N. C.

Rôle of active acidity of the medium in the enzymic inversion of sucrose. S. M. Kobrin (J. Gen. Chem. Russ., 1934, 4, 477—486).—The $[H^{\cdot}]$ remains const. during the enzymic hydrolysis of sucrose, pointing either to non-participation of $H^{\cdot}$ in the enzyme–substrate complex, or to the very low concn. of the latter.
R. T.

Effect of very high pressures on enzymes. M. Macheboeuf, J. Basset, and G. Levy (Ann. Physiol. Physicochim. Biol., 1933, 9, 713—722; Chem. Zentr., 1934, i, 3352).—Pressures of 5000—6000 atm. did not affect enzymic activity. Partial inhibition occurred in some cases with 9000 atm., the effect being influenced by external conditions (*e.g.*, p_H), but not by the rate at which pressure was raised or lowered. Pressure-resistance of enzymes is > that of ultravirus or bacteriophage, but < that of bacterial spores.
A. G. P.

Osmotic pressure and rate of enzymic reactions. S. Mardaschev and M. Mogilevski (Biochem. Z., 1934, **273**, 430—434).—Rate of fermentation (arginine by arginase, sucrose by invertase) markedly although not proportionally decreases as the (potential) osmotic pressure of the solution is increased by increasing the concn. of electrolytes (KCl, KNO_3, NaCl, $NaNO_3$) or non-electrolytes (urea). There may also be sp. ionic effects.
W. McC.

Fate of enzymes in the digestive tract. W. Heupke and H. Wirtz (Klin. Woch., 1933, **12**, 1866—1867; Chem. Zentr., 1934, i, 2297).—Myrosin, emulsin, urease, and catalase remain active in the large intestine, but zymase and peroxidase are destroyed.
A. G. P.

Activation of enzymes. II. Papain activity as influenced by oxidation–reduction and by the action of metal compounds. L. Hellerman and M. E. Perkins (J. Biol. Chem., 1934, **107**, 241—255).—Papain (I) is reversibly inactivated by catalysed ($Cu^{\cdot\cdot}$ or $Fe^{\cdot\cdot}$) oxygenation, I, benzoquinone, and $Fe(CN)_6'''$, activity being restored by many reducing substances. Cu_2O and mercurials of the type RHgX (which give mercaptides) completely inactivate (I), elimination of the metal restoring activity, suggesting that this depends on the presence of free $\cdot SH$ in (I). C. G. A.

Inhibitors of milk-curdling enzymes. H. Tauber (J. Biol. Chem., 1934, **107**, 161—168).—Urease inhibits the milk-coagulating power of pepsin (I) and trypsin (II), but not the protease activity of (II). Rennin (III) and (I) are distinct entities, and there is no (III) in the stomach of adult mammals. Gastric proteases of animals differ with the species. H. G. R.

Pepsin and rennin activity of preparations from dried stomach substance from the cardia, fundus, and pyloric regions of pig's stomach. E. Meulengracht and E. Schiødt (Ugeskr. Laeger, 1934, **96**, 187—190; Acta Med. Scand., 1934, **82**, 375—383).—Pepsin and rennin activity is greatest in preps. from the fundus. The location of the anti-anæmic substance is different from that of pepsin. These substances are therefore physiologically and anatomically separated in the mucous membrane of the stomach. Nutr. Abs. (*m*)

Biochemical micro-methods. IV. Nephelometric determination of pepsin. B. J. Krijgsman (Z. physiol. Chem., 1934, **227**, 251—262; cf. this vol., 337).—Nephelometric determination of the residual (protein) substrate is recommended for following enzymic hydrolysis and is applied to the fission of serum-proteins, edestin, and caseinogen by pepsin. J. H. B.

Rate of liberation of amino-acids and ammonia in tryptic hydrolysis. T. Tomiyama and S. Shigematsu (J. Biochem. Japan, 1934, **20**, 131—140).—The rates of liberation of NH_2- and NH_3-N on digestion of the proteins of sardine muscle (I), silk-worm pupæ, and soya bean (II) by trypsin+enterokinase do not conform with a unimol. reaction: that of NH_2-N (as % of total N or NH_2-N) is greatest with (I), whilst that of NH_3-N (as % of total N but not NH_2-N) is greatest with (II). F. O. H.

Activation of pancreatic juice by acidification. M. Lisbonne and A. Frank (Ann. Physiol. Physicochim. Biol., 1933, **9**, 723—732; Chem. Zentr., 1934, i, 3354).—Liberation of trypsin from pancreatic juice by small amounts of acid is confirmed. The action is slower than that of kinase, max. activity being attained in 24—30 hr. at room temp., more quickly at 42—45°, but ceasing at 60°. A. G. P.

Micro-methods for the detection of proteases and amylases. G. E. Pickford and F. Dorris (Science, 1934, **80**, 317—319).—For detecting proteases in biological liquids one drop of buffered fluid or extract is placed on the gelatin surface of an unexposed photographic plate which has been cleared with aq. $Na_2S_2O_3$. After about 2 hr. at $\ngtr 20°$, the slide is fixed in aq. CH_2O, washed, and stained in either acid fuchsin or Delafield's hæmatoxylin. A clear spot appears when digestion is complete, a clear ring when it is only partly complete. For amylases, a thin starch film on glass replaces the gelatin and digestion is allowed to proceed at 39°. When this is complete the plate is rinsed with dil. I, and a clear spot is obtained. With partial digestion the spot is only partly cleared and is often reddish. The method can detect 1 in $0{\cdot}5\times 10^6$ of Merck's pancreatin. Pyrex glass, but not soft glass or quartz, inhibits trypsin and amylase. L. S. T.

Proteases of the frog. S. R. Mardaschev (Biochem. Z., 1934, **273**, 321—323).—As regards the effect on it of temp. and $[H^{\cdot}]$ the tryptase (I) of frog pancreas does not differ from (I) of warm-blooded animals. Frog liver contains a peptidase exhibiting max. activity at p_H 8·1 and a catheptic protease (II) most active at p_H 4. (II) is activated by H_2S. W. McC.

Proteolytic enzymes of seeds. A. V. Blagovestschenski and R. M. Melamed (Biochem. Z., 1934, **273**, 435—445).—The proteolytic enzymes (I) (cathepsin, catheptic polypeptidase, dipeptidase) of seeds from different species of plants exhibit specificity as regards their activity. Sometimes (I) from a particular seed act more powerfully on the protein of the same seed than on that of any other seed. W. McC.

Stability of the dipeptidase in extracts of the muscles of the serpent, *Natrix annularis* (Hallowell). M. Sato (Mem. Fac. Sci. Agric. Taihoku, 9, No. 1).—The decomp. of leucyl- and of alanylglycine by the extracts are probably independent processes, effected by two different enzymes. The stability of extracts made with aq. glycerol (I) increases with their (I) content. Ch. Abs. (*p*)

Specificity of dipeptidases. Enzymic hydrolysis of peptides from aspartic and glutamic acids. W. Grassmann and F. Schneider (Biochem. Z., 1934, **273**, 452—462).—Glycine Et ester (I) reacts with the α-CH_2Ph ester of carbobenzyloxyaspartyl chloride (cf. Bergmann *et al.*, A., 1933, 1149) to give the *compound* $CH_2Ph\cdot O\cdot CO\cdot CH(NH\cdot CO_2CH_2Ph)\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2Et$, m.p. 101°. The corresponding *acid*, m.p. 144—145°, yields β-*glycylasparagine*, $CO_2H\cdot CH(NH_2)\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2H$ (II), m.p. 153° $[\alpha]_D^{22}+7{\cdot}2°$ in H_2O+1 mol. of HCl, on reduction (H_2–Pd-black). Carbobenzyloxy-*l*-aspartic anhydride with (I) in $CHCl_3$ gives the *compound* $CO_2H\cdot CH(NH\cdot CO_2CH_2Ph)\cdot CH_2\cdot CO\cdot NH\cdot CH_2\cdot CO_2Et$, m.p. 113°; the corresponding *acid*, m.p. 160°, is converted (H_2–Pd-black) into α-*glycyl*-l-*asparagine* (III). Carbobenzyloxy-*l*-aspartic acid with PCl_5 yields the *dichloride*, m.p. 46°, which gives the $(CH_2Ph)_2$ ester (IV), m.p. 164°, of the corresponding diglycyl derivative on treatment with glycine CH_2Ph ester. Hydrolysis of (IV) gives *diglycyl*-l-*asparagine* (V). Carbobenzyloxy-*l*-glutamic anhydride and (I) give the *Et* α-*glycylcarbobenzyloxy*-l-*glutamate*, m.p. 122°; the corresponding *acid*, m.p. 143°, with H_2–Pd-black yields α-*glycyl*-l-*glutamic acid* (VI), m.p. 180°, $[\alpha]_D^{22}$ $+80{\cdot}3°$ in H_2O. (III), (V), and (VI) but not (II) are hydrolysed by dipeptidase from yeast and by extracts of intestine or kidney. Aminopolypeptidase does not attack (II), (III), (V), or (VI). Dipeptidases hydrolyse the $CO\cdot NH$ linkings (VII) of appropriate natural NH_2-acids only when a free α-NH_2 and a free CO_2H are in the neighbourhood of (VII). W. McC.

Micro-titration in enzymic peptide and protamine synthesis. H. von Euler and B. Sjöman (Arkiv Kemi, Min., Geol., 1934, **11**, **A**, No. 16, 8 pp.).—Using a micro-technique (A., 1931, 1455), peptide synthesis by pig's intestinal mucosa preps. was detected with *d*-alanine (I)+glycine, (I)+*l*-histidine (II). (I)+*d*-arginine, and with (I) or (II) alone in 0·5*M* solution (containing glycerol) at p_H 7·5—8·0; with periods of up to 6 days, approx. 20% synthesis (as dipeptide) occurs. On dilution almost total hydrolysis of the formed peptide occurs. F. O. H.

Influence of carotene on the guanase content of rat's spleen. I. Rydh-Ehrensvärd and G. Schmidt (Z. physiol. Chem., 1934, **227**, 177—180).—Absence of vitamin-*A* from the diet produces a decrease in guanase (I) content in rat's spleen and a change in the time–action curve, the effects being nullified by carotene administration. In the spleen of rats with Jensen sarcoma, the (I) activity is considerably > in normal animals. J. H. B.

Specificity of arginase. H. O. Calvery and W. D. Block (J. Biol. Chem., 1934, **107**, 155—160).—The CO_2H of arginine (I) is probably a point of attachment of arginase (II) before hydrolysis, since (II) will hydrolyse argininic acid (III), but not the Me ester of (I) or the Et ester of (III). (I) and (III) probably exist in solution as stable ring structures. H. G. R.

Activators of arginase. F. Leuthardt and F. Koller (Helv. Chim. Acta, 1934, **17**, 1030—1047).—At p_H 9·2 and 38° the action of arginase (I) does not conform to the unimol. law and is never complete owing to inactivation of the enzyme, which occurs more rapidly with extracts of dry materials than with those of fresh organs. Inactivation is partly due to air, and in this respect the sensitiveness of liver-arginase of different animals differs widely. The activation of (I) by cysteine (II) is due in part to the absorption of mol. O_2 by the latter, which thus creates anaërobic conditions, but other factors appear also to be operative. The degree of activation of (I) by (II) in the organs of different animals was parallel with their sensitiveness to O_2. Ascorbic acid (III) absorbs O_2 more rapidly than does (II), but is not a more powerful (frequently less powerful) activator, since it is too rapidly consumed; its action is not generally enhanced by the presence of Cu. The action of (II) is increased by $Fe^{\cdot\cdot}$; this is not necessarily due to a (II)–$Fe^{\cdot\cdot}$ complex, since (II) shields $Fe^{\cdot\cdot}$ from oxidation and reduces $Fe^{\cdot\cdot\cdot}$ and also retains $Fe(OH)_2$ in solution. $Ca^{\cdot\cdot}$ activates fresh rat liver. Sections of tissue do not give reproducible results, probably owing to variations in thickness. Since activation is produced by such widely-differing substances as (II), (III), and N_2H_4,H_2O, it is more probably due to the reducing power of the compounds, independent of their mol. structure, rather than to a sp. chemical action. H. W.

Optimum buffer p_H for hydrolysis of urea by urease, and the preparation of stable urease powder. W. W. Kay and M. A. H. Reid (Biochem. J., 1934, **28**, 1798—1801).—An initial p_H of 6·6—7·0 for $\not>$6 mg. of urea is recommended. Urease powder is prepared by granulating a conc. aq. jack bean extract with $COMe_2$. H. G. R.

Reaction between crystalline urease and antiurease. J. S. Kirk and J. B. Sumner (J. Immunol., 1934, **26**, 495—504).—A definite compound is formed. Ch. Abs. (*p*)

Influence of different cations on the growth of yeast cells. A. Lasnitzki and E. Szörényi (Biochem. J., 1934, **28**, 1678—1683).—Alkali cations, in 0·01*N* concn., favour growth (I) of baker's yeast on a synthetic medium containing glucose, tartaric acid, asparagine, $MgSO_4,7H_2O$, and $(NH_4)_2HPO_4$, their effects agreeing with their positions in the Hofmeister series. Thus $Rb^{\cdot}$ and $K^{\cdot}$ show a large, $Na^{\cdot}$ and $Cs^{\cdot}$ a moderate, and $Li^{\cdot}$ a small (I)-promoting effect. $Mg^{\cdot\cdot}$ (but not $Ca^{\cdot\cdot}$) also exerts a marked (I)-promoting effect in a medium containing $K^{\cdot}$. $MgSO_4$ acts more strongly than $MgCl_2$, but the difference cannot be ascribed to the (I)-promoting action of SO_4''. A. E. O.

Growth of yeast below zero. J. A. Berry (Science, 1934, **80**, 341).—Of the several strains of yeast isolated from fermented cider one in particular is able to increase at −2·2°; it ferments glucose, fructose, and sucrose, but not maltose or lactose. L. S. T.

Influence of shaking on yeast. T. M. Kondrateva (Bull. Acad. Sci. U.R.S.S., 1934, 653—668).—When suspensions of *Saccharomyces cerevisiæ*, Race XII, *Schizosaccharomyces Pombe*, *Nadsonia fulvescens* (I), *Monilia variabilis*, and *Endomyces vernalis* are shaken in a machine, the cell-structure is modified. Vacuolisation becomes more marked, the vacuoles change their form, increase in no., and diminish in size, the homogeneity of the plasma disappears, and the amount of fat present increases; the form and size of the cells remain unchanged. With (I) the glycogen decreases in amount. These changes are accentuated by prolonging the shaking and are reversible, but the most pronounced alterations were transmitted, although only to the first generation of the first culture made. Shaking impairs the multiplication of the cells by budding or scission to an extent increasing with the period of shaking. The course of fermentation and the final products are unaffected. With (I) the sexual process and spore formation are accelerated. T. H. P.

Action of cocaine on yeast. N. N. Stadnitschenko (Bull. Acad. Sci. U.R.S.S., 1934, 669—684).—Cocaine (I) is weakly toxic to yeast, the cells being killed after several hr. in a solution containing $\not<$5% of (I). In concn. of 0·05—0·1%, (I) serves as a nutrient for certain yeasts. With *Saccharomyces cerevisiæ*, spore formation is unaffected. Asporogenous yeasts undergo morphological and physiological changes, giving variants of the saltant type. Cell multiplication is influenced by $\not<$ 0·1% of (I); with $\not>$0·5% it is transitorily increased, such increase being specially marked in media containing 0·2%. The fermentative functions are impaired only by distinctly toxic doses ($\not<$ 3%) of (I). No stimulating effect of (I) on the fermentative activity of *S. cerevisiæ*, Race XII, was detected. The action of (I) yields new strains of *S. cerevisiæ*. T. H. P.

Preparation of a new type of compound from yeast. K. Myrbäck (Svensk Kem. Tidskr., 1934, **46**, 211—219).—The cozymase of yeast (I) consists of adenylic acid (II) united to another component (III) through a P atom. (I) contains only one free acidic OH, but on deactivation by heat another appears, as in (II). (III) probably contains one N, and it has reducing powers like the sugars; the reducing power $\propto$ the enzymic activity of the sample. It was not possible to isolate (III) from the products of hydrolysis of (I), but an acid has been isolated having reducing powers like (III), but containing no N. R. P. B.

