BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

APRIL, 1932.

General, Physical, and Inorganic Chemistry.

Relations between corresponding quadruplets of N I, O II, S II, and Cl III. J. Gilles (Compt. rend., 1932, 194, 606—607). C. A. Silberrad.

Light intensities of neon discharges. P. Johnson (Phil. Mag., 1932, [vii], 13, 487—494).—Light intensities in the visible and ultra-violet spectrum of a d.c. discharge in Ne were measured and correlated with the pressure and current. H. J. Emeléus.

Study of a neon discharge by use of collectors. C. G. Found and I. Langmuir (Physical Rev., 1932, [ii], 39, 237—253).—Resonance radiation from a Ne arc can travel 20—30 cm. through non-ionised Ne; absorption by normal gives excited Ne atoms, which, in the metastable state, diffuse to the walls and metal electrodes and there liberate secondary electrons. N. M. Bligh.

Profile of the magnesium line at 5183 Å. in the solar spectrum. G. Righini (Atti R. Accad. Lincei, 1931, 14, 285—287). H. F. Gillbe.

Arc spectrum of magnesium, Mg I. F. Paschen (Sitzungsber. preuss. Akad. Wiss., 1931, 32, 9 pp.).—The spectrum is described and analysed. A. J. Mee.

Zeeman effect and Λ-type and spin doubling in the CaH bands. W. W. Watson (Physical Rev., 1932, [ii], 39, 278—288; cf. A., 1930, 1075). N. M. Bligh.

Extinction and transformation of resonance series spectra into band spectra. O. Heil (Z. Physik, 1932, 74, 18—30).—Mols. (Se_2 and Te_2) that are rapidly extinguished by the presence of inert gases do not readily transform to give band spectra in place of the resonance series doublets; S_2 is not rapidly extinguished and readily gives a band spectrum. A. B. D. Cassie.

Polarisation of resonance radiation and hyperfine structure: the cadmium resonance lines. A. Ellett and L. Larrick (Physical Rev., 1932, [ii], 39, 294—298).—The Cd resonance lines λλ 2288 and 3261 Å. excited by unpolarised radiation in a magnetic field parallel to the exciting light are 76·3 and 86—87% polarised, respectively. Mitchell's results (cf. A., 1931, 1104) are not supported. N. M. Bligh.

Absorption spectrum of I_2. I. I. Agarbiceanu (Compt. rend., 1932, 194, 702—703; cf. A., 1923, ii, 669).—The heads of about 20 new bands between λ 6450 and 5230 have been measured, and previous measurements of Mecke confirmed. C. A. Silberrad.

Absorption, fluorescence, and emission bands of cæsium. R. Rompe (Z. Physik, 1932, 74, 175—186). A. B. D. Cassie.

Band spectrum of barium hydride. A. Schaafsma (Z. Physik, 1932, 74, 254—266; cf. this vol., 104). A. B. D. Cassie.

Hyperfine structure of the mercury line 4916 Å. S. Tolansky (Nature, 1932, 129, 204).—A discussion. L. S. Theobald.

Polarisation of mercury resonance radiation. L. Larrick and N. P. Heydenburg (Physical Rev., 1932, [ii], 39, 289—293).—The polarisation of the line λ 2537 Å. in resonance radiation, and the relative transition probabilities within a hyperfine multiplet, are calc. N. M. Bligh.

Hyperfine structure of mercury. III. K. Murakawa (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 17, 299—306; cf. this vol., 2).—The hyperfine structure of the lines λ 5769·6, 5790·66, and 5789·69 is interpreted. The lines λ 4347·5, 4339·23, 3983·96, 6123·37, and 5461 were examined for isotope separation. N. M. Bligh.

$nh\nu$ Emission in xenon and thallium III. W. M. Hicks (Phil. Mag., 1932, [vii], 13, 329—354). H. J. Emeléus.

Theory of complex spectra. I. Energy levels. M. H. Johnson, jun. (Physical Rev., 1932, [ii], 39, 197—209; cf. this vol., 2).—Mathematical. N. M. Bligh.

Gas discharges at very high frequencies. L. Rohde (Ann. Physik, 1932, [v], 12, 569—599).—The behaviour of different gases in electric and magnetic fields of very high frequencies was investigated. The dependence of the min. ignition potential on pressure was determined. For gases other than inert there is a sharp min. in the pressure curve, of which the abs. val. is lower the lower is the wavelength. In the case of the inert gases, pressure was without effect. The ignition potential decreases with increasing frequency. The electrodeless ring discharge is also investigated. It can be produced up to 2·30 m. The use of high-frequency discharges for spectroscopic and other electro-optical purposes is mentioned. A. J. Mee.

"Ultimate" rays. T. Negresco (Bull. Math. Phys. Bucarest, 1931, 11, 191—194).—The lines last to disappear when the concn. of the element producing them is progressively diminished have been investigated. The most lasting spark spectra lines are not the same as those in the arc. A. J. Mee.

Material transport in the luminous arc. L. S. Ornstein and T. Koopmans (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 1099—1100).—The spectral lines of an electric arc, of which the anode and cathode consist of different metals, show a transition in intensity on passing from one electrode to the other. J. W. Smith.

Optical investigation of collisions of gas molecules with a solid wall. W. R. van Wijk (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 1201—1205).—An optical method of measuring the accommodation coeff. of gas mols. on a solid surface is described. The mols. reflected from a surface show no Boltzmann distribution of the rotation states, the higher rotation levels occurring in too great a proportion. This effect is qualitatively independent of the ratio N_1/N_2 of the mol. densities of the gas incident on the wall and emerging from it. J. W. Smith.

Exchange of energy between gas atoms and solid surfaces. II. Temperature variation of the accommodation coefficient of helium. J. K. Roberts (Proc. Roy. Soc., 1932, **A**, **135**, 192—205).—The accommodation coeff. of He with a W surface from which films of adsorbed gas have been removed is much lower than those ordinarily measured (A., 1930, 1340). Data are now given for the variation of the accommodation coeffs. between 22° and −194°. At −194° the very low val. of 0·025 is obtained. The results suggest that as 0° abs. is approached the accommodation coeff. would approach zero. L. L. Bircumshaw.

Atom factors. W. Ehrenberg and K. Schäfer (Physikal. Z., 1932, **33**, 97—122).—A *résumé* of work on atom factors with a table of vals. A. B. D. Cassie.

Scattering of X-rays by simple gases (N_2, O_2, CO_2, CS_2, NH_3, H_2O). H. Gajewski (Physikal. Z., 1932, **33**, 122—131).—Experimentally determined angular distributions of scattered radiation fit theoretical curves obtained by assuming a finite distribution of electronic charge and by adjusting nuclear separations. A. B. D. Cassie.

Absorption of X-rays in gases and vapours. II. J. A. Crowther and L. H. H. Orton (Phil. Mag., 1932, [vii], **13**, 505—523; cf. A., 1930, 1229).—The mass absorption coeffs. and relative ionisations of a number of gases and vapours were measured with Cu *K*- and Fe *K*-radiation. At. absorption coeffs. were deduced for C, N, O, Ne, Al, S, Cl, A, Zn, Br, I, and used to test the relation between at. absorption and at. no. and between at. absorption and wave-length. De Broglie's formula agrees with observations for elements in group I of the periodic table, but breaks down for elements of higher at. no. H. J. Emeléus.

Excitation potentials of light metals. I. Lithium. H. W. B. Skinner (Proc. Roy. Soc., 1932, **A**, **135**, 84—108).—The radiation emitted by metallic Li has been studied by the photo-electric method. The min. excitation potential for the *K*-radiation of Li is 9 volts below the *K*-ionisation potential of the Li atom, so that it is possible to excite a *K*-resonance radiation in the metal. The observed crit. potentials of Li metal are correlated with the calc. energy levels of the free Li atom. An attempt is made towards a theory of the approx. linear relationship found between the intensity of radiation emitted from a metal and the voltage of the exciting electron beam. L. L. Bircumshaw.

New lines in the *K* series of X-rays. W. Duane (Proc. Nat. Acad. Sci., 1932, **18**, 63—68).—In an examination of the *K* series lines of *X*-rays from Mo, reflected from the 100 plane of a calcite crystal, a new band has been discovered at a slightly shorter wave-length than the γ line of Mo. W. R. Angus.

Fine structure of X-ray absorption edges. D. Coster and J. Veldkamp (Z. Physik, 1932, **74**, 191—208; cf. A., 1931, 993).—Further experimental evidence is offered in favour of Kronig's theory. Fine structure was measured in the *K* edge of Cu, Fe, and Zn, the last at temp. up to 405°, and in the L_{111} edge of Au and Pt. A. B. D. Cassie.

Quadrupole lines in X-ray spectra. E. Segrè (Atti R. Accad. Lincei, 1931, [vi], **14**, 501—505).—All the forbidden lines of *X*-ray spectra can be attributed to quadrupole radiation. O. J. Walker.

Ionising efficiency of electronic impacts in air. J. Thomson (Proc. Roy. Soc. Edin., 1930—1931, **51**, 127—141).—The energy spent in producing one pair of ions by total absorption of electrons (velocity corresponding with 50—270 volts) in air, measured by an ionisation chamber method, varies with the initial velocity of the electron and is asymptotic to the val. 37±2 electron-volts when the energy of the electron is very great. H. E. Blayden.

Attempt to detect high photo-electric absorption in cæsium vapour at double the series limit. E. T. S. Appleyard (Phil. Mag., 1932, [vii], **13**, 300—305).—No absorption in Cs vapour in the region λ 1500—1600, as would be expected as a thermodynamic inverse to the experiments of Davis and Barnes on He (cf. A., 1930, 393), could be detected. N. M. Bligh.

Thermionic emission and space charge. N. H. Frank (Physical Rev., 1932, [ii], **39**, 226—236).—Mathematical. N. M. Bligh.

Effect of surface changes on the photo-electric emission of silver and gold. T. E. Clarke (Phil. Mag., 1932, [vii], **13**, 624—632).—The influence of annealing, polishing, and of adsorbed gas on the photo-electric emission of Ag and Au was investigated. H. J. Emeléus.

Collision of electrons with rotating dipoles. H. S. W. Massey (Proc. Camb. Phil. Soc., 1932, **28**, 99—105). N. M. Bligh.

New characteristic of the Dirac electron. A. Proca (Compt. rend., 1932, **194**, 691—693).—Mathematical. The Dirac electron has, besides the magnetic moment of Uhlenbeck and Goudsmit, a natural electric moment, distinct from that resulting from its magnetic moment; it behaves as if, besides its electric charge, *e*, it had a free magnetic charge $\mu = e$. C. A. Silberrad.

Influence of a cloud of electrons on structure of de Broglie waves. S. Szczeniowski and L. Infeld (Bull. Acad. Polonaise, 1931, A, 483—488).—Mathematical.

Angular distribution in the scattering of slow electrons by gas molecules. II. C. Ramsauer and R. Kollath (Ann. Physik, 1932, [v], 12, 529—561; cf. A., 1931, 782, 1107, 1206).—The zone apparatus previously described is improved and a method devised which gives the scattering as a function of scattering angle for small angles. The angular distribution was found in He, Ne, A, H_2, CO, and CO_2 for electron velocities between 1 volt and the excitation potential of the gas. The angular range investigated was 15—167°. A. J. Mee.

Collision of electrons with molecules. H. S. W. Massey and C. B. O. Mohr (Proc. Roy. Soc., 1932, A, 135, 258—275).—The collision theories of Born and Oppenheimer (A., 1928, 1170) are applied to various phenomena occurring on electron impact with mols. Elastic scattering is considered and general formulæ are obtained for the case of diat. mols., including the relation between *X*-ray and electron scattering. The intensity of elastic scattering in mol. H_2 is calc. for all angles and velocities for which the Born theory is valid. L. L. Bircumshaw.

Effect of electron attachment on the ion mobility curves in the Zeleny air-blast method of ion mobility measurement. L. B. Loeb and N. E. Bradbury (J. Franklin Inst., 1932, 213, 119—154).—Zeleny's results (cf. A., 1931, 1207) are interpreted by the application of the simplified theory of electron attachment. N. M. Bligh.

Polarisation of electrons. E. Rupp (Physikal. Z., 1932, 33, 158—164).—Experiments are described which show the polarisation of electrons, (*a*) at grazing reflexion, (*b*) by scattering at 90°, followed by transmission of the rays through a thin metal foil. The polarisation is connected with the magnetic moment of the electron. Application of a longitudinal magnetic field causes a rotation of the polarisation. The effect of a transverse field in various positions with respect to the direction of the rays is also given. A. J. Mee.

Artificial production of fast protons. J. D. Cockcroft and E. T. S. Walton (Nature, 1932, 129, 242).—Protons with a velocity of 10^9 cm. per sec. have a range in air of 8·2 mm., and in H_2, of 3·2 cm. at N.T.P. This supports Blackett's conclusions on the relative ranges of protons and α-particles. L. S. Theobald.

At. wt. of fluorine. H. S. Patterson, W. Cawood, and R. Whytlaw-Gray (Nature, 1932, 129, 245).—A discussion of certain points in previous work on the at. wt. of F. Chemical evidence at present indicates a val. of 19·01 in preference to 19·00 (cf. this vol., 106). L. S. Theobald.

Revision of at. wt. of lanthanum. I. Analysis of lanthanum bromide. II. Specific gravities of lanthanum chloride and bromide. III. Increased efficiency of calcium bromide as a drying agent at low temperatures. G. P. Baxter and E. E. Behrens (J. Amer. Chem. Soc., 1932, 54, 591—602; cf. A., 1922, ii, 298, 770).—By analysis of $LaBr_3$ the val. 138·923 has been obtained for the at. wt. of La. $LaCl_3$ has d^{25} 3·842 and $LaBr_3$ d^{25} 5·057. The efficiency of $CaBr_2$ as a drying agent improves on cooling at −21° or −72°. L. P. Hall (*c*).

Element 87. F. Allison, E. R. Bishop, A. L. Sommer, and J. H. Christensen (J. Amer. Chem. Soc., 1932, 54, 613—615).—By the magneto-optic method (A., 1930, 1541) characteristic minima are obtained for a cation with an equiv. wt. greater than $Tl^{\cdot}$, which are due, not to $SnCl_3^{\cdot}$ or $ReCl^{\cdot}$, but to element 87, which appears to have six isotopes and for which the name "virginium" and symbol Va are suggested. Small amounts of Va have been detected in pollucite, lepidolite, Searle's Lake brine, kainite, monazite sand, and samarskite. L. P. Hall (*c*).

Isotope of uranium. G. Elsen (Rec. trav. chim., 1932, 51, 284—288).—On the assumption that active U is the isotope U^{239} and the at. wt. of U is 238·189, the amount of Ac-U present is approx. 16%. Taking van Grosse's new val. of 238·084, however (A., 1931, 15), there is 10% Ac-U in U. On the basis of the first val. the radioactive const. is $6{\cdot}86\times10^{-11}$ year^{-1} and the period $1{\cdot}01\times10^{10}$ years. For 10% Ac-U the corresponding vals. are $1{\cdot}17\times10^{-11}$ year^{-1} and $5{\cdot}95\times10^{10}$ years. M. S. Burr.

High-tension supply for Geiger counters operated from a.c. mains. H. C. Webster (Proc. Camb. Phil. Soc., 1932, 28, 121—123).—An arrangement to give const. voltage and freedom from a.c. ripple and other disturbances is described. N. M. Bligh.

Influence of radioactive substances on the Volta effect. L. Bouchet (Compt. rend., 1932, 194, 695—697).—The radioactivity of U_2O_5 has very little influence on the Volta effect between gilt brass and Cd, Cu, Mg, Sn, or Zn (cf. A., 1882, 921). C. A. Silberrad.

Attempt to detect the spontaneous transformation of helium into penetrating radiation. G. T. P. Tarrant and L. H. Gray (Proc. Camb. Phil. Soc., 1932, 28, 124—127).—No evidence of production of any hard radiation by He in bulk in the neighbourhood of an ionisation chamber was obtained. Results indicate that atm. He cannot account for more than 2% of the effect of penetrating radiation, and interstellar He only if present in excess of 1%. N. M. Bligh.

Range and ionising power of H- and α-rays. E. Rüchardt (Ann. Physik, 1932, [v], 12, 600—606).—The results of Gerthsen (A., 1930, 1083) are in good agreement with those obtained by entirely different methods. A. J. Mee.

Loss of energy of α-particles and H-particles. P. M. S. Blackett (Proc. Roy. Soc., 1932, A, 134, 132—142).—Theoretical. The observed loss of energy of α-particles in H_2, He, and air is compared with the formula given by Bethe's theory of the loss of energy of fast particles (A., 1930, 972). The effect of capture and loss of electrons on the rate of loss of energy is discussed. L. L. Bircumshaw.