Equilibrium between hexosediphosphoric acid and dihydroxyacetonephosphoric acid. III. Fixing the triosephosphoric acid with hydrogen sulphite. Distribution of zymohexase in different cells. O. Meyerhof and K. Lohmann (Biochem. Z., 1934, **273**, 413—418; cf. this vol., 1261).—A procedure for the almost quant. enzymic conversion of Na hexosediphosphate into dihydroxyacetonephosphoric acid (I) [fixed as the $NaHSO_3$ compound (II)] is described. No glyceraldehydephosphoric acid is produced. (II) is converted into the Ba salt of (I). The zymohexase (III) content of muscle (IV) is twenty times that of yeast. Heart, brain, retina, blood-corpuscles, spleen, and carcinoma (mouse) contain smaller amounts, and liver and kidney almost none. (III) from (IV) is much less sensitive to temp. changes than is (III) from other organs. W. McC.

Mannose monophosphate. II. Fermentation of mannose by dried yeast. C. M. Jephcott and R. Robison (Biochem. J., 1934, **28**, 1844—1853; cf. A., 1933, 316).—In the fermentation of glucose (I), fructose (II), and mannose (III) by dried yeast in presence of PO_4''', mannose monophosphate (IV) may in all cases be isolated from the monophosphate fractions, either as the sparingly sol. cryst. *Ba* salt ($+2H_2O$), or, with greater certainty, as the *phenylhydrazine* salt of *mannose monophosphatephenylhydrazone*, m.p. 144—144·5°, which, by the action of PhCHO, yields (IV). The yield of (IV) from (III) is > from (I) and (II) both at 25° and, more especially, at 38°, when (IV) forms the chief part of the total hexose phosphates formed from (III). Reconsideration of the scheme previously put forward (*loc. cit.*) for the initial stage in the fermentation of (I), (II), and (III) is necessary. In aq. solution (IV) exists in two forms, only one of which is rapidly oxidised by (I). A. E. O.

Course of oxygen consumption in aërobic glucose fermentation. Lazzari and G. Scoz (Boll. Soc. ital. Biol. sperim., 7, 247—250; Chem. Zentr., 1934, i, 2438).—In PO_4'''-buffer solutions at p_H 5·6 the O_2 consumption reached a max. after 20 min. and then declined slowly. For 1 mol. of glucose utilised, 6 equivs. of O_2 were consumed in the principal fermentation, and 2 equivs. at the later stage. A. G. P.

Malarial pigment (hæmozoin). I. Action of solvents on hæmozoin, and spectroscopical appearances observed in the solutions. J. A. Sinton and B. N. Ghosh. **II. Reactions of hæmozoin to tests for iron.** B. N. Ghosh and J. A. Sinton (Rec. Malaria Survey India, 1934, 4, 15—42, 43—59).—I. Hæmozoin (I) peptised with NaOH or KOH, and alkaline solutions of hæmatin (II) or of pigment isolated from parasites by papain digestion does not dialyse through parchment. (I) is sol. in $(NH_4)_2S$, AcOH, HCO_2H, and butyric acid; H_2SO_4 affords hæmatoporphyrin. (I) dissolves slowly in NH_2Ph, C_5H_5N, and 4% quinine–$CHCl_3$. The spectra of (I) solutions are identical with those of (II). NH_2Ph solutions of (I) and (II) afford *aniline*-p-*hæmatin.*

II. (I) contains non-ionisable, but not ionisable, Fe. Ch. Abs.

Nitrogen content of *Aspergillus niger* in relation to the salt content of the culture medium. G. Rossi and G. Scandellari (Biochem. Terap. sperim., **19**, 92—98; Chem. Zentr., 1934, i, 559).—Absence of NO_3' or PO_4''' from media has harmful effects. $MgSO_4$ is not essential for growth, but has a favourable influence. High salt concns. are harmful. Small proportions of $MnSO_4$ facilitated N accumulation. A. G. P.

Production of citric acid by *Aspergillus niger*. E. Sotnikov (Compt. rend. Acad. Sci. U.R.S.S., 1934, **3**, 544—547).—Growth of mycelium on four successive changes of medium gave the following approx. yields of citric acid calc. on the sugar consumed: sterile medium in flasks, 70%; unsterile medium in loosely covered dishes, 60%; unsterile medium in open dishes, 20%. L. D. G.

Gluconic fermentation. X. Influence of iron on gluconic fermentation by *Penicillium luteum-purpurogenum*. A. Angeletti and L. Merlo (Annali Chim. Appl., 1934, **24**, 468—472).—On addition of small amounts of Fe (0·01145 g. per litre) as $FeCl_3$, the gluconic fermentation of a nutrient solution containing 20% of glucose is at first retarded, but the yield of gluconic acid obtained in 20 days is increased by about 11·5%. T. H. P.

Alleged stimulation of moulds by paraffin in heavy water. S. L. Meyer (Nature, 1934, **134**, 665).—A reply to criticism (this vol., 1035). L. S. T.

Assimilation of nitrites by micro-organisms. I. Culture solution for moulds containing nitrites as nitrogen source. K. Sakaguchi and W. Y. Chang (J. Agric. Chem. Soc. Japan, 1934, **10**, 459—476).—The optimum $[NO_2']$ in media for growth of various moulds was 0·1—0·25%. Neutral or slightly alkaline media are preferable. The utilisation of NO_2' by moulds is followed by formation of NH_3, but not of NO_3'. Yeasts and bacteria assimilating NO_3' grow easily on NO_2'. Ch. Abs. (*p*)

Energy and wave-length limits of mitogenetic rays. R. Ruyssen (Acta Brevia Neerland. Physiol., 1933, 3, 141—142; Chem. Zentr., 1934, i, 1204).—The effect of radiation on the growth of *Staphylococcus* cultures has been examined. With 2500 Å. a 30—100% increase was observed, 3000 Å. had no action, and at 2600—2900 Å. there was an intermediate effect. H. J. E.

Action of a filterable staphylococcal toxin on kidneys of normal rabbits. R. H. Rigdon, A. L. Joyner, and E. T. Ricketts (Amer. J. Path., 1934, **10**, 425—433).—Animals showing kidney lesions

after injection of the toxin had high blood-N without a corresponding increase in uric acid content.
Ch. Abs. (*p*)

Reversible inactivation of pneumococcal hæmolysin. Effects of oxidation and reduction and of metal compounds. H. Shwachman, L. Hellerman, and B. Cohen (J. Biol. Chem., 1934, **107**, 257—265).—Hæmolysin (I) extracted from type II pneumococci is reversibly inactivated by O_2, I, $Fe(CN)_6'''$, H_2O_2, SeO_2, azochloroamide, Cu_2O, and organomercurials. Reactivation is effected by H_2S, $Na_2S_2O_4$, reduced glutathione, thioglycollic acid, NaCN, cysteine, and ascorbic acid. The effects are analogous to those with urease and papain (A., 1933, 1332; this vol., 1402).
C. G. A.

Serological specificity of bacterial carbohydrates with special reference to type II pneumococcus and a heterophile strain of *B. lepisepticum*. J. H. Dingle (Amer. J. Hyg., 1934, **20**, 148—168).—Sp. carbohydrate materials are isolated from types of various bacteria. Serological reactions are described.
Ch. Abs. (*p*)

Respiration mechanism of pneumococcus. III. M. G. Sevag and L. Maiweg (J. Exp. Med., 1934, **60**, 95—105).—Transformation from a virulent (I) into an avirulent form causes a large but temporary increase in O_2 consumption, followed by a decline to vals. $<$ that of (I).
Ch. Abs. (*p*)

Physical method of deproteinisation. Separation of carbohydrates from egg-proteins and pneumococcus. M. G. Sevag (Biochem. Z., 1934, **273**, 419—429).—The material [egg-white (I), pneumococcus (II)] is repeatedly frozen with liquid air and allowed to thaw, shaken with a mixture of H_2O, $CHCl_3$, and amyl alcohol (III), and centrifuged. Almost all of the protein (IV) is thus pptd. The supernatant liquid which contains the carbohydrate (V) is freed from (IV) by shaking with $CHCl_3$+(III). (I) contains 16% of non-(IV), half of it being sol. in EtOH. Part of (V) from (I) is immunologically active, contains 11·5% N, has $[\alpha]_D^{24}$ −6° (+25° after hydrolysis), and reduces Fehling's solution. It contains no S. Dried virulent (II) yield 5·5% of (V) which contains about 7% N, has $[\alpha]_D^{24}$ +22° (+54° after hydrolysis), contains 8% Ac, and is immunologically active.
W. McC.

Comparison of the combining, antigenic, and toxic properties of chemically altered diphtheria toxoid and toxin. L. Reiner (J. Immunol., 1933, **24**, 213—220).—Conversion of the toxoid into azo-dye by coupling with diazotised arsanilic acid results in loss of antigenic power, but not of combining power (Ramon test), of sp. toxic action, or of ability to give non-sp. reactions. The toxoid dye has a high As : N ratio.
Ch. Abs. (*p*)

Adsorption of diphtheria toxoid by cellulose derivatives and ferric hydroxide gel. L. Reiner (J. Immunol., 1933, **24**, 221—227).—Adsorption of the toxoid by cellulose nitrate (I) is $>$ by the acetate and is favoured by an acid reaction and low temp. Toxoid can be obtained in a purified form by elution of the adsorbate from (I) or $Fe(OH)_3$ gel at p_H 7·6—7·8.
Ch. Abs. (*p*)

Antigenic power of a mixture of diphtheria toxin and vitamin-*C*. E. Harde and M. Philippe (Compt. rend., 1934, **199**, 738—739).—The effect of diphtheria toxin on guinea-pigs was reduced if ascorbic acid (I) was added to it before injection, and to a smaller degree when it was diluted with saline, or when (I) was injected separately into the animals.
R. N. C.

Decomposition of citric acid by *B. aertrycke*. W. F. Bruce (J. Biol. Chem., 1934, **107**, 119—129).—Aërobic cultivation of *B. aertrycke* (I), on a citrate medium, yields HCO_2H, AcOH, succinic acid, and CO_2. The rough form of (I) produces more HCO_2H and AcOH, less succinic acid and CO_2, than the smooth, and small amounts of lactic acid.
H. G. R.

Immunising fractions isolated from *B. aertrycke*. H. Raistrick and W. W. C. Topley (Brit. J. Exp. Path., 1934, **15**, 113—129).—The presence of a phosphatide and a polysaccharide is indicated.
Ch. Abs.

Blood-sugar changes and toxic effects produced in rabbits by certain fractions derived from *B. aertrycke*. M. E. Delafield (Brit. J. Exp. Path., 1934, **15**, 130—137).—Polysaccharide fractions produce hyperglycæmia.
Ch. Abs.

Toxicity for mice of certain fractions isolated from *B. aertrycke*. A. R. Martin (Brit. J. Exp. Path., 1934, **15**, 137—142).—The toxic substance is probably present in the fractions which induce an active antibacterial immunity.
Ch. Abs.

Content of specific antigenic polysaccharide substance in *B. aertrycke*. A. Boivin, L. Mesrobeanu, and I. Mesrobeanu (Compt. rend. Soc. Biol., 1934, **117**, 271—273).—The method of extraction (this vol., 929) of the sp. polysaccharide complex (I) is modified by a preliminary digestion of the bacteria with trypsin before the $CCl_3{\cdot}CO_2H$ extraction. (I) is present to the extent of 10% of the dry wt.
A. L.

Hyperglycæmic action of the specific toxic and antigenic complex isolated from *B. aertrycke*. A. Boivin and L. Mesrobeanu (Compt. rend. Soc. Biol., 1934, **117**, 273—275).—Aq. solutions of the sp. preps. from *B. aertrycke* injected intraperitoneally into rabbits have a considerable hyperglycæmic action.
A. L.

Metabolism of the strict anaërobes (genus *Clostridium*). I. Chemical reactions by which *Cl. sporogenes* obtains its energy. L. H. Stickland (Biochem. J., 1934, **28**, 1746—1759).—Washed suspensions of *Cl. sporogenes* activate H donation by the naturally occurring isomerides of alanine (I), valine, and leucine, and H acceptance by glycine (II), proline, and hydroxyproline. (I) is deaminated in the first stage of the oxidation. Any of these donators will react with any of the acceptors, *e.g.*, (I) will reduce 2 mols. of (II): $NH_2{\cdot}CHMe{\cdot}CO_2H + 2NH_2{\cdot}CH_2{\cdot}CO_2H + 2H_2O \longrightarrow 3AcOH + 3NH_3 + CO_2$. The rates of these reactions are of the same order as those of aërobic oxidations by other bacteria.
C. G. A.

Bacterial anaërobiosis. III. Oxidation–reduction potential of the butyric bacillus in presence of thiol compounds. W. A. Messing (Biochem. J., 1934, **28**, 1894—1900).—SH-compounds

(I) promote the growth (II) of *B. saccharobutylicus*, (II) being initiated prior to, but subsequently being accompanied by, a lowering of the redox potential of the medium (III). (III) containing (I) does not acquire a negative potential in absence of bacteria.
A. E. O.

Occurrence of *B. aërogenes* in sewage and fæces. N. Atkinson (Austral. J. Exp. Biol., 1934, **12**, 141—149).—In crude sewage (I) and sewage effluent (II) *B. aërogenes* (III) was present in considerable quantities and the proportion to the total lactose fermenters was approx. the same for (I) and (II). (III) was commonly found in human fæces (about 5% of the total lactose fermenters). It therefore appears unnecessary to differentiate (III) from *B. coli* in testing H_2O for fæcal pollution. W. O. K.

Nuclease activity of *B. subtilis*. D. A. MacFadyen (J. Biol. Chem., 1934, **107**, 297—308).—*B. subtilis*, *B. mesentericus vulgatus*, and *B. megatherium* rapidly decompose yeast nucleic acid (I), particularly at p_H 6·6, at both low and normal O_2 tensions. The liberated nucleotides (II) are further broken down, mainly to ribose phosphate and nitrogenous bases. UO_2Cl_2 in $CCl_3{\cdot}CO_2H$ ppts. (I) at p_H 1·5—2·0, and (II) at p_H 3·0—7·0. A. E. O.

Innate individuality of the bacteriophagous properties of three bacteriophages isolated from canal-water. P. C. Flu (Proc. K. Akad. Wetensch. Amsterdam, 1934, **37**, 417—423).—Three strains of bacteriophage isolated from Leiden canal-H_2O have been tested over a no. of years on plague (I), Shiga (II), and coli bacteria and it is concluded that each bacteriophage is a substance independent of the microbe undergoing lysis. Under certain conditions each colony can be caused to lose its lysogenic properties for (II), but a rapid recovery occurs by transmission through (I). S. C.

Bacteriophage of *Bacterium megatherium*; origin of the bacteriophage. P. C. Flu (Proc. K. Akad. Wetensch. Amsterdam, 1934, **37**, 423—429).—Non-lysogenic strains of *B. megatherium* can be infected with *B. megatherium* phage and then develop into resistant spore-bearing varieties, in which the phage is preserved after heating for 1 hr. at 80°. The latter is not necessarily a product of the bacterium undergoing lysis. S. C.

Chemical composition of bacteriophage. M. Schlesinger (Biochem. Z., 1934, **273**, 306—311; cf. A., 1933, 1084).—Qual. and quant. (C 42, H 6·4, N 13·2, P 3·7%, and S) examination indicates that bacteriophage consists chiefly of protein. Fat is also present, but probably no polysaccharide. The content of dry matter exceeds 50%. W. McC.

Hydrogen-ion concentration as a factor in the toxicity of amines for *Amœba proteus*. R. B. Howland and A. Bernstein (Biol. Bull., 1934, **66**, 276—285).—In the p_H range examined amine solutions at p_H 7·8 were the most toxic. The order of toxicity of amines was $NH_2Me>NH_2Et>NH_2Bu>NH_2Pr$, and $NH_2Me>NHMe_2>NMe_3$.
Ch. Abs. (*p*)

Protective action of pure proteins in photodynamic phenomena. O. Jirovec and Z. Ziegler (Z. ges. exp. Med., 1933, **90**, 651—660; Chem. Zentr., 1934, i, 1664).—The effect of proteins on the toxicity and the sensitising power of rose-Bengal, erythrosin, eosin, and pyronin has been investigated with *Paramecium aurelia* and *Colpidium colpoda*. The protective action against photodynamic action is in the order serum-albumin > ovalbumin > peptone.
L. S. T.

Biliary antiseptics. R. Ottenberg (J. Infect. Dis., 1933, **53**, 29—44).—Of substances examined, mercurochrome and salyrgan were promising. Flumerin (a Hg–fluorescein derivative) gave best results.
Ch. Abs. (*p*)

Mercuric phenyl nitrate. K. E. Birkhaug (J. Infect. Dis., 1933, **53**, 250—261).—$HgPhNO_3$ produces bacteriostatic effects in biliary, cerebrospinal, genito-urinary, and vascular tracts. Ch. Abs. (*p*)

Mode of action of antiseptics. R. Freund (Biochem. Z., 1934, **273**, 365—380).—Urea and bile (ox) greatly increase the bactericidal efficiency of antiseptics (rivanol). Since adsorbent materials on which very finely-divided Ag has been deposited act in the same way, oligodynamic factors are probably involved. W. McC.

Comparison of the antiseptic power of hexamethylenetetramine and the hydriodide of hexamethylenetetramine–ethyl alcohol. G. Toussaint, R. Gœtz, and M. Vérain (Compt. rend. Soc. Biol., 1934, **117**, 194—196).—At p_H 4—8, the antiseptic power of the hydriodide of $(CH_2)_6N_4$–EtOH towards *B. coli* is > that of $(CH_2)_6N_4$. A. L.

Action of sodium hypochlorite, chloramine-*T*, and azochloroamide on organic substrates. A. F. Guiteras and F. C. Schmelkes (J. Biol. Chem., 1934, **107**, 235—239).—The loss of available Cl to org. substrates increases in the order azochloroamide (I) (this vol., 993), chloramine-*T*, NaOCl, (I) being very inactive over a p_H range 3—11. This property is important in connexion with germicidal val.
C. G. A.

Spirochæticidal action of bismuth. C. Levaditi and Y. Manin (Compt. rend., 1934, **199**, 739—741).—Syphilitic rabbits were injected with basic Bi β-methyl-α-carboxyethylnonoate (bivatol). The variations of the syphilomatous Bi during 12 days were quite independent of the corresponding Bi variations in kidney, spleen, and blood. The spirochæticidal action of Bi is therefore catalytic, like that of Te, As, V, and Au. R. N. C.

Autacoid function of parasympathetic nerves. A. B. L. Beznák (J. Physiol., 1934, **82**, 129—153).—The moving-surface curve of the decrease in the heart's action by acetylcholine (I) is a hyperbola; the equation of the (I) concn.–decrease curve corresponds with that of the Freundlich adsorption isotherm. The inotropic effects on the frog's heart in Ringer's solution of tissue extracts (II) decrease rapidly on dilution compared with that of a pure (I) solution giving the same effect, suggesting that (I) is not the active substance in the tissues. The reaction of the heart to (I) is not altered by changes in osmotic pressure or histamine; choline in amounts >0·1 mg. decreases the effect, whilst fall of p_H generally increases it.

Evidence is given that (II) contain a substance inhibiting the effect of (I). The effect of (I) on the frog's rectus (III) and leech (IV) increases to a max. on repeated treatment with the same concn. of (I); it is decreased by raising the total [NaCl] of the Ringer's solution. The optimum p_H is 6·8 for (III), and 7·8 for (IV). (III) and (IV) are both sensitive to $K^{\cdot}$, a $[K^{\cdot}]$ of 0·20% being toxic to (III); the effects of small concns. of (I) and $K^{\cdot}$ together are mutually increased. Choline increases the effect of (I) on both (III) and (IV). Parasympathetic stimulation does not alter the total choline ester content (V) of (II). Degenerative chorda section does not alter submaxillary (V). Perfusion of the frog's heart with Ringer's solution containing excess $H^{\cdot}$ or $K^{\cdot}$ causes an increase in (I) similar to that from vagus stimulation. The (I) of the press-juice from frogs' hearts obtained in presence of eserine increases on incubation at 37°. R. N. C.

Chemical transmission of secretory impulses to the sweat glands of the cat. H. H. Dale and W. Feldberg (J. Physiol., 1934, **82**, 121—128).—Stimulation of the sympathetic nerve supply to the sweat glands results in the appearance of acetylcholine in the venous fluid. R. N. C.

Acetylcholine: a peristaltic hormone. F. T. Harvey (Vet. Rec., 1934, **14**, 1219—1221).—A description of the action of acetylcholine on intestinal peristalsis, and its use in the treatment of ileus in horses. R. N. C.

"Fat metabolism hormone" and hyperglycæmia. B. Harrow, I. M. Chamelin, and A. Mazur (Amer. J. Physiol., 1934, **109**, 436—439).—To obtain an extract of "fat metabolism hormone" (I), male urine is acidified with AcOH, and BzOH in EtOH added slowly; the ppt. is treated twice with 95% EtOH to remove BzOH, and extracted with aq. NH_3, and the extract is kept alkaline until required for testing. Injection of (I) into rabbits causes large increases in blood-sugar, -ketones, and -lactic acid; CO_2-combining power is decreased, and carbohydrate and fat metabolism undergo a profound disturbance. R. N. C.

Inactivation of callicrein. II. E. Werle (Biochem. Z., 1934, **273**, 291—305; cf. A., 1930, 1624; this vol., 224).—The inactivating material (I) occurs in blood-serum but not in corpuscles, does not pass through semi-permeable membranes (high mol. wt.), and is destroyed by papain. (I) is destroyed by heating (completely in 45 min. at 58°) and hence inactivated callicrein (II) can be reactivated by heating to 58°. The rate of inactivation depends on the temp., concn. of (I) and (II), and $[H^{\cdot}]$ (optimum at p_H 7·5, quite inactive at 4 and 11). Horse-serum contains also a second (I) which has an additional optimum at p_H 5·5. These two (I) exhibit differences with regard to sensitivity to the action of heat. As regards inactivating power sera from various animals form the series man>ox>dog>horse>pig. The effects of (I) are counteracted by germanin and novocaine. There seems to be an equilibrium, governed by the mass action law, between (I), (II), and a compound of (I) with (II). W. McC.

Action of insulin on the heart and blood-pressure. R. K. Pal and S. Prasad (J. Physiol., 1934, **82**, 154—159).—Insulin in small doses causes slowing of the heart rate with some irregularities, and in larger doses complete stoppage of the heart, the action being physiologically antagonistic to that of atropine. Blood-pressure also falls after insulin. R. N. C.

Effect of insulin in conjunction with posture on blood concentration in depancreatised dogs. A. M. Waterhouse and E. P. Ralli (Amer. J. Physiol., 1934, **109**, 422—429).—Administration of hypoglycæmic doses of insulin to depancreatised dogs kept on their backs caused increase of blood concn. This did not occur when the animals were kept upright, or on their backs without insulin. R. N. C.

Effect of insulin and glucose on the metabolism of amino-acids. J. P. Bouckaert, P. P. de Nayer, and W. Cassiman (Compt. rend. Soc. Biol., 1934, **117**, 257—258).—The blood of rabbits injected simultaneously with insulin, amounts of glucose sufficient to maintain the normal amount of blood-sugar, and glycine (I) shows an increase in the NH_2-acids as compared with that of animals receiving (I) only. A. L.

Effect of insulin on the blood amino-acid level. R. Martens (Compt. rend. Soc. Biol., 1934, **115**, 752—754).—In the depancreatised dog the NH_2-acid content of liver, muscle, and blood is high and is reduced by insulin (I). From comparisons of the NH_2-N of femoral vein and artery, and hepatic and portal veins in normal and depancreatised dogs before and after (I) it is deduced that (I) reduces loss of NH_2-acids from muscle and liver; (I) is therefore thought to inhibit proteolysis and favour synthesis. Nutr. Abs. (*b*)

Effect of insulin and adrenaline on carbohydrate metabolism in hyperglycogenæmia. H. Biedermann and W. Hertz (Deut. Arch. klin. Med., 1934, **176**, 272—280; Chem. Zentr., 1934, i, 3077).—Blood-sugar of persons with hyperglycogenæmia scarcely reacts to adrenaline, but shows great sensitivity to insulin. R. N. C.

Glycæmic curve of adrenaline and insulin in castrated animals. G. B. Contardo (Boll. Soc. ital. Biol. sperim., 1932, 7, 98—101).—Castration (I) is followed by a fall in blood-sugar and an increase in the hyperglycæmia due to adrenaline (II) or the hypoglycæmia due to insulin (III). Before puberty, (I) does not produce these effects. The actions of (II) and (III) are influenced in similar ways by the ovarian hormone. R. N. C.

Effect of adrenaline on liver-glycogen in adrenalectomised rabbits. J. Asaeda and P. T. Shen (J. Biochem. Japan, 1934, **19**, 391—401).—Bilateral adrenalectomy in rabbits diminishes the blood-sugar (I), liver-glycogen (II), and, to a smaller extent, muscle-glycogen (III). Subsequent administration of adrenaline increases the survival period and (I) but not (II) or (III). F. O. H.

Adrenaline, lymphatic extract, and hyperglycæmic reaction. M. Coppo (Boll. Soc. ital. Biol. sperim., **6**, 378—381; Chem. Zentr., 1934, i, 560).—Thymus extract causes hyperglycæmia and reduces or prevents adrenaline-hyperglycæmia (I). Lymphatic extracts behave similarly, but are less effective in respect of (I). A. G. P.

Determination of adrenaline in blood. G. Viale (Compt. rend. Soc. Biol., 1934, **117**, 267—268).—A reply to criticisms. A. L.

Influence of adrenals on the function of muscle, particularly on its metabolism. G. Kuschinsky and D. Nachmansohn (Klin. Woch., 1934, **13**, 265—266; Chem. Zentr., 1934, i, 3077).—The gastrocnemius of an adrenalectomised guinea-pig (I) when stimulated produces more phosphagen (II) than that of a normal animal (III) equally stimulated, and is sooner fatigued. Lactic acid (IV) formation in (I) is diminished or prevented; in (III) it supplies energy for the resynthesis of (II). Administration of adrenaline (V) restores the activity of the muscle, (V) therefore playing an important part in the resynthesis of (II) and in (IV) production. R. N. C.

Effect of fluid deprivation and fluid intake on the revival of dogs from adrenal insufficiency. Effect of sodium chloride administration on adrenalectomised dogs not receiving extract. Relation between blood-pressure, blood-urea-nitrogen, and fluid balance of the adrenalectomised dog. W. W. Swingle, J. J. Pfiffner, H. M. Vars, and W. M. Parkins (Amer. J. Physiol., 1934, **108**, 144—150, 159—167, 428—437).—As the blood-pressure falls the blood-urea rises. Adrenalectomised dogs lose a greater proportion of H_2O than do normal dogs and correspondingly there is retention during treatment with extract. Nutr. Abs. (*m*)

Influence of various internal secretion glands on the formation of indican in the organism. Influence of (i) thyroid, (ii) insulin and adrenaline, (iii) testicles, (iv) ovaries, (v) spleen; relation between spleen and thyroid in indican formation. S. Shingu (Folia Endocrinol. Japan, 1932, 8, 17—18, 18—19, 21, 21—22, 22—23).—(i) In normal rabbits 15% of injected indole (I) appeared in urine as indican (II). Feeding with powdered thyroid increased, and thyroidectomy decreased, urinary (II).

(ii) Excretion of (II) was increased by injection of insulin or of glucose and further increased by injection of both. Adrenaline reduced the (II) eliminated.

(iii) Feeding powdered testicle increased and castration decreased elimination of (II).

(iv) The (II) in urine decreased after ovariectomy or feeding powdered corpus luteum and increased after feeding follicular fluid containing powdered connective tissue.

(v) Spleen extirpation increased (II) in urine. Removal of spleen and thyroid caused a return to normal (II) excretion. Ch. Abs. (*p*)

Adrenal capsules and electrolyte metabolism. IV. Influence of adrenaline, choline, and cortical substance of adrenal capsules on potassium and calcium contents of skeletal muscles. S. Sugimoto (Folia Endocrinol. Japan, 1932, 8, 23—24).—In 30 min. after injection of adrenaline the K content of muscle had increased and that of Ca decreased. After 2 hr. the changes were reversed. Injection of choline chloride increased K. Feeding of cortex increased K and decreased Ca. Ch. Abs. (*p*)

Influence of hormones on hydrogen-ion concentration of blood-plasma. I. Influence of thyroid and of insulin. N. Nakatsugawa (Folia Endocrinol. Japan, 1932, 8, 39—40).—Feeding of thyroid powder lowered, and thyroidectomy raised, the blood-p_H. Injection of insulin (I) caused a temporary decrease followed by a transition to an alkaline period. On simultaneous injection of glucose with (I) the acid change is less marked, but the alkali phase is prolonged. Large injections of (I) produce marked acidosis. Ch. Abs. (*p*)

Reduction of blood-lipase by thyroxine and its prevention. J. Bauer and L. Feil (Wien. med. Woch., 1934, **84**, 566—568).—Thyroxine does not produce a general reduction of activity of lipolytic enzymes, but affects only blood-lipase. Lipase is reduced in the liver, but not in the kidney. The reduction of serum-lipase is attributed to lowered production in the liver. Nutr. Abs. (*m*)

Effect of thyroxine and antithyroid substances on the serum-lipase. M. H. Hoffmann (Arch. Int. Med., 1934, **54**, 427—435).—The reduction in serum-lipase (I) after thyroxine (II) injection as a means of studying antithyroid substances is applied to the blood-extract (III) of Anselmino and Hoffmann (A., 1933, 754) and to olive oil (IV). Both substances inhibit the reduction of (I), (III) being twice as active as (IV). Injection of insulin before the (II) did not protect (I). A. L.

Investigation of the thyroid–liver effect by continual examination of the complement content of the serum. Examination of antithyrotropics by this method. F. Fischer and W. Loew (Med. Klin., 1934, **30**, 200—203; Chem. Zentr., 1934, i, 2149).—Injection of thyroxine (I) in guinea-pigs causes a fall in serum complement, which can be used as a test for thyroid effect, and depends on the influence of (I) on the liver function. The effect is inhibited by di-iodotyrosine, cholesterol, the Hoffmann–Anselmino serum extract, and insulin. R. N. C.

Concentration of thyroxine in the blood of man and animals. A. W. Elmer, Z. Luczynski, and M. Scheps (Compt. rend. Soc. Biol., 1934, **115**, 1714—1716).—By a modification of Leland and Foster's method it was found that the thyroxine content of human blood was in two cases 0·0394 and 0·0482 mg. per litre; in the blood of a horse it was 0·029 and of a dog 0·034 mg. This represents 25—32% of the total I and 40—60% of the org. I. Nutr. Abs. (*b*)

Extrathyroid origin of iodine compounds with action resembling that of thyroxine. I. Abelin (Klin. Woch., 1934, **13**, 940—942).—One of the fractions obtained by the hydrolysis with aq. $Ba(OH)_2$ of iodised protein has an action similar to that of thyroxine on the metabolism of rats, the depigmentation of feathers of fowls, and the MeCN resistance test. Nutr. Abs. (*m*)

Functional inter-relationship between the adrenal and parathyroid glands. J. M. Rogoff (Science, 1934, 80, 319—320). L. S. T.

Variations in blood- and bile-calcium following injections of calcium gluconate and parathyroid extract. M. CHYRAY, A. MARCOTTE, R. LE CANUET, and P. FIRMIN (Presse méd., 1933, **41**, 2109—2111). NUTR. ABS. (*b*)

Detoxicating principle in the organism. I. Extraction of the active principle of the liver. II. Complementary experiments and investigation of the active principle in various organs and tissues. A. DE BARBIERI (Boll. Soc. ital. Biol. sperim., 1931, **6**, 196—197, 197—199).—I. An EtOH extract of the liver was adsorbed with kaolin, the adsorbate eluted with H_2O, extracted with Et_2O, repeatedly treated with PhMe, decolorised with animal C, extracted again with EtOH, and finally dissolved in H_2O. Guinea-pigs injected subcutaneously with this extract (I) were not killed by quantities of NH_4Cl that proved fatal to untreated animals.

II. Frogs injected with (I) and NH_4Cl in the dorsal lymphatic sac remained in normal condition, whilst those injected with NH_4Cl alone developed muscular paralysis and tetanic convulsions. Extracts similar to (I) in effect were obtained from muscle and kidney. Positive results were also obtained from serum, suggesting that the active principle is hormonal. R. N. C.

Action of tonephin or pitressin and orasthin in increasing blood-sugar and antagonising insulin. H. SCHROEDER (Klin. Woch., 1933, **12**, 1766—1768; Chem. Zentr., 1934, i, 560).—Injection of pituitary extracts increases blood-sugar (I) by approx. 20%. Components affecting the uterus do not influence (I). The antagonistic action of pitressin towards insulin (II) is not brought about by restriction of resorption of (II). A. G. P.

Biological determination of anti-diuretic activity of posterior pituitary extracts. H. PÉNAU and H. SIMONNET (J. Pharm. Chim., 1934, [viii], **20**, 304—319).—Modified technique using dogs is described. Results of Molitor (cf. A., 1932, 885) are confirmed. F. O. H.