Passage of α- and β-particles through matter and Born's theory of collisions. E. J. Williams

(Proc. Roy. Soc., 1932, **A**, **135**, 108—130).—The non-relativity theory of the passage of electric particles through matter developed by Bethe on the basis of Born's theory of collisions (A., 1930, 972) is compared with experimental results for the stopping power, primary ionisation, total ionisation, straggling, and production of branches by α- and β-particles. Some of these phenomena (*e.g.*, the stopping power of H_2 for slow β-particles) are accounted for by the new theory, but the total ionisation of the monat. gases and the straggling of α-particles in light elements still present difficulties. The experimental results for fast β-particles indicate a small relativity correction to Bethe's formulæ. L. L. Bircumshaw.

Artificial disintegration by α-particles. II. Fluorine and aluminium. J. Chadwick and J. E. R. Constable (Proc. Roy. Soc., 1932, **A**, **135**, 48—68).—The proton emission from Al bombarded by α-particles from Po can be resolved into 8 groups, due to penetration of the α-particles through 4 resonance levels, each level giving rise to a pair of groups. The disintegration of F, which gives 6 groups of protons when bombarded by α-particles, is explained in a similar way. L. L. Bircumshaw.

Scattering of β-rays. J. A. Gray (Trans. Roy. Soc. Canada, 1931, [iii], 25, III, 57—64).—Experiments described indicate that the scattering of β-rays is accompanied by loss of energy, which is the greater the smaller is the at. no. of the scattering atom, and the greater is the angle of scattering. For single scattering, a radiator must be so thin that both the intensity and the average energy of the scattered rays are proportional to the thickness of the radiator. A. J. Mee.

Upper limit of energy in the β-ray spectrum of thorium-*C*″. F. R. Terroux and N. S. Alexander (Proc. Camb. Phil. Soc., 1932, **28**, 115—120).—The upper part of the spectrum investigated by the expansion chamber method showed no "tail," and no tracks of $H\rho$ greater than 10,800; the end-point is placed at 9400 $H\rho$. N. M. Bligh.

Number of secondary β-rays emitted by radium. E. Stahel (Compt. rend., 1932, **194**, 608—610).—Using Ra free from emanation and active deposit spread on a diamond surface and the arrangement previously described (cf. A., 1931, 543), the no. of secondary β-rays per 100 atoms of Ra decomposed is 5±1. Preliminary experiments show that the no. of γ-rays emitted is approx. the same. The Ra atom must therefore decompose, either with emission of only a single α-particle, or with simultaneous emission of an α-particle and also of a γ-ray or the corresponding secondary β-ray. C. A. Silberrad.

Nomenclature for lines in the β-ray spectra of radioactive bodies. C. D. Ellis (Nature, 1932, **129**, 276).—A nomenclature is suggested. L. S. Theobald.

Effect of absorption of γ-rays of very high frequency by projection from light nuclei. (Mme.) I. Curie and F. Joliot (Compt. rend., 1932, **194**, 708—711).—The H particles ejected from paraffin by γ-rays of Po+Be (cf. this vol., 210), examined in a Wilson expansion chamber, show tracks of all lengths to >12 cm., and also β-rays, some of energy $>10^6$ volts, due probably to a Compton effect. Comparison of μ/ρ of these γ-rays and of γ-rays from Th-*C*″ in Cu, C, and paraffin show that much energy is absorbed by the H nuclei, and a considerable amount by C; also the ionisation current produced by the Po+Be γ-rays in He is 4·6 times that produced in air at the same pressure. The phenomenon thus appears to be general. From considerations of the absorption by diffusion it is concluded that the absorption attributable to emission of H particles is a new method of interaction between radiation and matter. Deduction of wave-length from coeff. of absorption in cases of high quantum energies is erroneous. C. A. Silberrad.

Interval between the departure of the disintegration particle and the emission of the gamma radiation. P. Wright (Proc. Camb. Phil. Soc., 1932, **28**, 128—135).—No evidence of γ-ray emission from the space above a source of Ra-*C* liberating recoil atoms of Ra-*C*′ was obtained, indicating that the interval between the departure of the disintegration particle and emission of the γ-ray quantum is $<10^{-5}$ sec. N. M. Bligh.

Absorption of hard monochromatic γ-radiation. II. G. T. P. Tarrant (Proc. Roy. Soc., 1932, **A**, **135**, 223—236; cf. A., 1930, 1085).—The absorption coeffs. of the γ-rays from Th-*C*″ have been measured, using an ionisation chamber containing gas at 120 atm. pressure. The vals. for the light elements are 3·1% > those calc. from the Klein–Nishina formula (A., 1929, 373), indicating the possibility of nuclear absorption occurring for the light elements as well as for the heavy. The vals. per electron vary between the light and heavy elements as the square of the at. no. L. L. Bircumshaw.

Abnormal absorption of heavy elements for hard γ-rays. C. Y. Chao (Proc. Roy. Soc., 1932, **A**, **135**, 206—213).—Approx. homogeneous γ-ray beams of varying wave-length are obtained from a strongly filtered Th-*C*″ primary radiation, by utilising the change of wave-length accompanying scattering. A rapid decrease of the extra-absorption of the scattered rays in lead is found between $\lambda=5·9$ and 6·6 X. This suggests the existence of an excitation or a disintegration potential. L. L. Bircumshaw.

Active nitrogen. IX. Electric conductivity of active nitrogen. E. J. B. Willey and W. A. Stringfellow. **X. Supposedly oxidisable variety of nitrogen.** E. J. B. Willey and S. G. Foord (J.C.S., 1932, 142—152, 153—161).—IX. Charged particles probably play no part in the chemical reactions of active N. The conductivity of active N is a surface effect, due to the ejection of electrons from the testing electrodes by impact and deactivation of 8-volt metastable N_2. The conductivity was shown not to be due to photo-electric emission from the testing electrodes.

X. No evidence was obtained for the existence of an oxidisable active species of N, or of an oxide of N, which reacts with O_3 but not with O_2. Lowry's results (J.C.S., 1912, **101**, 1152) may be explained by the very rapid reaction of NO and O_3 compared with that of NO and O_2. H. J. Emeléus.

Determination of the Stefan-Boltzmann radiation constant, using a Callendar radio-balance. F. E. Hoare (Phil. Mag., 1932, [vii], **13**, 380—392).—With a source of radiation at approx. 100° the mean val. obtained was $5\cdot737\times10^{-5}$ erg/sec./cm.^{2}/degree^4. H. J. Emeléus.

Quantum mechanical theory of energy exchanges between inert gas atoms and a solid surface. J. M. Jackson (Proc. Camb. Phil. Soc., 1932, **28**, 136—164).—Mathematical. N. M. Bligh.

Continuous atomic matrix. W. R. Morgans (Phil. Mag., 1932, [vii], **13**, 664—673).—Mathematical. H. J. Emeléus.

Chemistry and the quantum theory of atomic constitution. N. Bohr (J.C.S., 1932, 349—384).—Faraday Lecture.

Beryllium molecule. W. H. Furry and J. H. Bartlett, jun. (Physical Rev., 1932, [ii], **39**, 210—225).—Mathematical. The stability of Be mol. states is investigated. N. M. Bligh.

Search for the band spectra of boron fluoride. N. R. Tawde and R. C. Johnson (Phil. Mag., 1932, [vii], **13**, 501—504).—New bands between λλ 6400 and 4438 Å., which may be due to BF, were measured. H. J. Emeléus.

Absorption spectrum of iodine bromide in the visible. H. Cordes (Z. Physik, 1932, **74**, 34—44).—The heat of dissociation of IBr is 1·80 volts, and of ICl 2·043. A. B. D. Cassie.

Absorption spectra of various series of rare-earth double nitrates. II. D. Wyllie and J. A. Harris (Trans. Roy. Soc. Canada, 1931, [iii], **25**, III, 107—113).—Various double and simple nitrates of Ce-free, Ce group rare earths have been repeatedly recryst. to test the val. of these salts in the separation of rare earths. A study of absorption spectra indicates that crystallisation of simple nitrates from conc. HNO_3 and formation of double nitrates with Pb and Cd do not provide satisfactory methods for the separation of the rare earths of the Ce group. Fractional recrystallisation of the double nitrates with NH_4 is the most efficient method for a preliminary separation of Pr from La and Nd. Mg, Co, and Zn double nitrates crystallise well, but give no marked separation. For the rapid separation of Sm the use of the double nitrate of the Ce group earths with Ni is recommended. A. J. Mee.

Absorption spectra of rare-earth glazes. F. H. Norton and D. T. H. Shaw (J. Physical Chem., 1931, **35**, 3480—3485).—The spectro-photometric reflecting curves of glazes containing oxalates of Ce, Pr, Nd, Sm, and "didymium" have been obtained. The reflexion minima correspond closely with the absorption bands of aq. solutions of the salts, thus indicating that the absorption characteristics of the rare-earth atoms are not appreciably altered in the change from an aq. solution to a silicate glass. The characteristic absorption bands by which the elements may be easily identified are: Ce, 585 mμ; Pr, 592 mμ; Nd, 525 and 585 mμ; Sm, 470 and 560 mμ. C. C. Kiess (*c*).