Action of pituitrin [on urinary excretion]. S. BIANCARDI (Boll. Soc. ital. Biol. sperim., 1931, **6**, 227—231).—Injection of pituitrin (I) into fasting animals to which H_2O had been administered produced a marked reduction of diuresis. Administration of dil. NaCl solution instead of H_2O reduced the vol. of urine; this masked the reduced diuresis from (I), but the blood-chlorine was unaffected. R. N. C.

Corticotropic hormone of the anterior pituitary. K. J. ANSELMINO, F. HOFFMANN, and L. HEROLD (Klin. Woch., 1934, **13**, 209—211; Chem. Zentr., 1934, i, 3223).—To obtain an extract of the hormone, fresh ox anterior pituitary is dried with $COMe_2$, powdered, and agitated for 1 hr. with H_2O; the solution is freed from other hormones by ultrafiltration at p_H 5·0—5·5. The hormone is sol. in H_2O, but insol. in EtOH, $COMe_2$, Et_2O, and $CHCl_3$; it withstands boiling for 15 min., and is stable to dil. acids and alkalis. It is not adsorbed by animal C. It can be ultrafiltered through collodion, and is consequently not associated with protein. R. N. C.

Determination of the [pituitary] anterior lobe hormone in human urine, and its importance in the recognition of the functioning conditions of different endocrine glands. M. ARON (Bull. Acad. Méd., 1934, **111**, 273—275; Chem. Zentr., 1934, i, 2442).—In primary hyperthyroidism the thyroxine of the urine is diminished; in primary hypothyroidism it is increased. This fact is applied in determining whether thyroid abnormalities are primary or secondary. R. N. C.

Effects of anterior pituitary extracts of cattle on carbohydrate metabolism in the guinea-pig. R. F. HOLDEN, jun. (Proc. Soc. Exp. Biol. Med., 1934, **31**, 773—776).—In the male guinea-pig, repeated injections of an extract (I) of the anterior pituitary of the cow cause a diminution in liver-glycogen which reaches a min. in 6 days and is thereafter restored despite continued injections. The min. val. varies with the dose. These observations accord with the view that (I) increases the activity of the thyroid gland. NUTR. ABS. (*m*).

Effect of operative interference with the anterior pituitary on the metabolism of diabetic dogs. H. LUCKE, E. R. HEYDEMANN, and O. BERGER (Z. ges. exp. Med., 1933, **92**, 711—723; Chem. Zentr., 1934, i, 2148).—Depancreatised dogs were given sufficient insulin (I) to prevent glycosuria (II), and the anterior pituitary (III) was cauterised. The carbohydrate metabolism was considerably improved, and after the effect of (I) had worn off, (II) did not appear at once. In some cases the destruction of (III) resulted in a rapid and heavy fall of blood-sugar, ending in death from hypoglycæmic shock. Dogs treated in this way were unusually variable in blood-sugar retention, suggesting an increased sensibility to hypo- and hyper-glycæmic substances. (III) probably secretes a hormone necessary for the control of carbohydrate metabolism. R. N. C.

Effect of intermedin and the thyrotropic substance from the anterior pituitary on the adrenaline and ascorbic acid content of the adrenals. A. G. HOLMQUIST (Klin. Woch., 1934, **13**, 664—666).—Extracts from the intermediate and anterior lobe of the pituitary, although producing hypertrophy of the adrenal cortex when injected into guinea-pigs, did not affect the adrenaline or ascorbic acid content of the gland. NUTR. ABS. (*b*)

Solubility of anterior pituitary substances in solutions of different p_H. R. MULLER (Endokrinol., 1934, **14**, 1—12; Chem. Zentr., 1934, ii, 626).—The optimum p_H for dissolution of thyrotropic hormone was 12·7 and for the gonadotropic hormone 8·7. A. G. P.

Thyrotropic substance of the anterior pituitary gland. I. II. Metabolic relation to other organs of internal secretion. A. LOESER (Arch. exp. Path. Pharm., 1934, **176**, 697—728, 729—739).—I. The thyrotropic principle (I) (A., 1932, 970) has a max. stability at p_H 9; at p_H 1—3, 7, and 13, decomp. at room temp. is complete in approx. 6 days. With rats, rabbits, and guinea-pigs, the blood-level of (I), which normally has a low val., rises after thyroidectomy and falls after hypophysectomy. Intravenously injected (I) is rapidly excreted unchanged in the urine, no accumulation occurring in the liver, spleen, kidney, thyroid gland (II), or muscle. (I) is relatively stable in blood *in vitro*. The action of (I) is independent of the nervous system, but dependent on the activity of (II); thus it is diminished by thyroxine, di-iodotyrosine, 3 : 5-di-iodothyronine, or KI+I, but not tyramine, tyrosine, or thyronine. The relation between the activity of (II) and that of the pituitary gland is discussed.

II. The metabolic activity of (I) is related to the functioning of the ovary and adrenal glands (III). Thus ovariectomy in guinea-pigs produces an increased secretion of (I) which influences (II). The changes in (III), which occur mainly in the cortex, are not directly due to hormonal influence, but are probably caused by the metabolic disturbance due to (I) and (II). F. O. H.

Thyrotropic hormone of the anterior pituitary. E. M. Anderson and J. B. Collip (J. Physiol., 1934, **82**, 11—25).—The metabolic rate (I) of the rat or guinea-pig is increased by injection of extracts of the thyrotropic hormone (II) of the anterior pituitary. Hypophysectomised animals (III) are more sensitive to (II) than normal animals. A prolonged series of injections results in a fall of (I) to the level of (III); the antithyrotropic hormone causing this is not produced in the pituitary, since (III) also develop the same resistance. (I) rises very steeply in goitrous animals injected with (II). Purified extracts of (II) are prepared by concn. in vac. of the $Ca_3(PO_4)_2$ filtrates from the original extracts, saturation with $(NH_4)_2SO_4$, filtration and extraction of the ppt. with H_2O twice, pptn. with EtOH and dissolution in H_2O twice, and repeated pptn. from EtOH or $COMe_2$. The adrenotropic hormone can be separated from (II) in the filtrates from the last pptns. by isoelectric pptn. (II) is stable for long periods in the cold in aseptic conditions, but is destroyed by boiling. R. N. C.

Hypoglycæmic action of the thyrotropic hormone of the anterior pituitary. E. Zunz and J. La Barre (Compt. rend. Soc. Biol., 1934, **117**, 262—264).—Intravenous injection of the thyrotropic hormone of the anterior pituitary gland into dogs causes a decrease in blood-sugar due to increased insulin secretion. A. L.

Thyrotropic activity of anterior pituitary extracts. I. W. Rowlands and A. S. Parkes (Biochem. J., 1934, **28**, 1829—1843).—The thyrotropic activity of anterior pituitary extracts was tested by their capacity to increase the wt. of the thyroids of immature female guinea-pigs. A curve for response/dose has been constructed, and a provisional unit adopted. It is probable that a clean and simple separation of the growth hormone and prolactin from the thyrotropic and gonadotropic substances may be effected by C_5H_5N extraction, only the latter being sol. in aq. C_5H_5N. A. E. O.

Mechanism of action of the insulin-antagonistic hormones of the anterior pituitary. II. Anterior pituitary, adrenal insufficiency, and carbohydrate metabolism. III. Anterior pituitary, adrenal denervation, and carbohydrate metabolism. H. Lucke, E. R. Heydemann, and H. Hahndel (Z. ges. exp. Med., 1933, **91**, 483—491, 492—501; Chem. Zentr., 1934, i, 2148).—II. In adrenalectomised dogs, injection of the insulin-antagonistic hormones (I) (fresh anterior lobe preps.) produces no rise of blood-sugar.

III. (I) have no hyperglycæmic effect in dogs with denervated adrenals. The hyperglycæmia is therefore due to a stimulation of the adrenal nerves. R. N. C.

Influence of anterior pituitary on bile secretion. G. Baltacéano, C. Vasiliu, and M. H. Paraschiv (Compt. rend. Soc. Biol., 1934, **117**, 279—283).—Anterior pituitary preps. injected into dogs increase the quantity of bile (I) secreted. The amount of salts in (I) is increased, the cholesterol content diminishes, and the pigments remain unchanged. A. L.

Anterior pituitary hormones. VI. Comparison of the effect of the different hormones on deamination processes. R. Agnoli (Boll. Soc. ital. Biol. sperim., 6, 754—756; Chem. Zentr., 1934, i, 560).—The lipin hormone (Agnoli) and prolan (Zondek) intensify deamination. A. G. P.

Pituitary and fat-accumulation following castration. K. W. Schultze (Arch. Gynäkol., 1934, **155**, 327—334; Chem. Zentr., 1934, i, 2938).—Injection of the Anselmino–Hoffmann extract of the anterior pituitary into rats raises the blood-ketones. The active substance (I) can de detected in human blood after a meal of fat. In persons with fat-accumulation following castration or climacteric, there is no diminution below the normal of the blood-(I). The ketonæmia induced by injection of the anterior pituitary extracts is probably the result of an increased fat exchange. R. N. C.

Extraction of gonad-stimulating substances of the anterior pituitary. A. E. Meyer and H. L. Fevold (Proc. Soc. Exp. Biol. Med., 1934, **31**, 570—571).—Almost complete extraction is obtained with 5% aq. C_5H_5N, 6% BuOH, or 3% *n*-amyl alcohol. Ch. Abs. (*p*)

Bio-assay of the anterior pituitary-like sex-hormone (antuitrin-*S*). L. W. Roe, A. Simond, and W. O. Nelson (J. Amer. Pharm. Assoc., 1934, **23**, 882—891).—Using 26-day-old rats and examining for corpora lutea gives a method accurate to 10—20%. 1 mouse unit is equiv. to 4 rat units. The rabbit ovulation unit is equiv. to 1 rat unit per kg. body-wt. of the rabbit. C. G. A.

Effect of pineal extracts on the action of the anterior pituitary hormone. P. Engel (Klin. Woch., 1934, **13**, 266—267; Chem. Zentr., 1934, i, 3076).—In mice and rabbits injected with anterior pituitary hormone (I) and then with an extract of the human pineal gland (II), the stimulating effect of (I) on the ovary did not appear. A human (II) contained enough active material to inhibit the action of 30 rat units of (I). R. N. C.

Demonstration of an œstrus-inhibiting substance in the pineal gland of young female rats. W. Fleischmann and H. Goldhammer (Klin. Woch., 1934, **13**, 415; Chem. Zentr., 1934, i, 3076).—Attempts to inhibit the action of the anterior pituitary by implantation (I) of pineals (II) in young animals failed; the implants also did not antagonise injected folliculin. (I) of two (II) from young female rats in mice suspended œstrus (III), often for 4—6 weeks. The inhibitory effect was max. when the (I) took place at the height of (III). After the effect had subsided, (III) occurred normally again. R. N. C.

Elimination of prolan in the urine in the involution period and in age. H. Saethre (Klin. Woch., 1933, **12**, 1727—1729; Chem. Zentr., 1934, i, 3481).—Prolan elimination (I) in the urine of women in the climacteric and post-climacteric stages was always increased. No increased (I) was established in pre-puberty or puberty. R. N. C.

Complete recovery of gonadotropic substances from the urine of pregnant women. L. Davy (Endocrinol., 1934, **18**, 1—17).—Acidified urine is shaken with Lloyd's reagent, which is dried, eluted with 50% C_5H_5N, and the active substance pptd. with 95% $COMe_2$. Ch. Abs.

Action of ovarian extract on the alkali reserve of castrated rabbits. G. B. Contardo (Boll. Soc. ital. Biol. sperim., 1932, **7**, 102—104).—Injection of ovarian extract or folliculin in castrated rabbits shows no effect on the alkali reserve (I). The increase in (I) on castration is probably due to the activity of other endocrine organs. R. N. C.

Preparation of the female [sex] hormone, and a new phenomenon of the hormone. M. Ito and S. Hayazu (Münch. med. Woch., 1933, **80**, 1969; Chem. Zentr., 1934, i, 3222).—Mare's urine is acidified with HCl, filtered through kieselguhr, the hormone adsorbed on C, and the C washed with dil. alkali and EtOH and extracted with aq. PhOH, the PhOH being distilled off in steam. The solution is evaporated, the residue dissolved in aq. EtOH, and boiled with 10 vols. of C_6H_6. The yellow C_6H_6 layer is washed with 2% aq. Na_2CO_3 until colourless, conc., and then shaken with 4% NaOH; this extracts 90—95% of the hormone, which is pptd. on neutralisation. By repeated saponification of the ppt. with 5% NaOH, followed by extraction with Et_2O and evaporation, 60% of the hormone is obtained as crystals, m.p. 254°. Analysis indicates the formula $C_{18}H_{22}O_2$; the mouse unit is $0{\cdot}07 \times 10^{-6}$ g. 100 litres of urine yield 640 mg. of crystals. The same crystals are obtained from urine of pregnancy. The hormone content of these extracts increased slowly, in one case from 7 to 60 million units in one year, suggesting that a prohormone was being converted slowly into the hormone. R. N. C.

Theelin prepared from human and mare's urine and from theelol. Preparation of theelin from mare's urine. J. M. Curtis, D. W. MacCorquodale, S. A. Thayer, and E. A. Doisy (J. Biol. Chem., 1934, **107**, 191—205).—There is no evidence of the existence of α- and β-isomerides of theelin (I). (I) is obtained from mare's urine by pptn. with BzOH in acid solution and purified by the usual methods. $< 0{\cdot}1$% of the activity is due to a less active form, if this is present. H. G. R.

Influence of folliculin on the flowering of plants. R. Harder and I. Stormer (Jahrb. wiss. Bot., 1934, **80**, 1—19).—The hormone had no effect on the rate of growth or period of flowering of any plant species examined. A. G. P.

Action of œstrin on the coagulating glands and on certain vestigial structures in the mouse (*Mus musculus*). H. Burrows (Nature, 1934, **134**, 570).—The changes described indicate that œstrin may have a sp. action on structures derived from the Müllerian apparatus. L. S. T.

Crystalline progestin. O. Wintersteiner and W. M. Allen (J. Biol. Chem., 1934, **107**, 321—336).—From the cryst. fraction containing progestin previously isolated from corpus luteum extracts (A., 1933, 194) four cryst. substances have been isolated by fractionation from C_6H_6 and light petroleum. The chief constituent is a *substance*, $C_{21}H_{34}O_2$ (or less probably $C_{22}H_{36}O_2$) (I), m.p. 190°, a saturated hydroxy-ketone [*phenylurethane*, m.p. 214·5°; p-*nitrobenzoate*, m.p. 216°; *semicarbazone*, m.p. 248—249° (decomp.)] devoid of progestin activity. The mother-liquors from (I) contain an active *substance*, $C_{21}H_{30}O_2$ (II), m.p. 128°, an unsaturated diketone [*dioxime*, m.p. 238° (decomp.); *semicarbazone*, amorphous, m.p. 280° (decomp.)], exhibiting selective absorption at 240 mμ, together with a second very similar active *substance*, $C_{20}H_{28}O_2$ (?), m.p. 120—121°, which may consist of mixed crystals of (II) with small amounts of impurities. A second inactive *substance*, m.p. 74°, was also isolated in minute amount. The above results are in good agreement with those of Butenandt (this vol., 1039) and of Slotta *et al.* (*ibid.*, 931). Oxidation of (I) by CrO_3 yields a diketone, m.p. 191—194°, not identical with pregnandione. A. E. O.

Hormones of the corpus luteum. K. H. Slotta, H. Ruschig, and E. Fels (Helv. Chim. Acta, 1934, **17**, 1361—1362).—The cryst. hormone of Hartmann *et al.* (this vol., 1039) is a mixture of 75% of luteosterone-*A* and 25% of luteosterone-*C* (I) + -*D*. Their dioxime is probably derived from (I). H. W.

[Hormones of the corpus luteum.] M. Hartmann and A. Wettstein (Helv. Chim. Acta, 1934, **17**, 1363—1364).—A reply to Slotta *et al.* (preceding abstract) and Butenandt *et al.* (this vol., 1039). A bibliography is appended. H. W.

Corpus luteum hormones. II. M. Hartmann and A. Wettstein (Helv. Chim. Acta, 1934, **17**, 1365—1372; cf. this vol., 1039).—Preliminary enrichment is effected by the method of Corner *et al.* (Amer. J. Physiol., 1929, **88**, 326). After freezing from dil. MeOH, partition between 80 vol.-% EtOH and light petroleum (I) causes the active material to remain in the EtOH while much inactive material passes into the (I). The EtOH is diluted to 33% and shaken with (I), into which the corpus luteum hormones pass, whilst the follicular hormone and ballast remain in the EtOH–H_2O. Purification can also be effected by adsorbing the hormones from anhyd. (I) or CS_2 by fuller's earth followed by elution with boiling EtOH; the method is particularly applicable to ox corpus luteum. A third method consists in extracting the C_6H_6 solutions with 75% H_2SO_4, diluting the extract to 20%, and extraction with Et_2O. The quant. separation of diketones and OH-ketones in the products thus obtained is effected by use of more freely sol. ketonic products; thus the *dioximes*, $C_{21}H_{30}(N\cdot OH)_2$, m.p. 269° (corr.) and m.p. 251° (corr.), respectively, have been obtained. Further, the OH-compounds may be removed by treatment with o-$C_6H_4(CO)_2O$ in C_5H_5N; the non-reactive portion yields homogeneous hormones, m.p. 129° (corr.) and m.p. 120° (corr.), respectively, whilst the H phthalate fraction is hydrolysed to a OH-ketone, m.p. 196·5—197·5° (corr.). H. W.

Effect of the male sex hormone on the genital tract of the female. S. Skowron (Nature, 1934, **134**, 627).—Female rabbits give a macroscopic positive reaction after subcutaneous injections of the male hormone of the rabbit. L. S. T.

Standardisation of the male hormone. R. Fussgänger (Med. chem. Abh. med.-chem. Forsch. I.G. Farbenind., 1933, 213—226; Chem. Zentr., 1934, i, 2440—2441).—The comb method is recommended, the unit being the amount of hormone which after five daily injections into the castrated cock produces a comb-growth of 30% in seven days from the beginning of the experiment. R. N. C.

Colour test for vitamin-*A*. J. Rosenthal and J. Erdélyi (Magyar Orvosi Arch., 1934, **35**, 232—237).—5% guaiacol (I) solution produces with vitamin-*A* the same red-violet colour as does 5% pyrocatechol. The stability of the colour renders the (I) test suitable for quant. purposes. Nutr. Abs. (*m*)

Colour reaction for carotene. V. E. Levine and G. E. Bien (Proc. Soc. Exp. Biol. Med., 1934, **31**, 581—582).—Carotene (I) in $CHCl_3$ reacts with CH_2O in H_2SO_4 (1 vol. of 40% CH_2O in 50 vols. of acid) to form a deep violet zone between the layers. The violet zone, on shaking, spreads through the acid layer, leaving the $CHCl_3$ colourless. Addition of Ac_2O causes a transitory blue to appear in the acid layer if the concn. of (I) is sufficiently high.

Nutr. Abs. (*m*)

Liebermann–Burchard reaction with carotene. V. E. Levine and G. E. Bien (Proc. Soc. Exp. Biol. Med., 1934, **31**, 804—808).—Carotene (I) can be detected by means of Ac_2O and conc. H_2SO_4, in concns. of $\nless$ 0·01 mg. of (I) in 10 ml. of $CHCl_3$. The reaction resembles the Liebermann–Burchard test for cholesterol (II) except that the green colour is more rapidly formed and much more transitory. (I) does not interfere with the determination of (II) in blood.

Nutr. Abs. (*m*)

Storage of vitamin-*A* in cattle. H. R. Guilbert and G. H. Hart (J. Nutrition, 1934, **8**, 25—44).—Carotene in adipose tissue may be withdrawn during vitamin-*A* (I) privation without the withdrawal of the fat. The premature expulsion of the fœtus resulting from (I)-deficiency is examined. The liver-tissue of mature beef cows reared under favourable conditions contained (I) in amounts approximating to that of cod-liver oil. The (I) in livers of newly-born calves from well-fed cows was relatively low. A. G. P.

Vitamin-*A* storage in livers of turkeys and chickens. H. R. Guilbert and W. R. Hinshaw (J. Nutrition, 1934, **8**, 45—56).—Storage of vitamin-*A* (I) in chicken livers is directly related to the (I) content of the ration. The influence of age on the (I) reserves of chicken and turkeys is examined. A. G. P.

Cholesterol and vitamin-*A* content of the human liver. G. L. Muller and M. M. Suzman (Arch. Int. Med., 1934, **54**, 405—411).—The cholesterol content (I) of livers obtained at autopsy was 0·098—1·003% (average 0·301%). (I) was $<$ average in cases of death from infectious and $>$ average in death from arterial hypertension. No relation could be established between (I) and the vitamin-*A* content of the liver or the sex or age of the patient. A. L.

Vitamin content of the pituitary. E. Vogt (Med. Klinik, 1933, **29**, 1734—1735; Chem. Zentr., 1934, i, 880).—Normally the pituitary (I) of adults under 50 possesses a definite vitamin-*A* (II) content. In chronic, exhausting illnesses (II) gradually disappears completely. With malignant tumours, especially of the quick-growing type, the (II) of (I) can be $\nless$ normal. Only in the final stages of the disease does (I) become deprived of (II). L. S. T.

Carotene, vitamin-*A*, and vitamin-*C* in cow's milk. J. C. H. van Wijngaarden (Acta Brev. Néerland., 1934, **4**, 49—52).—Vitamin-*A* and carotene, determined after saponification of the milk, by means of the $SbCl_3$ test and Lovibond tintometer, respectively, are low in the milk of cows kept in stall on a diet of hay and oil-cake, or hay and mangolds, but higher on pasture or when silage is given. The same variation of conditions produces little change in the vitamin-*C* content of the milk. Nutr. Abs. (*m*)

Carotene and vitamin-*A* in human milk with special reference to colostrum. M. van Eekelen and J. H. de Haas (Acta Brev. Néerland., 1934, **4**, 52—54).—The carotene and vitamin-*A* contents are very high for the first week after parturition, but decline gradually until after some weeks the vals. are about one sixth of the initial figures and approach the vals. for cow's milk. Nutr. Abs. (*m*)

Effect of prolonged feeding of raw carrots on vitamin-*A* content of liver and kidneys in the dog. R. G. Turner (Proc. Soc. Exp. Biol. Med., 1934, **31**, 866—868).—The vitamin-*A* content of the liver and kidneys of dogs fed on fresh carrots is $>$ that of dogs on a meat or boiled rice diet.

Nutr. Abs. (*m*)

Relation between effects of vitamin-*A* and -*D* and amount of calcium salts and phosphates in food. H. Møllgaard (Ugeskr. Laeger, 1934, **96**, 565—570).—Dietary promotion of rapid growth in the pig without too great accumulation of fat greatly strains growth capacity and makes great demands on the vitamin supply and the amount and composition of mineral salts in the food. Administration of vitamin-*A* (I) and -*D* (II) produces different effects according to the Ca and P content of the food, and overdosage of these vitamins depends not only on the size of the dose, but also on the composition of the diet. Administration of (II) or of (I) + (II) causes tetany and osteoporosis when the Ca is low. Human beings should never be treated with highly conc. preps. of (II) or (I)+(II) unless the diet contains sufficient Ca.

Nutr. Abs. (*m*)

Calcium and phosphorus metabolism. II. Influence of carotene and gallosterol on blood-calcium and -phosphorus. III. Influence of carotene on organ- and tissue-calcium. I. Ishida (J. Biochem. Japan, 1934, **20**, 5—16, 17—22; cf. this vol., 323).—II. Rabbits fed on barley and vegetables show an increase in blood-Ca (I) which is diminished by repeated bleeding. Administration of gallosterol (vitamin-*A*–choleic acid) or β-carotene (II) increases the blood-inorg. and -org. P, but decreases (I).

III. Subcutaneous injection of (II) increases the Ca content of muscle, bone, liver, and kidney by 26·87, 14·27, 10·99, and 5·15%, respectively; that of lung and heart diminishes by 34·05 and 6·21%, respectively.

F. O. H.

Nutritional significance of vitamin-*A* throughout the life cycle. E. L. Batchelder (Amer. J. Physiol., 1934, **109**, 430—435).—Rats on diets containing variable quantities of vitamin-*A* as butter-fat (I) showed significant differences in their life-cycles. The rate of growth and wt. of young at 28 days declined with the (I) in the diet when (I) was $< 4\%$. The no. of young reared decreased below 2% of (I), and no. of young born, duration of reproductive life, and length of life, below 1%; on this diet fourth generation rats were born, but only a few were reared. R. N. C.

Metabolism of carotene. B. Ahmad, K. S. Grewal, and K. S. Malik (Indian Med. Gaz., 1934, **69**, 320—323).—Carotene (I) suspended in aq. glucose given to rats intravenously does not relieve the symptoms of vitamin-*A* (II) deficiency, and does not cause the storage of detectable amounts of (II) in the liver. Similar experiments with dogs fail to show any transformation of injected (I) into (II). The liver of the rabbit, however, seems able to make (II) from this source. Nutr. Abs. (*m*)

Influence of the solvent on the biological effect of carotene and vitamin-*A*. K. C. Lathbury and G. N. Greenwood (Biochem. J., 1934, **28**, 1665—1673).—Different batches of arachis oil and of coconut oil vary in their suitability as solvents for the biological testing (I) of vitamin-*A* or carotene, on account of an unknown factor not arising by deterioration of the solutions on keeping. Quinol does not render an inferior oil suitable for (I). A. E. O.

Influence of vitamin-*A*, -*B*, and -*C* and Collip's hormone on the development of tadpoles after treatment with irradiated ergosterol. P. Coccheri and G. Rossi (Boll. Soc. ital. Biol. sperim., **6**, 750—753; Chem. Zentr., 1934, ii, 562).—Large amounts of irradiated ergosterol (I) were injurious, but smaller proportions stimulated the growth (II) and metamorphosis (III) of tadpoles. Ill effects of (I) were counteracted by vitamin-*A* in respect of (II), but (III) was only slightly influenced. Vitamin-*C* restricted the injurious action of (I). Collip's hormone acts similarly to small amounts of (I) and accentuates the injurious effect of (I) when administered simultaneously. A. G. P.

Fatty constituents of marine plankton. I. Biology of the plankton. E. R. Gunther. **II. General character of the plankton oils.** G. Collin, J. C. Drummond, T. P. Hilditch, and E. R. Gunther. **III. Vitamin-*A* and -*D* content of the oils.** J. C. Drummond and E. R. Gunther (J. Exp. Biol., 1934, **11**, 173—197, 198—202, 203—209).—I. The representative occurrence of different species of organisms in zoo- (I) and phyto-plankton (II) was studied in relation to the yield of oil obtained from different samples. In plankton giving a high yield, the *Copepoda*, particularly *Calanus finmarchicus*, were predominant. The plankton oils resemble fish oils of the Clupeoids and Gadid liver oils, which are probably therefore derived ultimately from the plankton.

II. Methods of extraction and examination of the oils are given, with analyses of samples of (I) and (II) oils, and of the unsaponifiable fraction of (I) oil. The presence of an unsaturated C_{20} *alcohol* of the oleyl or eicosenyl type is recorded.

III. Colorimetric and biological tests indicated that vitamin-*A* was present in (II) oil, but probably absent from (I) oil. (I) oil has some small vitamin-*D* activity, but (II) oil is inactive. Nutr. Abs. (*b*)

Influence of vitamins on the catalase content of blood. II. H. J. Jusatz (Klin. Woch., 1934, **13**, 727—728).—Administration of carrots or of vitamin-*A* (I) causes no rise in the catalase content (II) of the blood of rabbits maintained for two months on a diet devoid of (I). Administration of 100 mg. of ascorbic acid daily, orally or intravenously, raises (II) of the blood of rabbits maintained on a scorbutic diet. Nutr. Abs. (*m*)

Vitamin-*D* content of eggs. H. D. Branion (Canad. Pub. Health J., 1934, **25**, 171—174).—Egg-yolk is a rich source of vitamin-*D* (I), of which a store is laid up in summer, the vals. being lowest in February and March. Addition of 2% of cod-liver oil (II) to the diet of the laying hens increased the amount of (I) in the egg-yolk 7·5 times; it also increased the no. of eggs laid and of chicks hatched from fertile eggs. With 2% of viosterol of strength comparable to (I), the (I) content was again raised 7·5 times; with viosterol 10 times as strong the increase was 15-fold; with viosterol 10,000 times as strong the increase was about 6000-fold, but with this last amount no chicks could be hatched from the eggs. Exposure of the hens daily for 20 min. to ultra-violet light slightly increased the (I) content in the yolk. Eggs kept in cold storage for several months did not deteriorate in (I). Nutr. Abs. (*b*)

Accuracy of biological determinations of vitamins. K. H. Coward (Analyst, 1934, **59**, 681—685).—Biological tests for vitamins are exceedingly sensitive. Assuming that the vitamin-*D* of cod-liver oil (I) and of butter (II) is calciferol, 0·0001 mg. can be detected in any wt. of (I), (II), or other foodstuff that can be given to a rat in 10 days. Thus the concn. of -*D* in (I) may be 1 in 2×10^5, and in (II) 1 in 4×10^7 parts. In any other foodstuff it is less. The accuracy of the tests is discussed. E. C. S.

Vitamin-*D* assay of the "reference cod-liver oil." L. L. Lachat and H. A. Halvorson (Science, 1934, **80**, 342).—A statement of the problem of reducing the chick assay of antirachitic supplements to terms of International rat units (I). Each chick requires 80—135 (I) to produce satisfactory calcification (normal growth and average bone-ash content >45%). The view that the vitamin-*D* requirement of the chick is very large when compared with that of the rat for the antirachitic substance in cod-liver oil is supported. L. S. T.

A. Rôle of bile in the absorption of vitamin-*D* in the rat. B. Action of viosterol in jaundiced rachitic rats. J. D. Greaves and C. L. A. Schmidt (Univ. California Pub. Physiol., 1934, **8**, 43—48, 49—60).—A. Healing of rickets due to loss of wt. makes the direct assay of vitamin-*D* (I) absorption in icteric rachitic rats (II) unfeasible. By feeding Et_2O extracts of the livers of jaundiced (II) receiving viosterol to other (II), it was shown that (I) is stored in the liver of icteric rats when subcutaneously, but not when orally, administered. The presence of bile in the intestinal tract is, therefore, essential for absorption of (I).

B. Viosterol given orally or subcutaneously to jaundiced (II) raised the level of inorg. PO_4''' in the blood, but did not aid calcification. There was no definite evidence of injury to the osteogenic cells. Phosphatase activity was decreased in the livers and kidneys of icteric rats and slightly increased in the bones. Nutr. Abs. (*b*)

Lung and vitamin-*D*. G. A. Metz and P. A. Coppens (Nederland. Tijdschr. Geneesk., 1934, **78**, 769).—In the dog, orally administered irradiated ergosterol is destroyed in the lungs. Nutr. Abs. (*b*)

Solar irradiation of children with special reference to hypervitaminosis-*D*. E. C. Dodds, J. D. Robertson, and H. J. Roche (Arch. Dis. Childhood, 1934, **9**, 91—103).—Hypervitaminosis was not observed. Blood-Ca and -inorg. P were increased by exposure to sunlight. Ch. Abs.

Vitamin content of Philippine foods. III. Vitamin-*B* in various fruits and vegetables. A. J. Hermano and G. Sepulveda (Philippine J. Sci., 1934, **54**, 61—71).—Himbaba-o, cauliflower, and tamarind are excellent sources of vitamin-B_1, as are mango, pineapple, melon, and many other both immature and ripe fruits; bananas contain none. P. G. M.