Number of excited atoms and the absorption spectra of various metallic vapours. A. T. Williams (Physikal. Z., 1932, **33**, 152—158).—By investigating the vapours of Cu, Ag, and Au, it was shown that the relationship $N_1/N=e^{-E/RT}$, where N_1/N is the ratio of the no. of excited to total atoms, and E is the absorbed exciting energy, is valid, apart from a few anomalies. A. J. Mee.

Intensity measurements in ultra-violet spectra by means of photo-electric cells sensitised by sodium salicylate. A. Chevallier and P. Dubouloz (Compt. rend., 1932, **194**, 452—454; cf. this vol., 213).—The method is applied to the determination of the intensity of the fluorescent light as a function of the wave-length of the exciting light, giving a curve closely resembling that relating energy to wave-length in H_2 (cf. A., 1929, 616); also to the determination of the ultra-violet absorption spectrum of $COMe_2$ (cf. A., 1926, 774). C. A. Silberrad.

Change in colour on heating of pyridine solutions of cobalt chloride. I. Rohde and E. Vogt (Z. physikal. Chem., 1932, **B**, **15**, 353—364).—Absorption curves of $CoCl_2$ dissolved in pyridine have been determined between −45° and 105°. The variation in the absorption with change in temp., visible as a colour change from red to blue between about 10° and 50°, actually goes on over the whole temp. range from the f. p. to the b. p. of the solution. The absorption spectrum consists of two superimposed curves, corresponding with two distinct mol. species. Change in temp. does not affect the separate spectra, but only the relative amounts of the two mol. species. At 503 mμ both forms have the same extinction coeff., for the absorption curves at all temp. intersect at this wave-length. The variation in temp. of the absorption coeff. for a selected wave-length (610 mμ) agrees with the assumption that the change red ⟶ blue is a unimol. reaction in respect of Co, the heat of reaction being 11,700 g.-cal. At 50°, when the solution appears to have a pure blue colour, the ratio of the blue form to the red form is 1 : 10, and reaches 1 : 1 only at 97°. The results tend to confirm the theory that the colour changes are due to such a reaction as
$CoCl_2,4C_5H_5N\ (\text{red}) \rightleftharpoons CoCl_2,2C_5H_5N\ (\text{blue}) + 2C_5H_5N$
(cf. A., 1927, 205). R. Cuthill.

Absorption spectra of sulphur compounds of various valencies. H. Ley and B. Arends (Z. physikal. Chem., 1932, **B**, **15**, 311—324).—Solutions of H_2S in H_2O and hexane have practically the same absorption curve, with a max. at 189 mμ, which is attributed to the undissociated mol. In aq. Na_2S the max. has shifted to 227 mμ, and corresponds with the HS′ ion. EtSH has a band at 193·5 mμ, and indications of another at about 225 mμ. No definite max. appear on the curves for EtSNa and Et_2S. Et_2S_2 has a band at 249 mμ and another below 185 mμ. The absorption bands of the alkali and alkyl sulphates, and probably also of the sulphonium salts, lie far in the ultra-violet, and could not be located with the apparatus used, the lower limit of which was about 185 mμ. R. Cuthill.

Ultra-violet absorption of some aromatic hydrocarbons. W. Pestemer and J. Cecelsky (Monatsh., 1932, **59**, 113—127).—Ultra-violet absorption data are recorded for diphenyl, dinaphthyl, anthracene, phenanthrene, and perylene dissolved in hexane. From the results it is difficult to regard perylene as having a definite naphthalene or anthracene character. Perylene cannot be considered as a simple union of two $C_{10}H_8$ chromophores, as in the case of dinaphthyl, but as an individual chromophore or an individual system of chromophores. M. S. Burr.

Absorption in the ultra-violet of solutions of optically active organic compounds. R. Lucas and M. Schwob (J. Phys. Radium, 1932, [vii], 3, 43—56).—Data for camphor in CCl_4, *cyclo*hexane, EtOH, AcOH, C_6H_6, HCO_2H, and H_3PO_4, fenchone in C_6H_{12}, *d*-cyanocamphor in *cyclo*hexane and C_6H_6, and tartaric acid in various solvents show that rotatory power varies with the solvent and concn., and absorption varies with the solvent and, contrary to Beer's law, with the concn. Possible explanations are discussed. N. M. Bligh.

Ultra-violet absorption spectra of solutions of substituted phenyluracils. J. Evans (J. Amer. Chem. Soc., 1932, 54, 641—646).—Ultra-violet absorption spectra curves of 6-phenyluracil, its 1-*N*- and 3-*N*-Me and 1 : 3-*NN*-Me_2 derivatives, Et 6-phenyluracil-3-*N*-acetate, Me 6-phenyl-1-*N*-methyluracil-3-*N*-acetate, 6-phenyl-1-*N*- and 3-*N*-methylhydrouracils, and Et 6-phenyl-1-*N*-methylhydrouracil-3-*N*-acetate are given. The absorption spectra of 1-*N*-substituted uracils differ from those of the 3-*N*- or non-substituted derivatives; the difference can be used to distinguish the 1-*N*- from the 3-*N*-substituted 6-phenyluracils. C. J. West (*b*).

Infra-red radiation of refractory substances. B. Wrede (Mitt. Kaiser-Wilh.-Inst. Eisenforsch., 1931, 13, 131—142; Chem. Zentr., 1931, ii, 1972).—The spectral distribution of the emission of silica (95% SiO_2), chamotte (55% SiO_2), sillimanite (33% SiO_2), corundum (70% Al_2O_3), and magnesite (80% MgO) refractories in the region 1—9 μ was determined. A. A. Eldridge.

Normal vibrations of acetylene. A. R. Olson and H. A. Kramers (J. Amer. Chem. Soc., 1932, 54, 136—138).—The ratios of the frequencies corresponding with the five normal modes of vibration of the C_2H_2 mol. have been recalc. on the basis of classical mechanics. The vals. of ν_1, ν_2, and ν_3 are not inconsistent with Mecke's interpretation of the spectrum, but if the new vals. of δ_1 and δ_2 are correct, Mecke's correlation with experiments must be revised. C. J. Humphreys (*c*).

Raman effect from the viewpoint of unimolecular reactions. A. Ganguli (Phil. Mag., 1932, [vii], 13, 306—310; cf. A., 1931, 1130).—Mathematical. N. M. Bligh.

Raman spectrum of sulphuric acid and the action of an electric field on it. V. Ricca (Atti R. Accad. Lincei, 1931, [vi], 14, 288—290).—With 50 wt.-% H_2SO_4 there is a displacement of the Raman lines towards the violet when the electric current applied is such that the H^+ ions move away from the spectrograph and towards the red in the opposite case, and in both cases the intensity of the lines is diminished. O. J. Walker.

Raman effect and molecular structure of some simple inorganic substances. A. Dadieu and K. W. F. Kohlrausch (Physikal. Z., 1932, 33, 165—172).—The Raman spectra of NH_3, SO_2, H_2S, and COS were investigated, and on the basis of these results and those of infra-red determinations, the mol. consts. were obtained. Experiments with butane, NOCl, and N_2O_4 led to no results, owing, in the last two cases, to their deep colour. A. J. Mee.

Relative efficiency of some of the mercury arc lines in exciting the Raman spectrum of benzene. (Miss) Werth (Physical Rev., 1932, [ii], 39, 299—310).—The observed Raman frequencies are Δν 606, 845, 992, 1175, 1585, 1603, 2947, 3060, 3185, and the corresponding exciting lines are 3650, 3654, 3663, 4047, 4078, 4108, 4339, 4347, and 4358 Å. Total intensities are tabulated. Relative intensities of Raman patterns for lines of single origin were measured. Rayleigh's fourth-power law was verified. N. M. Bligh.

Raman spectra in liquid and gaseous methane. S. C. Biswas (Phil. Mag., 1932, [vii], 13, 455—458).—The possibility of two physically distinct forms of CH_4 is discussed on the basis of differences in the Raman spectra of the liquid and gas. H. J. Emeléus.