Effect of *X*-rays on the vitamin-*B* content of wheat seedlings. K. Sugiura (Radiology, 1933, **21**, 438—448).—Treatment with *X*-rays caused only a small decrease in the " vitamin-*B* " content of whole, dry wheat grains as tested by the growth method with rats. If the wheat was soaked and allowed to germinate, its " vitamin-*B* " content increased, but at the same time it became more vulnerable to *X*-rays. Irradiation of dry seeds, before germination, with massive doses of *X*-rays inhibited subsequent growth of the plant > did irradiation of the growing seedlings. This effect was reversed with small doses of *X*-rays. Nutr. Abs. (*b*)

Isolation of oryzanin (antineuritic vitamin). III. S. Otake (J. Agric. Chem. Soc. Japan, 1934, **10**, 409—416).—Dry yeast was extracted with 60% EtOH. Vitamin-B_1 was pptd. by $Ba(OH)_2$ and $AgNO_3$ at p_H 4·5—6·8. After repptn. with phosphotungstic acid -B_1 was obtained as cryst. hydrochloride, identical with that from rice bran. Ch. Abs. (*p*)

Antineuritic vitamin. III. A. Windaus, R. Tschesche, and R. Grewe (Z. physiol. Chem., 1934, **228**, 27—32; cf. A., 1932, 310).—Oxidation of the nitrate of the vitamin with conc. HNO_3 at 60°, removal of SO_4'' (equiv. to 20% of the total S) with $Ba(OH)_2$ and of HNO_3 in vac., treatment of the residue with EtOH, and addition of 3 vols. of Et_2O, filtration, and evaporation of the filtrate in vac. affords a cryst. *substance* (I), $C_7H_{11}O_5N_3$, decomp. 146—153°, which is a nitrate and Et ester of $C_5H_6O_2N_2$. This is apparently not a glyoxaline derivative, but is possibly a dihydroxymethylpyrimidine. The residues from the prep. of (I) gave at 160°/12 mm. a cryst. *sublimate* (II), $C_5H_5O_2NS$, reddens at 200°, decomp. > 250° [*Me* ester (with CH_2N_2), m.p. 73—74°, giving a *phosphotungstate*]. (II) probably contains a free $\cdot CO_2H$ and a C:S or C·SH group. It gives the pyrrole reaction when heated with Zn dust. J. H. B.

Effect of the Clayton process on the vitamin-B_1 content of rice. A. G. van Veen and M. T. Koks (Geneesk. Tijdschr. Ned.-Ind., 1934, **74**, 482—485).—The Clayton process (action of SO_2 up to 3—4·5% concn. for about 3 hr.) caused a loss of vitamin-B_1 (I), depending on the H_2O and degree of milling of the rice and on the method of packing. When the rice was packed in small sacks the loss of (I) in dry paddy could just be detected, that in slightly milled (" silverskin ") rice was > 30%, and that in half-milled rice about 50%. With rice packed in large sacks the loss in " silverskin " rice was negligible. Pure (I) withstood aq. SO_2 at p_H 3—7, but was slowly destroyed in more conc. solution. Nutr. Abs. (*b*)

Use of unwashed, slightly milled rice as food. A. G. van Veen (Geneesk. Tijdschr. Ned.-Ind., 1934, **74**, 672—680).—All methods involving washing seriously diminish the vitamin-B_1 content of rice, whatever the degree of milling; steaming, in which the loss is relatively small, even with highly milled rice, is the preferable method of cooking. Nutr. Abs. (*b*)

Lactoflavin (vitamin-B_2) from liver. R. Kuhn and T. Wagner-Jauregg (Ber., 1934, **67**, [*B*], 1770—1773).—The flavin from ox-liver (isolation described) has m.p. 276° (Berl; decomp.) after darkening, $[\alpha]_D^{20}$ $-118°\pm10°$ in 0·05*N*-NaOH. In composition, m.p., mixed m.p., $[\alpha]_D$, and spectroscopic behaviour it is indistinguishable from lactoflavin (I). Since it is also hydrolysed by alkali to 4 : 5-diamino-*o*-xylene it is regarded as identical with (I). H. W.

Liberation of vitamin-B_2 adsorbed on acid earth by the action of pancreatin. W. Nakahara, F. Inukai, and S. Kato (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, **24**, 325—334).—Vitamin-B_2 (I) in liver extract is adsorbed completely on acid earth (II) and partly eluted (> 66%) by 1% aq. pancreatin at p_H 7·6 during 24 hr. at 32°. Pepsin has no eluent action. The eluent relieves symptoms of (I)-deficiency in a rat, the eluted (I) being more easily utilised by the animal than when fed adsorbed on (II). J. L. D.

Flavins and vitamin-B_2. I. H. von Euler, P. Karrer, and E. Adler (Arkiv Kemi, Min., Geol., 1934, **11**, B, No. 33, 6 pp.).—Ovoflavin, administered to animals simultaneously with yeast-juice [vitamin-B_4(?) (I)], induces no growth with doses $< 20 \times 10^{-6}$ g. With pure (?) lactoflavin, doses of 2×10^{-6} g. effect growth, whilst with preps. adsorbed on C or PbS and eluted with aq. C_5H_5N or hot H_2O, 5—15×10^{-6} g. produces initial but not permanent growth; fractionally eluted preps. also differ from each other. The data confirm the chemical but not biological identity of flavins, and also indicate a possible lack of (I) or some other factor from basal diets used. The purity of flavin preps. and their relation to vitamin-B_2 are discussed (cf. A., 1933, 522, 847). F. O. H.

Action of flavins on growth. H. von Euler, P. Karrer, E. Adler, and M. Malmberg (Helv. Chim. Acta, 1934, **17**, 1157—1165).—The growth-promoting action of flavins is definitely established and quant. agreement is observed in the effects produced by lactoflavin, ovoflavin *e*, hepaflavin, and the flavin from egg-yolk. The complex, non-dialysable flavin from liver and that from grass exert a B_2 action analogous to that of other flavins. H. W.

Effect of heat on vitamin-B_2 potency of desiccated yeast. F. C. Bing and D. G. Remp (Proc. Soc. Exp. Biol. Med., 1934, **31**, 624—626).—Dried yeast, heated for 2 weeks at 105°, showed no significant loss of vitamin-B_2 (I) when tested by wt. changes and production of dermatitis on mice 3 weeks old receiving a diet deficient only in (I). When heated at 150° activity was completely lost in 2 weeks. The dose of dried yeast was 1·5 g. per head per week. Nutr. Abs. (*b*)

Vitamin-B_2 concentration and possible supplementary relationships with the vitamin-B_2-deficient diet. J. W. Page, jun. (Proc. Soc. Exp. Biol. Med., 1934, **31**, 779—783).—Extraction of skim-milk powder with hot EtOH removed half the vitamin-B_2 (I), the conc. extract yielding a product ten times as active as the original powder. Pptn. of the extract with Et_2O resulted in loss of activity from both fractions. There was evidence of a variant of (I) when the preliminary depletion period was extended from 28 to 56 days. For the longer period EtOH-extracted milk powder was inadequate as a source of (I), but the Et_2O ppt., either alone or as a supplement to the extracted milk powder, enabled growth to be maintained. Nutr. Abs. (*b*)

Determination of vitamin-B_2 by fluorescence. F. H. Cohen (Acta Brev. Néerland., 1934, **4**, 46).—For the determination of vitamin-B_2 by means of its fluorescence, Kleinmann's nephelometer is used with light from a Hg lamp, filtered through a screen of Ni oxide. Nutr. Abs. (*b*)

Fluoroscope for the assay of vitamin-B_2. B. Josephy (Acta Brev. Néerland., 1934, **4**, 46—47).—In this apparatus the fluorescence of an unknown solution can be compared with that of a solution of Na fluorescein in monochromatic light. 2 ml. of material suffice. Nutr. Abs. (*b*)

Vitamin-C content of body-fluids. M. van Eekelen, A. Emmerie, B. Josephy, and L. K. Wolff (Klin. Woch., 1934, **13**, 564—565; Chem. Zentr., 1934, i, 3229; cf. A., 1933, 1090).—The vitamin-C reaction with 2 : 6-dichlorophenol-indophenol is also given by cystine and ergothionine, but these substances may be separated by pptn. with $Hg(OAc)_2$. In aq. humour and cerebrospinal fluid, ultra-violet absorption spectra show max. absorption with the same wave-length as pure vitamin-C and extinction vals. corresponding with ascorbic acid. A. G. P.

Distribution of vitamin-C in the organism. A. Giroud, C. P. Leblond, and M. Rabinowicz (Compt. rend. Soc. Biol., 1934, **115**, 1088—1091).—The wide distribution suggests that the vitamin plays an important part in general metabolism. Nutr. Abs. (*b*)

Vitamin-C in the pituitary. A. Giroud and C. P. Leblond (Compt. rend. Soc. Biol., 1934, **116**, 629—631).—Staining with $AgNO_3$ (acidified with AcOH) is believed to indicate the distribution of ascorbic acid in the pituitary, and it is suggested that the vitamin may be concerned with the function of this organ. Nutr. Abs. (*b*)

Vitamin-C in the lens. F. P. Fischer (Klin. Woch., 1934, **13**, 596—597).—Conditions in the lens are optimal for production of vitamin-C (I) because normal aq. humour is very rich in lactose, whilst that of the lensless eye (which shows practically no O_2 consumption) reaches the blood level. The lens-sugar is partly oxidised and partly glycolysed; part, however, is utilised differently. The lens has a high cystine content, and 1 mol. of sugar in presence of 2 mols. of cystine gave rise *in vitro* to 1 mol. of ascorbic acid and 4 of cysteine. The lens capsule has a peculiar selective permeability; (I) always passed through the capsule even when Fe salts and the ·SH group were retained. Lenses with cataracts allowed diffusion of all the (I) except a residue, which was retained in the capsule and subepithelial layer where the glutathione colour reaction (with CN′) was negative and yet strongly reducing properties were present. Derangement in any of the factors in the respiration of the lens leads to cataract. Whether faulty (I) formation leads to cataract or is only an associated condition is uncertain. Nutr. Abs. (*b*)

Vitamin-C content of fruit. J. Becker (Mezög. Kutat., 1934, **7**, 12—23; Chem. Zentr., 1934, i, 2779).—The vitamin-C contents of a no. of Hungarian and foreign fruits are recorded. R. N. C.

Isolation of vitamin-C from vegetables, and the relations between vitamin-C and ascorbic acid. S. Maruyama (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, **24**, 287—303).—Ascorbic acid (I) is isolated from *Rhapanus sativus*, L. (radish), and from the juice of *Citrus aurantium*, L. (a Japanese lemon), by a modification of Szent-Györgyi's method (A., 1929, 98). Japanese green tea also contains (I). J. L. D.

Antiscorbutic value of lemon juice in relation to preserving media. Comparison of Tillmans' chemical method and the biological method for determining vitamin-C. R. Cultrera (Ind. ital. Conserve aliment., 1934, **9**, 1—8; Chem. Zentr., 1934, i, 1668).—The methods give vals. which are in good agreement. Preservation with 0·35% SO_2 destroys the vitamin-*C* almost completely in 98 days, but sterilisation by Matzka's method left 70% after 180 days. L. S. T.

Biological and titrimetric determination of vitamin-*C*. H. Lund, B. Spur, and L. S. Fridericia (Biochem. J., 1934, **28**, 1825—1828).—Assays of vitamin-*C* (I) by biological and titrimetric methods [Tillmans' method (A., 1932, 310) slightly modified] yield results in fairly good agreement. For the guinea-pig, the necessary daily addition of (I) to a (I)-free diet is about 0·7 mg. Dried hips contain 1·5% of (I). Lemon juice is unsuitable as a (I) standard. A. E. O.

Effect of chemico-physical agents on the Szent-Györgyi and Tillmans reducing factor. R. Cultrera (Ind. ital. Conserve aliment., 1934, 9, 9—18; Chem. Zentr., 1934, i, 1668).—Ultra-violet light quickly destroys the reducing factor (I). H_2O_2 has a strong oxidising action, but nascent H does not reduce. A rise in temp. destroys (I): at p_H 1·4—5·2 the decomp. proceeds relatively slowly; it is quicker at p_H 6·7, and at p_H >7 it occurs at room temp. L. S. T.

Determination of vitamin-*C* in animal tissues by a modification of the silver method. E. Harde (Compt. rend. Soc. Biol., 1934, **116**, 153—155).—MeOH extracts of various tissues of normal and scorbutic guinea-pigs, and of rats and mice on normal and vitamin-*C*-free diets reduced $AgNO_3$. The distribution of this $AgNO_3$-reducing substance in the bodies of these animals agreed with that recorded for ascorbic acid (I), with which it is concluded to be identical. A similar extract of tumour tissue, which reduced indophenol, also reduced $AgNO_3$, but it is doubted whether, in this case, reduction was due to (I). Nutr. Abs. (*b*)

Effect of ageing on potency of spray-dried antiscorbutic material. H. J. Gerstenberger, D. N. Smith, and G. L. Hacker (J. Pediat. St. Louis, 1933, **3**, 93).—Fresh orange juice (I), spray-dried as a constituent of a lactose–(I) mixture, retains its antiscorbutic potency undiminished for at least 15 months. Scorbutic guinea-pigs were cured by the daily administration of an amount of the prep. equiv. to 3 ml. of (I), and a human infant by a daily dose equal to 45 ml. of (I). Fresh lemon juice, spray-dried as a constituent of an acid protein milk to which are added at the time of manufacture 20 ml. of lemon juice per litre, was adequate to cure scurvy in scorbutic infants 5—23 months after its manufacture. Nutr. Abs. (*b*)

Assay of ascorbic acid with respect to its effect on oxygen consumption in young guinea-pigs. N. Törnblom (Skand. Arch. Physiol., 1934, **68**, 171—180; Chem. Zentr., 1934, i, 3488).—A daily dose of 9 mg. of ascorbic acid (I) per kg. protects young guinea-pigs on an otherwise vitamin-*C*-free diet against scurvy (II). No marked difference was found in the O_2 consumption (III) from that of animals receiving standard lemon juice instead of (I). Animals on a vitamin-*C*-free diet showed, towards the end of (II), a somewhat reduced (III) compared with both of the above groups. R. N. C.

Origin of vitamin-*C* in the mouse. E. Harde and J. Wolff (Compt. rend. Soc. Biol., 1934, **116**, 288—290).—The intestinal mucosa of the mouse, maintained on a vitamin-*C*-free diet, possessed a substance which reduced both $AgNO_3$ and indophenol. Its concn. here was > in the liver, but, in the absence of biological tests, it could not be definitely identified with ascorbic acid. Nutr. Abs. (*b*)

Protection of ascorbic acid from oxidation by animal tissue. L. de Caro and M. Giani (Z. physiol. Chem., 1934, **228**, 13—24).—Aq., EtOH, or $CCl_3{\cdot}CO_2H$ extracts of tissue (guinea-pig) inhibit atmospheric oxidation of ascorbic acid *in vitro*. The aq. extract preserves this power in the filtrate after pptn. with Pb or Hg salts. Ringer's solution and its salt constituents at 0·1*M* concn. show marked inhibition. Glucose, fructose, and sucrose are inactive, glycine and alanine have a weak, yeast-adenylic acid a stronger, cysteine and glutathione, even in oxidised form, a very strong inhibitory action comparable with that of KCN. J. H. B.

Colour reaction of *iso*ascorbic acid (*iso*-vitamin-*C*). M. Bachstez and G. Cavallini (Z. physiol. Chem., 1934, **228**, 25—26).—Aq. *iso*ascorbic acid (1%), when made slightly alkaline and treated with 2 drops of 10% $UO_2(OAc)_2$, gives a weak brownish colour which becomes deep brown-red but with no formation of ppt. on addition of conc. NaOH. With ascorbic acid similarly treated, conc. NaOH causes disappearance of the colour and formation of a ppt. J. H. B.

Occurrence of vitamin-*E* in soya-bean oil. U. Suzuki, W. Nakahara, and Y. Sahashi (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1934, **24**, 283—286; cf. this vol., 705).—The vitamin-*E* (I) content is low, since pregnancy in female albino rats with soya-bean oil as sole source of (I) is frequently terminated by abortion. J. L. D.

Growth factor in liver. O. L. Kline, C. A. Elvehjem, J. A. Keenan, and E. B. Hart (J. Biol. Chem., 1934, **107**, 107—118).—A growth factor for chicks has been demonstrated in liver (I). It is stable to heat and insol. in H_2O, but sol. after mild hydrolysis of (I), when it is slightly sol. in $Bu^{a}OH$. It is destroyed by autoclaving at p_H 9 for 5 hr. at 1 atm. H. G. R.

Synergistic and antagonistic behaviour of vitamins in the organism. H. J. Jusatz (Z. Vitaminforsch., 1934, **3**, 268—279).—A review.

Long and short wave-length limits of photosynthesis. G. R. Burns (Plant Physiol., 1934, 9, 645—652).—Leaves of white pine and Norway spruce utilised all the visible spectrum except part of the blue and all the violet range. A. G. P.

Assimilation of carbon dioxide by plants. P. Klason (Svensk Kem. Tidskr., 1934, **46**, 208—211).—A discussion of the origin of xylose and lignin in photosynthesis. R. P. B.

Carbon dioxide storage. VI. Lowering the acidity of fungal hyphæ by treatment with carbon dioxide. VII. Changes in flower colour as evidence of the effectiveness of carbon dioxide

in reducing the acidity of plant tissue. N. C. Thornton (Contr. Boyce Thompson Inst., 1934, **6**, 395—402, 403—405; cf. B., 1933, 1032).—VI. In cultures of *Sclerotinia fructicola* exposure to CO_2 increased the p_H of the hyphæ to extents which retard growth. The action of CO_2 at 2° was > that at 15° or 28°.

VII. Colour changes of the anthocyanin pigment in petals of rose, verbena, peony, and iris, confirmed by direct p_H determinations, indicate the action of CO_2 in increasing the p_H of living plant tissues.

A. G. P.

Colonial formation of unicellular green algæ under various light conditions. F. E. Meier (Smithsonian Miscell. Coll., 1934, **92**, No. 5, 14 pp.).—The effect of lighting on growth, chlorophyll (I) formation, etc. is recorded for 18 species. The majority form (I) even in continuous darkness. L. D. G.

Effects of intensities and wave-lengths of light on unicellular green algæ. F. E. Meier (Smithsonian Miscell. Coll., 1934, **92**, No. 6, 27 pp.).—Intermittent illumination is the most favourable to growth. Between the limits of 3·76 and 10·20 microwatts per sq. mm. increase in no. of cells $\propto$ intensity of light for 12 out of 16 species tested. *Stichococcus bacillaris* grows well at a wide range of red and infra-red from 0·6 to 1·4 μ. L. D. G.

Effect of alkyl halides on the respiration of potato tubers. L. P. Miller (Contr. Boyce Thompson Inst., 1934, **6**, 279—296).—The increase in CO_2 output of tubers was approx. the same following treatment with Et, Pr^a, Bu^a, *n*- or *iso*-amyl bromide (0·05 c.c. per litre), and considerably smaller for Pr^β and *sec.*-Bu compounds. The efficacy of Bu bromides was in the descending order, *n*, *iso*, *tert.*, *sec.* At similar concns. the activity of bromides and iodides was approx. the same and > that of chlorides. In general, the effect of the halides increases with the dosage. The action of these substances on respiration is unrelated to that on dormancy. A. G. P.

Effect of *X*-rays on growth and respiration of wheat seedlings. D. S. Francis (Bull Torrey Bot. Club, 1934, **61**, 119—153).—Exposure to radiation retarded fresh- and dry-wt. production and, except in very young seedlings, depressed respiration. The effects varied with dosage and time. Sensitivity was greatest in lateral roots and least in coleoptiles.

Ch. Abs. (*p*)

Distribution of activity in the chemistry of higher plants. A. Tschirch (Helv. Chim. Acta, 1934, **17**, 992—996).—Evidence is adduced that chemical reactions in higher plants occur in the cell-sap colloid and in the intercellular material as well as in the plasma. Electro-chemical work in plants is due to the morphology of the participating bio-colloids.

H. W.

Action of certain salts on the germination of grain embryos outside the grain. G. Dragone-Testi (Atti R. Accad. Lincei, 1934, [vi], **20**, 59—63).—The growth of grain embryos on Knop's solution is stimulated by addition of various salts, notably by borax and $ZnSO_4$. T. H. P.

Chemical changes in carrots during growth. H. Platenius (Plant Physiol., 1934, **9**, 671—680).—With advancing growth carrots do not deteriorate in quality or in food val. Older carrots have higher sucrose and carotene and lower crude fibre contents. Roots, but not tops, contain small amounts of starch.

A. G. P.

Influence of dyes and hormones on the growth of plants. J. Sellei (Arch. Pharm., 1934, **272**, 737—743).—Addition of eosin, quinine, or methylene-blue to the soil hinders the development of wheat grains. Various animal hormone extracts have similar effects, but ovarian and testicular hormones cause an increased growth at a relatively late stage.

R. S. C.

Potentially unlimited growth of excised tomato root tips in a liquid medium. P. R. White (Plant Physiol., 1934, **9**, 585—600).—Root tips appeared capable of indefinite growth in culture solutions in which sucrose provides carbonaceous matter normally supplied by the aërial parts of the plant. A. G. P.

Effects of clipping the tops on root development of lucerne (*Medicago sativa*, L.). H. G. Thornton and H. Nicol (J. Agric. Sci., 1934, **24**, 532—539).—Clipping lucerne plants did not affect the no. or size of nodules formed, or the N content of the whole plants. Root-N, however, was reduced by 40%. A. G. P.

Test method for rhizocalin, the root-forming substance. F. W. Went (Proc. K. Akad. Wetensch. Amsterdam, 1934, **37**, 445—455).—Etiolated pea (*Pisum sativum*) shoots are cut off just above the first node and the tip is removed below the third node. The cut plants are placed with their bases in H_2O (4 hr.) and then in 0·05% aq. $KMnO_4$ (4 hr.). The apex of the shoot is slit and the plants are inverted in the rhizocalin (I) solution under test (15 hr.), a set of controls being placed in H_2O. The test plants and controls are then placed with their bases in 2% sucrose (6 days) and finally in H_2O (7 days) and the no. of roots (II) is counted. A linear relationship exists between the concn. of (I) and (II) and the amount of (I) is calc. (in root units) from concns. giving suboptimal root formation. The very few roots grown on controls are due to small amounts of (I) stored in the nodular scales. The polar transport of (I) is due to p.d. inside the pea shoot. A paste of (I) in lanolin is suggested as suitable for inducing root formation in practice. S. C.

Chemical nature of the root-forming hormone. K. V. Thimann and F. W. Went (Proc. K. Akad. Wetensch. Amsterdam, 1934, **37**, 457—459).—The root-forming hormone is an unsaturated acid, *pK* 4·5 approx., oxidised by H_2O_2, neutral $KMnO_4$, and I but not by BzO_2H, very similar to but not identical with auxin. Root-producing and growth-promoting activities of hormones from various sources including Kögl's auxin-*a* and- *b*, heteroauxin, and conc. rhizocalin preps. from urine and *Rhizopus suinus* are recorded. S. C.

Plant growth-substances. XI. Auxin ("hetero-auxin") from urine. XII. Influence of auxins on root-growth and chemical nature of the auxin of grass coleoptiles. F. Kögl, A. J.

HAAGEN-SMIT, and H. ERXLEBEN. **XIII. Hetero-auxin as metabolic product of the lower plant organisms. Isolation from yeast.** F. KÖGL and D. G. F. R. KOSTERMANS (Z. physiol. Chem., 1934, **228**, 90—103, 104—112, 113—121; cf. this vol., 1332).—XI. A substance, having similar growth-stimulating properties to auxin-*a* (I) and -*b* (II), isolated from human urine proved to be β-indolylacetic acid, now termed "hetero-auxin" (III). Indole-2- and -3-carboxylic and β-3-indolylpropionic acids are physiologically inactive. (III) as isolated showed optical rotation due to an isomorphous *substance*, m.p. 167°, $[\alpha]_D^{20}$ —34·3° in EtOH, which was separated by chromatographic analysis.

XII. (III) inhibits the growth (in length) of the roots of oat plants when present in the H_2O in which the plants are grown in concns. of 0·01—1 mg. per litre. In this respect it behaves like (I) and (II). The mol. wt. of the growth-substance in the growing tip by the diffusion coeff. method (Went technique) is 300—400, which agrees with (I) or (II) but excludes (III). The activity of the maize-tip auxin is destroyed by 0·5*N*-KOH at 100° (3·5 hr.) but unchanged by 5% HCl at 100° (3 hr.). This excludes (II) and (III) but agrees with the properties of (I), which is therefore most probably the growth hormone present in plant tips.

XIII. The plant growth-substance present in yeast was isolated from an autolysate after preliminary enrichment by Et_2O extraction. Its identity with (III) was confirmed by m.p., sensitivity to acid and alkali, and mol. wt. by diffusion coeff. The growth-substance produced by *Rhizopus nigricans* and *Aspergillus niger* when grown on substrates containing org. N is also (III). J. H. B.

Influence of growth-promoting substances on barley mutants. I. H. VON EULER, D. BURSTRÖM, and M. MALMBERG. **II.** H. VON EULER, D. BURSTRÖM, and H. LARSSON (Arkiv Kemi, Min., Geol., 1934, **11**, B, No. 38, 6 pp., No. 39, 5 pp.).—I. Bios preps. from malt (this vol., 696) have a slight growth-promoting action (I) (indicated by dry wt. and length of root) on seedlings of normal and chlorophyll-defective Albina barley mutants; the content of bios is not changed either in the nutrient media or in the roots. Neither inositol (A., 1928, 1152) nor folliculin (II) (this vol., 224) has any marked (I); most of (II), however, disappears from the medium.

II. Pike eggs are rich in bios but poor in flavins, whilst hen's egg-yolk has high contents of bios, vitamin-B_2, and flavins. Birch and elm pollen contain little bios, whilst $9\times10^{-4}\%$ of flavins occurs in the former. Neither $ZnCl_2$ nor $ZnCl_2$+bios has any (I) on the mutants. $ZnCl_2$ inhibits yeast fermentation and accelerates the reduction of methylene-blue or (II) (to testicular hormone) by barley roots. F. O. H.

Nature of indole base from barley mutants Albina 1 and 3. H. VON EULER, H. HELLSTRÖM, and J. HAGEN (Arkiv Kemi, Min., Geol., 1934, **11**, B, No. 36, 6 pp.; cf. A., 1933, 877).—Extraction of the chlorophyll-defective mutant Albina 1 with EtOH followed by Et_2O and aq. HCl digestion gives an aq. layer with absorption bands (I) at 270 and 325 mμ and a weaker one at 288 mμ, the latter being also found in Et_2O extracts. Adsorption on acid clay and elution with C_5H_5N yield solutions with (I) of 330 mμ max., stable to aq. NaOH. On keeping, aq. extracts acquire (I) between those of C_6H_6 and PhMe. This Ph derivative is not volatile in steam and is derived from the indolyl base by bacterial action. The base is not a growth-promoting factor for yeast. F. O. H.

Vegetative and reproductive responses associated with fruit development in the cucumber. J. P. MCCOLLUM (Cornell Univ. Agric. Exp. Sta. Mem., 1934, No. 163, 27 pp.).—The inhibitive effect of the development of fruits on the general growth of plants is not related to mineral nutrition or to carbohydrate accumulation within the plant. The presence of a growth-regulating substance in the fertilised ovary is indicated. A. G. P.

Accumulation of tannin in the cells of chestnut wood. M. QUENDIAC (Compt. rend., 1934, **199**, 799—801).—In early spring tannins are localised in areas in which sap flow is restricted, notably in the parenchyma of the sap wood. In May accumulation zones extend towards the extremity of branches. Subsequently the sapwood develops two distinct regions, one normal and one with tannin accumulations corresponding with the zone of transition between heart- and sap-wood. A. G. P.

Growth and elasticity of cell walls in the hypocotl of *Helianthus*. F. GESSNER (Jahrb. wiss. Bot., 1934, **80**, 143—168).—Elasticity of cell walls (I) decreases with rising temp. and is not influenced by variations in the H_2O content within vital limits. Elimination of "growth substance" by decapitation causes a decline in (I). In NaOAc solutions (I) varies with $[H^{\cdot}]$ in the range p_H 5·5—4·0. (I) is not altered by changes in lighting, but decreases on exposure to ultra-violet light. Living cells only are affected. Reduced (I) and growth restriction are not necessarily parallel phenomena. A. G. P.

Seasonal cycles of nitrogenous and carbohydrate materials in fruit trees. I. Seasonal cycles of total nitrogen and of soluble nitrogen in wood, bark, and leaf portions of terminal shoots of apple trees under two cultural systems—grass *plus* annual spring nitrate, and arable without nitrogenous fertiliser. D. V. KARMARKAR (J. Pomology, 1934, **12**, 177—221).—Well-defined cycles in the total sol. matter, total N (I), protein- (II), and various fractions of non-protein-N (III) of wood and bark are established. Max. vals. for wood-N occur in June. In bark, peak vals. for (I), (II)-, humin-, and imide-N appear during dormancy, and those for (III), basic, and residual N at the beginning of the dormant period (November). The N cycle in leaves is different in character. (I) and (II) decline, especially in autumn, with a corresponding increase in (III) in leaves and in (I), (II), and (III) in bark. (I) and the % of (II) in (I) increase in the order, wood<bark<leaves. In manured grass plots the % of (II) and (I) in bark and wood is > that in arable. The distribution of the fractions of (III) is not greatly affected by differences in the method of culture. A. G. P.

Effect of ethylene, ethylene chlorohydrin, and ultra-violet light on carbohydrate content of stored apples. R. B. Dustman (Plant Physiol., 1934, 9, 637—643).—None of these treatments affected the composition of the fruit or the p_H of expressed juice. C_2H_4 hastened the colour change and accelerated the softening of the fruit. A. G. P.

Metabolism of citric, sulphuric, and nitric acids in the potato tuber. Explanation for the high p_H of the juice of tubers treated with ethylene chlorohydrin. J. D. Guthrie (Contr. Boyce Thompson Inst., 1934, 6, 247—268).—The expressed juice of tubers treated with $CH_2Cl{\cdot}CH_2{\cdot}OH$ shows decreased contents of SO_4'', NO_3', citrate, Ca, Mg, and total ash. The increased p_H is $<$ that anticipated as a result of the above changes. Three days after treatment the juice has less buffer power on the acid side (probably due to loss of citric acid), but regains normal val. after 6 days as a result of the appearance of amphoteric substances (NH_2- and other non-amide forms of N). Buffers occurring in juice include NH_2-acids and asparagine (p_H 8—10), and these together with citric and malic acids in the range p_H 8—3. Phosphates exert buffer effects between p_H 8 and 6. A. G. P.

Carbohydrate and nitrogen relations in wheat plants with reference to type of growth under different environmental conditions. A. M. Hurd-Karrer and A. D. Dickson (Plant Physiol., 1934, 9, 533—565).—Leaves of plants grown with short-period lighting (8 hr.) (I) had higher N and lower carbohydrate contents than those with prolonged lighting (17 hr.). Supplementary lighting of high intensity induced higher proportions of acid-hydrolysable matter (II) and lower % N than weaker lighting without affecting the rate of growth or external appearance. Growth on limed soils (p_H 8·1) produced lower proportions of sugar and higher (II) than did that on neutral soils. (II) was not affected by temp. (I) and low temp. are associated with high p_H in the plant juice. The latter was not appreciably influenced by the intensity of light or by soil reaction. A. G. P.

Separation of cellulose particles in membranes of cotton fibres by treatment with hydrochloric acid. W. K. Farr and S. H. Eckerson (Contr. Boyce Thompson Inst., 1934, 6, 309—313).—Treatment of mature fibres with HCl (*d* 1·19) for periods up to 5 days removed non-cellulose constituents, without affecting the essential characteristics of the cellulose. A. G. P.

Starch determination methods involving solubility in acids. F. E. Denny (Contr. Boyce Thompson Inst., 1934, 6, 381—393).—Low vals. obtained by Rask's method (B., 1927, 311) are not due to hydrolysis of starch (I) during contact with HCl, but probably to incomplete extraction of (I) by the procedure adopted. From solutions in HCl, after 1 hr. at 20—25° (I) may be recovered almost completely by coagulation in EtOH. H_2SO_4 may similarly be used. Repeated extraction of tissues with acid removes all (I), but the ppt. obtained with EtOH may be contaminated with foreign substances. Determination of (I) in the ppt. by hydrolysis leads to vals. comparable with those of other methods. The taka-diastase method gives higher results than other methods in some cases, owing to hydrolysis of non-starchy constituents to give Cu-reducing substances. A. G. P.

Pectic constituents of citrus fruits. L. W. Gaddum (Florida Agric. Exp. Sta. Bull., 1934, No. 268, 23 pp.).—In orange, grapefruit, and kumquat the % of total pectic material (I) in the albedo and in the pulp remains const. through a considerable part of the growth period. The H_2O-sol. pectins (II) rise to a max. val. immediately prior to the decline in (I), and subsequently decrease. The degree of methylation (*M*) of (II) is $<$ that of acid-extracted pectins (III). With advancing maturity the *M* of (II) declines but that of (III) remains approx. const. The *M* of pectins from various sections of the fruit increases in the order juice, pulp, albedo. The *M* of (II) is closely related to their viscosity. The Ca content of the various pectates approached a mean val. between 7·4 and 7·6%. A. G. P.

Determination of sugar in plant-saps by means of Fehling's solution. P. Crisci (Atti Congr. naz. Chim., 1933, 4, 705—714; Chem. Zentr., 1934, i, 2322).—Clarification with $Pb(OAc)_2$ if prolonged $>$ 30 min. may lead to low vals. for sugar. A. G. P.