Raman effect in non-ideal binary solutions and in a series of mono-, di-, and poly-hydric alcohols. R. E. Whiting and W. H. Martin (Trans. Roy. Soc. Canada, 1931, [iii], 25, III, 87—98).—A solution of pyridine and AcOH, and of $COMe_2$ and CS_2, both non-ideal, gave Raman spectra which were superpositions of those of the components. Careful purification and removal of dust caused disappearance of continuous portions from the spectra of MeOH, ethylene glycol, and sucrose solutions. Glycerol, under the same conditions, gave a strong continuous spectrum with a double structure. Raman frequencies for all these substances have been measured. Dust-free glucose solution gave a strong continuous spectrum which may be ascribed to photochemical decomp. A. J. Mee.

Raman effect in the terpenes. Hydrocarbons. G. B. Bonino and P. Cella (Mem. R. Accad. d'Italia, 1931, 2, [Chim., 4], 51 pp.).—The Raman spectra of *d*- and *l*-pinene, limonene, sabinene, menthene, pinane, sabinane, and menthane have been studied. The complex spectra obtained are discussed in relation to the mol. structure, and those of *d*-pinene and limonene are compared with the infra-red absorption spectra. H. F. Gillbe.

Raman spectrum of sugar solutions. V. Polara (Atti R. Accad. Lincei, 1931, [vi], 14, 293—298).—In the Raman spectrum of sucrose solutions five of the seven lines characteristic of glycerol and four lines of the alcohols are found as well as other lines usually attributed to various types of linkings in the aliphatic series. O. J. Walker.

Raman spectra of carotenoids. H. von Euler and H. Hellström (Z. physikal. Chem., 1932, B, 15, 342—346).—The spectra in Et_2O solution of α- and β-carotene, leaf-xanthophyll, lycopene, and β-ionone have been determined, the first three compounds giving the same frequencies, one of which also occurs with ionone. R. Cuthill.

Molecular symmetry and diffusion spectra. J. Cabannes and A. Rousset (Compt. rend., 1932,

194, 706—708; cf. this vol., 212).—From further results of a similar nature are deduced the angles between the linkings in NO_2 (in $PhNO_2$), NH_2 (in NH_2Me), and SO_2, and the vals. of ρ in PCl_3, $POCl_3$, and $CHCl_3$. The depolarisation of the H_2O band at 3240 cm.$^{-1}$ and non-depolarisation of that at 3418 are opposed to Kastler's theory (cf. A., 1931, 668). The case of allene (this vol., 109) is shown not to be exceptional. C. A. SILBERRAD.

Photography of fluorescence spectra and Raman spectra. F. ALMASY (Physikal. Z., 1932, **33**, 221—222).—An apparatus is described by means of which weak spectra such as the above may be photographed. A. J. MEE.

A peculiar form of activity of matter. G. REBOUL (Compt. rend., 1932, **194**, 602—603; cf. A., 1931, 666).—Experiments show that the action on a photographic plate of certain substances, *e.g.*, paper, exposed to the action of a resistance cell is consistent with its being due to emission by the paper, in a manner analogous to phosphorescence, of very easily absorbable radiation belonging to an invisible portion of the spectrum, and produced by radiation from the cell. C. A. SILBERRAD.

Cathodic phosphorescence of rare earths in calcium oxide. S. FAGERBERG (Nova Acta Reg. Soc. Sci. Upsalensis, 1931, [iv], **7**, No. 6, 59 pp.; Chem. Zentr., 1931, ii, 2424).—Modified apparatus and methods are described, and results are tabulated. New lines have been observed. A. A. ELDRIDGE.

Minute structure of phosphors and its relationships to atomic-chemical problems. E. TIEDE and E. WEISS (Ber., 1932, **65**, [*B*], 364—372).—The formation of phosphors is studied by exposing SiO_2 tubes containing a layer of activator (CuS or Sb_2S_3) between two layers of fundamental sulphide (ZnS or MgS) (layer method) or a homogeneous mixture of activator and fundamental sulphide (mixture method) to gradually rising temp. Activation and consequent development of characteristic phosphors commences at about 330° in all systems examined. The anion of the metallic salt has no marked influence, CuS being replaceable by CuO or $CuSO_4$. The activating influence of CdS or a pre-formed ZnS–Cu phosphor is observed at 650°. Very prolonged heating of ZnS–CuS at 280—320° does not produce a phosphor. It appears, therefore, that the active metal atoms penetrate the lattice of the fundamental sulphide without causing an actual displacement of the components of the latter. The relationship of at. distance to production of phosphors is discussed (cf. A., 1931, 1253). H. WREN.

Emission of praseodymium in alkaline-earth phosphors. II. H. EVERT (Ann. Physik, 1932, [v], **12**, 137—153).—The effect of temp. and type of excitation on the previously described phosphors (cf. this vol., 110) is studied. In the spectra of the sulphide and oxide Pr phosphors there are two bands, the lines differing in their properties as regards temp., excitation, distribution, and sharpness. A. J. MEE.

Dissociation of nitrogen and carbon monoxide by electron impact. J. T. TATE and W. W. LOZIER (Physical Rev., 1932, [ii], **39**, 254—269).—Energies of dissociation products, variation with electron energy of probability of ion production, and min. electron energy for the production of ions of specified energy were determined. Probable processes and heats of dissociation in volts were: $N_2 \longrightarrow N+N$ ($8{\cdot}4 \pm 0{\cdot}5$); $N_2^+ \longrightarrow N^+ + N + e$ ($7{\cdot}1 \pm 0{\cdot}5$); $N_2 \longrightarrow N^+ + N^+ + 2e$; $CO \longrightarrow C+O$ ($9{\cdot}3 \pm 0{\cdot}5$); $CO^+ \longrightarrow C^+ + O$ ($6{\cdot}4 \pm 0{\cdot}5$); $CO + e \longrightarrow C + O^-$; $CO \longrightarrow C^+ + O^-$. N. M. BLIGH.

Efficiencies of ionisation and ionisation potentials of various gases under electron impact. J. T. TATE and P. T. SMITH (Physical Rev., 1932, [ii], **39**, 270—277; cf. A., 1931, 665).—The gases investigated and ionisation potentials found were: N_2, 15·7; H_2, 15·6; CO, 14·1; O_2, 12·5 and 16·1; NO, 9·5; C_2H_2, 11·6 volts. Negative ions were formed by electron impact in the four last named. N. M. BLIGH.

Photo-electric association of sodium in rock-salt. E. REXER (Physikal. Z., 1932, **33**, 202—204).—Irradiation with blue light of a rock-salt crystal coloured by at. Na causes an association of the Na to larger complexes, depending on the inner photo-effect. A. J. MEE.

Photochemistry of crystal structure faults. A. SMEKAL (Physikal. Z., 1932, **33**, 204—206).—A discussion of work on coloured specimens of rock-salt. A. J. MEE.

Photo-electric effect in semi-conductors. L. BERGMANN (Physikal. Z., 1932, **33**, 209—213).—The use of the method described, which involves intermittent exposure of a special photo-cell to radiation, enables the photo-electric properties of exceedingly small quantities of substances to be investigated. A. J. MEE.

Transport phenomena in a degenerate gas. I. D. S. KOTHARI (Phil. Mag., 1932, [vii], **13**, 361—379).—Mathematical. H. J. EMELÉUS.

Effect of the character of the electrode surfaces on conduction in liquid dielectrics. H. EDLER and C. A. KNORR (Z. physikal. Chem., 1932, **158**, 433—440).—The form of the current–voltage curve obtained with Pt electrodes in C_6H_6 is greatly influenced by the H content of the electrodes. For a given voltage, electrodes free from H give vals. for the current which are lower and more nearly reproducible than those obtained with electrodes charged with H. Addition of thiophen considerably reduces the current passing. R. CUTHILL.

Electrical conductivity of the alkali carbides and the nature of the combination. A. VON ANTROPOFF and J. F. MÜLLER (Z. anorg. Chem., 1932, **204**, 305—314).—Na_2C_2 at temp. between 180° and 270° behaves as a typical ionic conductor. With direct current, polarisation and dendrite formation occur. The current is conveyed exclusively by $Na^{\bullet}$, and Faraday's law is applicable. The behaviour of Li_2C_2 containing about 20% of Li acetylide is similar. H. F. GILLBE.

Non-volatile and non-conducting crystals. F. HUND (Z. Physik, 1932, **74**, 1—17).—Properties of crystals are discussed from the point of view of occupying available crystal proper functions with available electrons (cf. this vol., 10, 215). The criterion for non-conductivity is that the ground term should not be bordered by a continuous succession of higher terms. Available proper functions divide into two equal classes, those giving binding and those giving loosening, and when the corresponding sets of energy vals. are separated by a finite interval, the crystal is non-conducting. Non-volatile, non-conducting at. crystals, such as diamond, have their binding proper functions filled, and fulfil the criterion for non-conductivity; non-volatile at. crystals have both classes filled, and must always be non-conductors.