Synthesis of sucrose in plant tissue. A. I. Virtanen and M. Nordlund (Biochem. J., 1934, 28, 1729—1732).—Leaves of red clover and wheat, deprived of starch by storage in the dark, synthesise sucrose from both glucose and fructose, to the extent of 6% of the dry wt. of the leaf, when kept in a 10% solution of the sugar in the dark for 24 hr. C. G. A.

Glucoside from madder. R. Hill (Nature, 1934, 134, 628).—A yellow cryst. glucoside of ψ-purpurin (I), named *galieide* (II), m.p. indefinite (decomp.), has been prepared from the roots of wild madder (*Rubia peregrina*) and the yellow bedstraw (*Galium verum*). (II) appears to be a 1-monopentoside of (I), and is easily hydrolysed. (II) is responsible for the dyeing properties of the above plants. L. S. T.

Glucoside of *Bryonia dioica*. A. Angeletti and D. Ponte (Gazzetta, 1934, 64, 569—577).—The roots of *B. dioica* ("stabilised" by inactivating the enzymes) contain KNO_3, a small amount of essential oil, an amorphous alkaloid, and the amorphous glucoside brionin, $C_{48}H_{66}O_{18}$, which yields on hydrolysis 1 mol. of glucose, 1 mol. of briogenin, $C_{30}H_{46}O_6$, and a resinous substance, $C_{12}H_{12}O_8$(?) (cf. Power and Moore, J.C.S., 1911, 99, 937). R. K. C.

Bitter glucoside of the olive. W. V. Cruess and C. L. Alsberg (J. Amer. Chem. Soc., 1934, 56, 2115—2117).—Details are given for the extraction and purification of the glucoside (oleuropein) (I) (C 53·65, H 6·51, O 39·84%), *M* 433 (f.p. in AcOH), 470 (b.p. in EtOH), $[\alpha]$ $-145°$ to $-148°$ in H_2O (cf. Bourquelot and Vintilesco, A., 1908, i, 904), which reduces Fehling's solution (reducing power 0·47; glucose 1) and aq. $KMnO_4$ (reducing power 0·45; tannin 1). When an aq. solution of (I) is boiled, an insol. resin, $[\alpha]^{20}$ $-116{\cdot}8°$ in EtOH, is pptd.; this is probably a "phlobaphen" similar to that obtained from o-$C_6H_4(OH)_2$-tannins. (I) is hydrolysed slowly by emulsin (not by invertase) and rapidly by "pectinol" (a mould enzyme prep.).

Hydrolysis (2% H_2SO_4) of (I) gives glucose and a bitter ester, which is readily hydrolysed by alkali with loss of the bitter taste. Cold dil. NaOH converts (I) into a non-bitter glucoside; 3% NaOH or 4% $Ba(OH)_2$ at 80—100° gives $3:4\text{-}(OH)_2C_6H_3\cdot CH{:}CH\cdot CO_2H$, whilst energetic alkaline hydrolysis affords a little unidentified phenol, m.p. 91·5°. The amounts of (I) in different varieties of olives are determined. H. B.

Presence of urson in *Arbutus unedo*, L. A. Sanna (Atti Congr. naz. Chim., 1933, **4**, 595—596; Chem. Zentr., 1934, ii, 622).—Urson, obtained from the EtOH extract from crushed leaves of *A. unedo* (I), has m.p. 278° (*Ac*, m.p. 264°, and *Bz* derivative, m.p. 214°). With Ac_2O and a trace of H_2SO_4, a violet colour is produced. Arbutin and methylarbutin also occur in (I). A. G. P.

Organic principle in *Eupatorium ayapana*, Vent. N. C. Nag and K. N. Bose (Trans. Bose Res. Inst., 1932—1933, **8**, 195—198).—The syrupy residue from a hot H_2O extraction of the dried leaves is extracted with 5 vols. of 91% EtOH. After filtration from inorg. salts, the EtOH is removed and the residue shaken with light petroleum, which affords a cryst. *substance*, $C_{12}H_{10}O_4$, m.p. 110—112°, giving a violet colour with conc. H_2SO_4. P. G. M.

Constituents of miso. IV. Acids. Y. Sakurai (J. Agric. Chem. Soc. Japan, 1934, **10**, 486—495).—AcOH, lactic and succinic acids are identified. Amounts of Et_2O-sol. free acid were small. Acidity is probably due to acid phosphates. Ch. Abs. (*p*)

Formation of phenols in plants. T. K. Gaponenkov (J. Gen. Chem. Russ., 1934, **4**, 466—471).—Thymol, carvacrol, and other phenols originate probably by oxidation of *p*-cymol, and terpenes (phellandrene) by reduction. The thymol content of Ashgon plants increases with their stage of maturity; that of the seeds increases on storing, but falls on germination. R. T.

Formation of terpenes. G. V. Pigulevski (J. Gen. Chem. Russ., 1934, **4**, 603—609).—The view that essential oils (I) arise from the decomp. of resin acids is supported by the co-existence in natural (I) of different compounds of the same general structure and of the same type of mol. asymmetry. R. T.

Chemical examination of *Celastrus scandens*. N. Wakeman (J. Amer. Pharm. Assoc., 1934, **23**, 873—874).—Leaves (I), stem (II), root (III), and fruit (IV) were separately submitted to successive extraction with light petroleum, Et_2O, and EtOH. (I) gives chlorophyll, sterols (V), and a white cryst. non-reducing *substance* (VI), m.p. 182°, yielding galactose on hydrolysis. (II) gave (V) and (VI) together with a substance, m.p. 186°, resembling dulcitol. The red bark of (III) yields β-carotene and an orange powder. C. G. A.

Constituents of *Ginkgo biloba*, L., fruit.—See this vol., 1345.

Preparation of humate–iron and other humate–metals. C. K. Horner, D. Burk, and S. R. Hoover (Plant Physiol., 1934, **9**, 663—669).—Synthetic and natural humates containing Fe, Al, Mn, Zn, Ni, Cu, and other metals have been prepared. Small applications of humates to plant culture media normally supply sufficient metal for entire growth requirements. The compounds are stable in alkaline, neutral, and moderately acid media and are not pptd. by PO_4'''. A. G. P.

Characteristics and composition of coffee-bean oil. H. A. Schuette, M. A. Cowley, and C. Y. Chang (J. Amer. Chem. Soc., 1934, **56**, 2085—2086).—The oil (I) extracted from green Santos beans (freed from wax with $C_2H_2Cl_4$) by light petroleum has d^{25} 0·9653, n^{25} 1·4790, I val. (Wijs) 100·72, sap. val. 195·53, Reichert–Meissl val. 0·36, Polenske val. 0·4, acid val. 7·05, OH val. 22·82, and contains 12·63% of unsaponifiable matter (I val. 153·8). (I) gives oleic (12·36%), linoleic (25·66%), myristic (2·19%), palmitic (20·17%), stearic (9·13%), and arachidic acid (2·11%) (cf. Heiduschka and Kuhn, this vol., 465; Bengis and Anderson, *ibid.*, 710). Data previously reported (lit.) for (I) refer (usually) to the wax-containing oil. H. B.

Embryo and testa of kaoliang (*Andropogon sorghum*, Brot.). I. Oils. R. Yamamoto and M. Ninōmiya. **II. Decomposition of oil.** R. Yamamoto, M. Ninomiya, and A. Otaka (J. Agric. Chem. Soc. Japan, 1934, **10**, 248—256, 257—264).—I. The embryo oil (I), m.p. −17° to −21°, *d* 0·8964—0·9263, *n* 1·4566—1·4735, has I val. 115·10—124·10, sap. val. 179·7—192·0, Reichert–Meissl val. 0·18—0·81, acid val. 3·11—21·21, and unsaponifiable matter 2·57—3·43%. Testa oil (II), m.p. 60—62·5°, *n* 1·4570, has I val. 110·8, sap. val. 185·8, Reichert–Meissl val. 0·73, Ac val. 18·8, Hehner val. 90·01, Polenske val. 0·46, acid val. 96·47, unsaponifiable matter 8·04%.

II. Acid vals. of (I), and particularly (II), increase *in situ*. The lipase in the embryro bud has optimum p_H 4·2; it is inactivated in 1 hr. at 90° or 3 hr. at 60°. Ch. Abs.

Sicilian sumach-seed oil. G. A. Bravo (Annali Chim. Appl., 1934, **24**, 427—430).—On extraction with light petroleum, the seeds of *Rhus coriaria* yield about 14% of a yellowish-brown oil, *d* 0·9128, n^{20} 1·4772, optically inactive and not fluorescent, acid val. 9·6, sap. val. 191·9, I val. (Hübl) 97·5, Reichert–Meissl val. 1·2, unsaponifiable matter (containing phytosterol and a resin) 1·63%. The colour reactions of the oil and properties of its fatty acids are given. The % composition is calc. on the assumption that the only glycerides present are triolein, trilinolein, tristearin, and tripalmitin. D. R. D.

Oils from leguminous pulses. H. N. Banerjee (Trans. Bose Res. Inst., 1932—1933, **8**, 199—210). Et_2O-extraction of green moog gave 0·5% of oil, sap. val. 171·2, I val. 111·9, unsaponifiable matter 12·3% from which phytosterol was obtained. Vitamin-*A* and -*D* were present in the oil obtained from *Kabuli chhola*, sap. val. 185·3, I val. 72·44, unsaponifiable matter 3·4%; phytosterol was also isolated. P. G. M.

Resin from *Achras zapota*, Linn. (Sawo Manila), fruit. A. J. Ultée (Pharm. Weekblad, 1934, **71**, 1152—1154).—The resin (ash 0·86, proteins 1·8, aq. extract 11·14, EtOH extract 84·03, gutta-percha 9·19%), gave 1% of γ-chicle-alban and consisted mainly of β-amyrin; α-amyrin and lupeol were not detected. Hexoic acid was isolated from the hydrolysed material. S. C.

Effects of potassium on the growth of sugar cane and on the absorption and migration of ash constituents. C. E. Hartt (Plant Physiol., 1934, **9**, 399—452).—In sand cultures K deficiency was marked by depressed growth, leaf discoloration, die-back of leaf tips, and reddening of midribs. The latter is attributed to the presence of phloroglucinol (I) and sufficient SO_4'' in the plants. (I) is probably derived from decomp. of tannic acid as a result of K deficiency. Plants deprived of K and Na were not inferior to those receiving Na but no K. Those previously deprived of Na and K recovered after K additions, more rapidly than those previously deprived of K only. In nearly all cases, all organs contained more K than Na even when Na was supplied in relative excess. Absorption of K during the first month $\propto$ the size of the plant, but at later stages $\propto$ the amount supplied. Addition of K to K-deficient plants was followed by rapid absorption and increased growth, but the intake of Mg and P was depressed. K absorption was not affected by light. Deficiency of K is associated with increased intake of P, Fe, Ca, Mg, and Si during the first few months of growth, and with nodal accumulations of Fe. The latter was translocated to leaves after replenishment of the K supply. A. G. P.

Effects of potassium on the amounts of protein- and amino-nitrogen, sugars, and enzyme activity of sugar cane. C. E. Hartt (Plant Physiol., 1934, **9**, 453—490).—The expressed juice of K-deficient plants (I) had similar p_H, titratable acidity, and buffer systems to that of controls (II). After 2 months' growth blades and stems of (I) had more NH_2- and less protein-N than (II) The relationship was reversed in stems at a later stage. K starvation restricts both synthesis and translocation of K, but reduction of NO_3' remains normal. The total sugars of leaf blades were not appreciably affected by the K supply, but reducing sugars were higher and sucrose was lower in (I). In stems a positive correlation was observed between the K supplied and the total sugar stored. Optimum invertase (III) activity occurred at p_H 4·4. K is not essential for the formation of (III), but is a sp. activator. Amylase activity (IV) in blades was optimum at p_H 5·9; that in stems was little affected by $[\text{H}^{\cdot}]$. (IV) was higher in (I) than in (II). Optimum p_H for the ereptase (V) of blades and roots was 4·9, and that of stems, 5·9. K deficiency affected (V) only in roots, in which activity increased. A. G. P.

Influence of potassium on the nitrogen and carbohydrate metabolism of plants. T. W. Turtschin (Z. Pflanz. Düng., 1934, **A**, **35**, 343—357).—Deficiency of K retards assimilation of mineral N, and, when the latter is in the form of $\text{NH}_4^{\cdot}$, leads to toxic accumulation of NH_3 within the plant. High Ca or Na in association with insufficient K causes accumulation of non-protein-N and in some instances of glucose. The unfavourable effects of excessive Cl′ in fertilisers result from the formation of CaCl_2 in soil (by base exchange), the subsequent increased intake of Ca by plants, and the disturbed metabolism due to high Ca : K ratio. K fertilisers counteract the injurious effects of heavy $\text{NH}_4^{\cdot}$ manuring. A. G. P.

Cuticular excretion of leaves. K. Arens (Jahrb. wiss. Bot., 1934, **80**, 248—300).—The excretion is alkaline and contains K, Ca, Mg, P, and org. matter. The total ash of leaves may be reduced by 50% by washing with distilled H_2O for 24 hr. A. G. P.

[Composition of] dandelions. G. E. Youngburg (Science, 1934, **80**, 337; cf. this vol., 1275).—The P content is given. L. S. T.

Use of tartrazine in the determination of chlorides in biological material. W. L. Fearon and W. A. Gillespie (Biochem. J., 1934, **28**, 1629—1630).—Tartrazine is recommended as an indicator in this determination. Proteins interfere and an indirect procedure, for use in their presence, is described. H. N. R.

Micro-determination of bromine in biological fluids. T. Leipert and O. Watzlawek (Z. physiol. Chem., 1934, **226**, 108—115).—The material (blood, milk, urine) is oxidised with Ag_2SO_4–CrO_3–H_2SO_4 and the liberated Cl_2 and Br are retained by NaOH. The NaBr and NaOBr are oxidised by NaOCl to NaBrO_3, which is determined iodometrically after addition of KI. J. H. B.

Colorimetric micro-determination of arsenic. G. Taubmann (Arch. exp. Path. Pharm., 1934, **176**, 751—756).—The material (containing 0·1—0·4 mg. As), *e.g.*, blood, is digested with H_2SO_4–H_2O_2 and treated by the Marsh method. The AsH_3 evolved is passed through aq. AgSO_4, excess of AgSO_4 removed, the dissolved As_2O_3 oxidised by Br, and As_2O_5 determined colorimetrically (A., 1932, 963). F. O. H.

Biological method for the determination of calcium-ion concentration. F. C. McLean and A. B. Hastings (J. Biol. Chem., 1934, **107**, 337—350).—The isolated frog's heart is sensitive to changes in $[\text{Ca}^{\cdot\cdot}]$ (I) but not to non-ionised Ca, the criterion for equal (I) being equal amplitude of contraction of the ventricle. A sensitivity to differences of (I) of 1 mg. per litre has been demonstrated. A. E. O.

Determination of nitrate-nitrogen by the Devarda process. Application to biological media. D. Bach (Bull. Sci. pharmacol., 1933, **40**, 459—470; Chem. Zentr., 1934, i, 1679).—Reduction of NO_3' to NH_3 in $< 0.05N$-NO_3' solution with $0.2N$-NaOH and 0·05 g. of Devarda alloy per c.c. at 70° is complete in 10 min. The reduction and NH_3 distillation are carried out as previously described (A., 1933, 921). There is a systematic error up to 0·02 mg., due to NH_3 from the alloy. With glycine, urea, urine, meat broth, and *Aspergillus* culture liquids there is an error of 0—1·94%, blood-serum 2·31, asparagine 2·48, and peptone 5·02%. This is remedied by removal of protein from the serum or by dilution. Li_2CO_3, $\text{Ba}^{\cdot\cdot}$, $\text{Ca}^{\cdot\cdot}$, $\text{Mg}^{\cdot\cdot}$, $\text{Zn}^{\cdot\cdot}$, $\text{Mn}^{\cdot\cdot}$, $\text{Co}^{\cdot\cdot}$, $\text{Ni}^{\cdot\cdot}$, $\text{Fe}^{\cdot\cdot}$, $\text{Cu}^{\cdot\cdot}$, PO_4''', AsO_3''', and BO_3''' inhibit reduction, and extra NaOH is required. $\text{Cr}_2\text{O}_7''$, MnO_4', and ClO_3' are also inhibitors. Hexoses, pentoses, and polyalcohols, but not bioses, interfere and must be diluted to a concn. of 2%. $\text{CCl}_3\cdot\text{CO}_2\text{Na}$ and polyphenols interfere, but not PhOH and $\text{C}_{10}\text{H}_7\cdot\text{OH}$. L. S. T.