A. B. D. Cassie.

Dielectric polarisation of hydrogen chloride in solution. I. Benzene, *cyclo*hexane, and carbon tetrachloride. F. Fairbrother (J.C.S., 1932, 43—55).—The dielectric const. of the dry HCl solutions was measured by a resonance method, *n* with a modified Pulfrich refractometer, and *d* with a dilatometer. The molar refractivity of HCl in C_6H_6 solution was somewhat less than that of HCl gas. The dielectric polarisation of HCl in each solvent was greater than that of the gas. The electric moment of HCl in C_6H_6 is $1{\cdot}28\times10^{-18}$ e.s.u.

H. J. Emeléus.

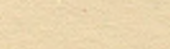
Dielectric constant and dipole moment of iron pentacarbonyl. W. Graffunder and E. Heymann (Z. physikal. Chem., 1932, **B**, **15**, 377—382).—From measurements at 20° of *n* and the dielectric const. of $Fe(CO)_5$ and C_6H_6 solutions, the dipole moment is found to be $0{\cdot}81\times10^{-18}$ e.s.u., which supports the view that the CO groups are not symmetrically arranged about the Fe atom. R. Cuthill.

Electric moments of certain *cyclo*hexane derivatives. O. Hassel and E. Næshagen (Z. physikal. Chem., 1932, **B**, **15**, 373—376).—Reasons are given for believing that β-hexachlorobenzene has zero dipole moment (cf. A., 1931, 900). The dipole moments of chloro-, bromo-, and iodo-*cyclo*hexane are $2{\cdot}1\times10^{-18}$, $2{\cdot}1\times10^{-18}$, and $2{\cdot}0\times10^{-18}$ e.s.u., respectively.

R. Cuthill.

Dipole moments of certain acetophenone derivatives. O. Hassel and E. Næshagen (Z. physikal. Chem., 1932, **B**, **15**, 417—420).—The dipole moments of *p*-chloro-, *p*-bromo-, *p*-iodo-, and *p*-amino-acetophenone are 2·29, 2·29, 2·23, and $4{\cdot}3\times10^{-18}$ e.s.u., respectively. These vals. correspond with an angle between the moment of PhAc and the group moment of the halogen of 53° in the Cl and Br compounds, and 49° in the I compound. This result indicates that in the CO group the C has excess positive charge and the O excess negative charge. R. Cuthill.

Structure and electric moments of certain dihalogeno*cyclo*hexanes. E. Halmöy and O. Hassel (Z. physikal. Chem., 1932, **B**, **15**, 472—473).—A preliminary report of dipole moment measurements with *cyclo*hexane derivatives of the type $C_6H_{10}X_2$ (X=Cl, Br, I). R. Cuthill.

Dielectric constant of liquids. VI. Aqueous solutions of sulphamide. G. Devoto (Atti R. Accad. Lincei, 1931, [vi], **14**, 432—434).—From the positive val. of the dielectric const.-concn. coeff., *dε/dc*, it is probable that sulphamide has the polar structure  $NH{:}SO<^{NH_3^+}_{O^-}$. O. J. Walker.

Dependence of dielectric constants of diluted strong electrolytes on frequency. H. Falkenhagen and E. L. Vernon (Physikal. Z., 1932, 33, 218—221).—A discussion of the general problem, and its application to sp. cases. An interpolation table is given by means of which the dispersion phenomena can be calc. in any special case. A. J. Mee.

Valency. XV. Dielectric constants of phosphorus trichloride and pentachloride. T. M. Lowry and J. Hofton (J.C.S., 1932, 207—211).—The dielectric const. of PCl_3 at 17° is 3·498 and at 59·8° 3·139. That of PCl_5 at 22·8° is 4·23 and at 160° 2·85. The abnormal increase for PCl_5 on solidification is attributed to a change in mol. structure, as in SCl_4 (cf. A., 1930, 666). Hot PCl_5 attacks Pt and Ag, but Ni, Mo, and W were unattacked at 180°.

H. J. Emeléus.

Molecular and atomic volumes. XXXIV. Densities of elements of the fourth to sixth groups at low temperatures. W. Biltz and A. Sapper [with E. Wunnenberg]. **XXXV. Volumetric determination of densities with small quantities of substance.** A. Sapper. **XXXVI. Density of cuprous oxide.** F. W. Wrigge and K. Meisel. **XXXVII. Volumes of crystallised hydrides of [elements of] the fourth to seventh groups at low temperatures. XXXVIII. Volumes of silicates.** W. Biltz and A. Lemke. **XXXIX. Calculation of volumes of technical glasses.** W. Biltz and F. Weibke (Z. anorg. Chem., 1932, 203, 277—306, 307—311, 312—320, 321—329, 330—344, 345—364; cf. A., 1931, 1214).—XXXIV. Densities of halogen compounds (excepting fluorides) of elements of groups IV, V, and VI, including derivatives of CH_4, have been determined at temp. down to −195°. Zero vols. of the compounds and of the halogen atoms concerned are calc.

XXXV. Technique of determining vols. of about 1·5 c.c. of substances at room temp. or −183°, with an accuracy of 0·01—0·06%, is described.

XXXVI. *X*-Ray diagrams of Cu_2O prepared both with and without org. reducing agents have been examined. No evidence of the existence of more than one form was obtained. The consts. were *a* 4·259±0·002 Å., *d* 6·11±0·01. Production of hollow spaces in the crystals of material made with org. reducing agents may lead to low pyknometric vals., but such irregularities do not affect the vals. derived from *X*-ray data.

XXXVII. Work described in Part XXXIV has been extended to the solid hydrides of elements of groups IV—VII, excepting CH_4, NH_3, and H_2O. The results are discussed theoretically.

XXXVIII. Previous measurements of densities of many silicates have been amplified and the data are collated.

XXXIX. Application of the principle of vol. additivity to the densities of a variety of glasses, with the aid of data given in Part XXXVIII, indicates that the glasses contain definite silicates in a state of mol. or submicronic dispersion in amorphous SiO_2. Densities of glasses containing Al_2O_3 or B_2O_3 can be accounted for only by assuming that the latter are present as complex alumino- or boro-silicates. F. L. Usher.

Refraction and dispersion of neon and helium. C. CUTHBERTSON and M. CUTHBERTSON (Proc. Roy. Soc., 1932, A, 135, 40—47).—Accurate measurements show that, although the difference between the free frequencies of the electrons in He and Ne is less than that formerly found (A., 1910, ii, 561), the anomaly in the frequency of Ne is real.

L. L. BIRCUMSHAW.

Atomic refractivity of fluorine. K. VON AUWERS (Z. physikal. Chem., 1932, **158**, 411—420).—The procedure adopted by Schiemann in determining the at. refractivity of F (A., 1931, 1355) is criticised.

R. CUTHILL.

[Atomic refractivity of fluorine.] G. SCHIEMANN (Z. physikal. Chem., 1932, **158**, 421).—A reply to von Auwers (cf. preceding abstract).

R. CUTHILL.

Magneto-optical dispersion of organic liquids in the ultra-violet region of the spectrum. IV. Magneto-optical dispersion of acetic anhydride, *n*-butyric acid, and ethyl *n*-butyrate. W. J. LEWIS and E. J. EVANS (Phil. Mag., 1932, [vii], **13**, 265—283; cf. A., 1931, 24).—Full data are recorded and an expression is deduced for the magneto-optical dispersion in the region 0·46—0·30 μ, and for the natural dispersion in the region 0·6678—0·2800 μ; the wave-lengths of the absorption band for the three liquids are 0·1031, 0·1064, and 0·1081 μ, respectively. The calc. vals. $\times 10^{-7}$ of *e/m* are 0·923, 0·992, and 1·008 e.m.u., respectively. N. M. BLIGH.

Magnetic rotatory power of blende as a means of measuring the field strength of an electromagnet with pierced pole-pieces. A. COTTON, G. DUPOUY, and M. SCHÉRER (Compt. rend., 1932, **194**, 405—409). C. A. SILBERRAD.

Double refraction of amorphous silica and quartz by compression, and its dispersion in the ultra-violet. G. BRUHAT and J. THOUVENIN (J. Phys. Radium, 1932, [vii], 3, 1—20).—A detailed account of work already noted (this vol., 6).

Double refraction of quartz along the optic axis. H. A. FERREIRA (Proc. Roy. Soc., 1932, A, 135, 214—223).—The vals. of the refractive indices of quartz along the optic axis are given for 22 wave-lengths between Li 6708 and Hg 2345. The mean of the two indices is the val. of *n* for the ordinary ray. The experimental vals. of the angular separation and of the difference of the two indices are in good agreement with those calc. from the Fresnel theory of rotatory polarisation. L. L. BIRCUMSHAW.

Variations in the refractive index of benzene during intensive drying. J. J. MANLEY (Phil. Mag., 1932, [vii], **13**, 249—264).—Using highly-purified C_6H_6 dried by Baker's method, μ for the liquid showed a gradual rise with time of drying; a similar rise was shown when the vapour was dried by P_2O_5 not in contact with the liquid. The irregular curve obtained on slowly melting dried and cryst. C_6H_6 indicates the formation in the liquid of complex and dense assemblages increasing in no. with drying to a max. val. and explaining the observed rise of b. p. During drying by various reagents the b. p. showed an irregular variation. $CaCl_2$ was inferior to KOH as a drying agent, and H_2SO_4 and P_2O_5 showed superior and nearly equal efficiency. N. M. BLIGH.

Optical rotatory power of vapours. I. Rotatory dispersion of camphor and camphorquinone, especially in the region of absorption. T. M. LOWRY and H. K. GORE (Proc. Roy. Soc., 1932, A, 135, 13—22).—Camphor vapour has $[M]^{180}_{5893}$ +83° and the rotatory dispersion curve shows a sharp max. at $[\alpha]^{180}_{3200}$ +2000° (approx.), followed by a reversal of sign at 3000 Å. and a negative max. $[\alpha]^{180}_{2800}$ −1860° (approx.). Camphor in solution in *cyclo*hexane shows a positive max. $[\alpha]^{20}_{3200}$ +2600° (approx.), followed by a step-out, a reversal of sign, and a negative max. $[\alpha]^{20}_{2720}$ −2100° (approx.). Camphorquinone vapour has $[M]^{200}_{5893}$ −146°, and the rotatory dispersion curve passes through a negative max. $[\alpha]^{200}_{4950}$ −500° (approx.). In *cyclo*hexane the negative max. is $[\alpha]^{20}_{4940}$ −450° (approx.), followed by a reversal of sign at 4740 Å., and a positive max. $[\alpha]_{4440}$ +300° (approx.). L. L. BIRCUMSHAW.

Optical rotatory powers of *d*-β-octyl hydrogen phthalate and its salts in various concentrations and the influence of added electrolytes. H. G. RULE and J. M. HILL (J.C.S., 1931, 2644—2652).—Salt formation lowers the rotatory power of *d*-β-octyl H phthalate, the effect being in the order Rb>K>Na>NH_4>Li; the rotation also decreases with concn. both with the acid and with the salts. Addition of alkali chlorides depresses the rotatory power of Na H phthalate, the effects being in the same order as above. Equiv. concns. of alkaline-earth cations produce still greater depressions, but $HgCl_2$, which is relatively non-ionised, has little effect. The changes are analogous to those observed with malic and tartaric acids, so it is concluded that the sensitivity of these acids to neutral electrolyte is related to the presence of the CO_2H group and not to the OH group as previously assumed. J. W. SMITH.

Solvent action. II. Rotatory powers of *d*-β-octyl hydrogen phthalate and its methyl ester. H. G. RULE and J. M. HILL (J.C.S., 1931, 2652—2658).—In solvents of the aromatic series the rotatory power of *d*-β-octyl H phthalate is the lower the higher is the dipole moment of the solvent, but the effect with aliphatic solvents is irregular. The dipole may be screened by an alkyl group, since PhAc has much less depressing action than PhCHO. In *m*- and *p*-disubstituted benzenes the dipoles appear to act independently. The results are compared with the effect of addition of electrolyte (cf. preceding abstract). Analogous effects are observed with tartaric acid, but here both electrolytes and dipolar solvents increase the rotation. J. W. SMITH.

Influence of thorium salts on the rotatory power of tartaric acid and tartrates. E. DARMOIS and YEU-KI-HENG (Compt. rend., 1932, **194**, 703—706).—In view of the great influence of temp. on the rotatory power of mixtures of a Th salt and a tartrate pointing to complex formation, [α] was plotted against the amount of $ThCl_4$ added to aq. Na tartrate (followed by addition of NaOH) with results pointing to the formation of $ThO_2,C_4H_4O_6Na_2$, stable in excess of alkali, and of $ThO_2,2C_4H_4O_6Na_2$, less stable. $Th(NO_3)_4$ behaves similarly (cf. A., 1903, ii, 601).

C. A. Silberrad.

Rotatory power of some amino-acids as a function of p_H. E. Vellinger (Compt. rend., 1932, 194, 718—720; cf. A., 1926, 778; 1927, 205).—Rotatory power–p_H curves for glutamic acid, leucine, and aspartic acid, calc. as before, are given. Darmois' scheme (cf. A., 1926, 1201) applies to the dispersion of glutamic acid, but not to that of leucine, aspartic acid, or alanine. C. A. Silberrad.

General theory for the quantitative determination of the dependence of refractive indices of non-absorbing substances on changes of density. N. Günther (Physikal. Z., 1932, 33, 175—177).—Mathematical. The theory has been verified experimentally with quartz. A. J. Mee.

Intermediate products in thermal decomposition of ammonia. A. B. F. Duncan and D. A. Wilson (J. Amer. Chem. Soc., 1932, 54, 401—402).—The NH band, assumed to be at 3360—3370 Å., could not be detected in the absorption spectrum of decomposing NH_3, a result which cannot be due either to insufficient decomp. of NH_3 or to the life of the NH mol. being too short. Either the mechanism of the surface decomp. is not $NH_3=NH+H_2$, or the absorption coeff. is so low that the effective absorbing layer was too short. C. J. West (c).

Co-ordination of hydrogen in associated liquids. J. C. Speakman (Nature, 1932, 129, 244).—The parachor for HF increases from 34·2 at −80° to 35·8 at 19·5°. The difference from the "theoretical" val. of 42·8 is nearly equal to that required for a liquid associated to double mols. and decreases steadily with a rise in temp. L. S. Theobald.

Non-adiabatic chemical processes. F. London (Z. Physik, 1932, 74, 143—174).—Theoretical. Perturbation coeffs. are developed as functions of the time and of mol. separations to express the dynamical interaction of two atoms or mols. Simple examples that require a dynamic as opposed to an adiabatic transition are sensitised ionisation and activation, and the formation of ionic mols. ($Na+Cl_2\longrightarrow NaCl+Cl$); these processes are superficially similar to inelastic electronic collisions, but the chemical transition occurs much more suddenly. Expressions are deduced for reaction velocities. A. B. D. Cassie.

Dependence of pre-dissociation on temperature. G. Joos and A. Herrmann (Physikal. Z., 1932, 33, 213—214).—The explanation of pre-dissociation given by Henri is somewhat different from that based on quantum mechanics (Herzberg). The question has been settled by investigating the sharpness of the single bands of the NO_2 spectrum over a temp. range of −15° to 500°; no sharp variation is found. This is in favour of the quantum-mechanics explanation. A. J. Mee.

Distribution of electrons in the aromatic nucleus and the early stages of aromatic substitutions. A. Lapworth and R. Robinson (Nature, 1932, 129, 278).—Hückel's conclusions (A., 1931, 1356) concerning the distribution of electrons in C_6H_6 derivatives and the mechanism of substitution are not accepted. L. S. Theobald.

Paramagnetic organic compound. J. Kenyon and S. Sugden (J.C.S., 1932, 170—171).—The compound $C_{18}H_{22}O_2N_2$ from $COMe_2$ and NHPh·OH (cf. A., 1926, 828) is diamagnetic, whilst its oxidation product $C_{18}H_{21}O_2N_2$, which is believed to contain N^{IV} or O^{I}, is strongly paramagnetic. The mol. has a moment close to 1·73 Bohr magnetons, corresponding with 1 unbalanced electron. H. J. Emeléus.

Thermoelectric properties of ferromagnetic substances. L. F. Bates (Phil. Mag., 1932, [vii], 13, 393—412).—The thermoelectric power of Mn_3As_2 changes when it passes from the ferromagnetic to the paramagnetic state; some specimens have a positive and others a negative Thomson coeff. A rod of pure Mn_3As_2 has a negative Thomson coeff. at the ferromagnetic crit. point and hence should show a decrease in sp. heat at this point, which agrees with direct calorimetric measurements. H. J. Emeléus.

Magnetism and valency. I. Copper and silver compounds. S. Sugden (J.C.S., 1932, 161—170).—The magnetic susceptibility of 10 Cu compounds and 9 Ag compounds was measured by the Gouy method. Compounds of Cu^I and Ag^I had zero moment, and in the bivalent state moments of 1·72—2·16 Bohr units, in agreement with predicted vals. for one unbalanced electron. H. J. Emeléus.

Rendering visible circuits of different ferromagnetic states of solid bodies. W. Gerlach (Z. Physik, 1932, 74, 128—129).—Polemical, against von Hámos and Thiessen (*ibid.*, 1931, 71, 442).

A. B. D. Cassie.

Interpretation of some ferromagnetic phenomena. F. Bitter (Physical Rev., 1932, [ii], 39, 337—344).—A review of contemporary theory.

N. M. Bligh.

New experimental methods in ferromagnetism. S. L. Quimby (Physical Rev., 1932, [ii], 39, 345—353).—Methods of observing the magneto-elastic, mechanical, and thermal properties of single and polycryst. specimens of Ni are described.

N. M. Bligh.

Effect of impurities on ferromagnetism. T. D. Yensen (Physical Rev., 1932, [ii], 39, 358—363).—The effect of "interstitial" impurities, C, O, N, and S on the *B–H* and hysteresis curves of Fe and of Fe–Ni alloys is considered. N. M. Bligh.

Hydrogenised iron. P. P. Cioffi (Physical Rev., 1932, [ii], 39, 363—367).—The improved magnetic characteristics of Fe with high-temp. heat treatment in H_2 are discussed. N. M. Bligh.

Magnetisation and thermal e.m.f. S. R. Williams (Physical Rev., 1932, [ii], 39, 368; cf. Sears, A., 1931, 1361).—The thermal e.m.f. between transversely and longitudinally magnetised wires is related to the Ettingshausen–Nernst effect.

N. M. Bligh.

Faraday effect in ferromagnetics. H. R. Hulme (Proc. Roy. Soc., 1932, A, 135, 237—257).—Theoretical. The rotation of polarised light transmitted through thin films of ferromagnetics is discussed, using the ordinary simple model for a ferro-

magnetic. For magnetisations in the region of saturation the rotation is found to be proportional to the magnetisation and to increase with the wave-length of the light. These results accord with experiment.
L. L. BIRCUMSHAW.

Gyromagnetic ratio for paramagnetic substances. III. Salts of the rare-earth group. W. SUCKSMITH (Proc. Roy. Soc., 1932, **A**, **135**, 276—281; cf. A., 1930, 1100).—The Van Vleck development of the Hund theory (A., 1928, 572) is most successful in explaining the experimental results. For the ions Gd^{+++}, Nd^{+++}, Eu^{+++}, and Dy^{+++} the theoretical vals. of *g*, the Landé splitting factor, are 2·0, 0·75, 6·4, and 1·33, respectively, the corresponding experimental vals. being 2·12, 0·78, $>$4·5, and 1·36.
L. L. BIRCUMSHAW.

Quenching of mercury resonance radiation. II. Further hydrocarbons and nitric oxide. J. R. BATES (J. Amer. Chem. Soc., 1932, **54**, 569—576; cf. A., 1930, 1489).—Vals. of the effective cross-section of the collision process $\times 10^{16}$ are: NO, 24·7; *n*-heptane, 24·0; ββγ-trimethylbutane, 19·7; Δ^{γ}-heptene, 55·9; Δ^{α}-heptene, 45·8; C_6H_6, 41·9. A general arrangement of mols. which correlates their effective cross-sections and structure is discussed.
J. B. AUSTIN (*c*).

Law of discontinuous distribution of Curie points. R. FORRER (Compt. rend., 1932, **194**, 697—699). C. A. SILBERRAD.

Physical properties and chemical constitution. I. Atomic refractions and observations on the parachor. J. D. A. JOHNSON (Ber., 1932, **65**, [*B*], 294—302).—Determination of the mol. refraction of the chloride, Et and Bu^{α} esters of phenylmethylphosphinic acid shows that the mean val. of the at. refraction of P^{III} is 2·03 units lower in aliphatic than in aromatic compounds and the refraction of the aliphatic $\equiv P \rightarrow O$ group is 1·59 units smaller than that of the aromatic $\equiv P \rightarrow O$ group. If O in $\equiv P \rightarrow O$ has the same val. as in others, the mean val. of the semipolar double linking is $-3·92$ and $-4·36$ units in aliphatic and aromatic compounds, respectively. Optical data indicate the structure $PH(OEt)_2 \rightarrow O$ for Et phosphite. In aliphatic As compounds the semipolar double linking has the val. $-3·5$. The causes of variation in the refraction of the semipolar double linking and of the parachor are discussed at length. Bu^{α} *phenylmethylphosphinate* has b. p. 166°/11 mm., d_4^{20} 1·0608.
H. WREN.

Effects of thermal strain on intensity of reflexion of *X*-rays by certain crystals. Y. SAKISAKA and I. SUMOTO (Bull. Inst. Phys. Chem. Res. Tokyo, 1932, **11**, 135—142).

Influence of lattice binding forces on *X*-ray emission spectra. R. GLOCKER and M. RENNINGER (Naturwiss., 1932, **20**, 122—123).—The theoretical significance of the influence of chemical binding on the long wave-length lines of the *K* series in simple elements may be best understood from consideration of allotropic modifications. Results for diamond and graphite are discussed. W. R. ANGUS.

Microstructure of pearlite. M. MIKAMI (Sci. Rep. Tôhoku, 1931, **20**, 710—714).—Photographs of pearlite taken with various methods of illumination show that it is impossible to say which constituent of the eutectoid appears white and which appears dark. The top portion of lamellar cementite in relief appears white, whilst the side faces are dark, and the bottom of the lamellar ferrite between two neighbouring cementite lamellæ also appears white, whilst both edges are dark. A. R. POWELL.

Vitreous state. I. Glass as a fourth state of matter. E. BERGER (Z. tech. Physik, 1931, **12**, 344—363; Chem. Zentr., 1931, ii, 1966).—A discussion.
A. A. ELDRIDGE.

Variation in the effective lattice constant of crystals with wave-lengths. J. M. CORK (Physical Rev., 1932, [ii], **39**, 193—196; cf. Bearden, A., 1931, 887).—*X*-Ray wave-lengths determined by a calcite crystal compared with reflexion angles for particular emission wave-lengths over 1—5·5 Å. using a quartz crystal are consistent to 0·03%. N. M. BLIGH.

Structure of very thin crystal sheets. F. KIRCHNER (Naturwiss., 1932, **20**, 123—124).
W. R. ANGUS.

Variation in dimensions caused by annealing cold-worked copper. A. SCHWEITZER (Compt. rend., 1932, **194**, 449—450).—The rate of variation increases with rise of temp. Up to 550° the variation is independent of the cold working, above that temp. it increases therewith. C. A. SILBERRAD.

Crystal structure of copper electro-deposited in presence of gelatin. H. KERSTEN (J. Physical Chem., 1931, **35**, 3644).—Comparison by *X*-ray examination of Cu deposited from a 10% gelatin solution on Au-plated brass with the deposit from a similar plating bath containing no gelatin indicates that the difference in the unit cell of the lattice is less than 0·01 Å. CHEMICAL ABSTRACTS (*c*).

Crystal structures of krypton, xenon, hydrogen iodide, and hydrogen bromide in relation to the temperature. B. RUHEMANN and F. SIMON (Z. physikal. Chem., 1932, **B**, **15**, 389—413).—Kr and Xe have the face-centred cubic lattice, and at 88—89° abs. have *a* 5·69 and 6·24 Å., and *d* 2·99 and 3·56, respectively. The existence of the transition point of Kr reported by Peters and Weil (A., 1930, 986) could not be confirmed. At 21°, 82°, and 125° abs., temp. between which lie the transition intervals revealed by sp. heat measurements, HI has a tetragonal face-centred lattice with c/a 1·08, which indicates that the transitions must be of the NH_4Cl type. At 125° abs. the lattice has *a* 6·19 Å. and *d* 3·17. *X*-Ray diagrams of HBr at 82—120° abs. suggest that the lattice is face-centred rhombic and that no fundamental crystallographic changes occur on passing through the transition intervals. R. CUTHILL.

Crystal structure of the tetrahalides of the lighter elements. II. O. HASSEL and H. KRINGSTAD (Z. physikal. Chem., 1932, **B**, **15**, 274—280; cf. A., 1931, 897).—$TiBr_4$ and TiI_4 have the same kind of cubic lattice structure as SnI_4, the lattice consts. (*a*) being 11·25 and 12·00 Å., respectively.
R. CUTHILL.

Crystal structure of β-zirconium. W. G. BURGERS (Nature, 1932, **129**, 281).—β-Zr is cubic

body-centred, with 2 atoms per unit cube, and *a* 3·61 Å. near the transition temp. (862°).
L. S. Theobald.

Crystal structure of lithium hydride. J. M. Bijvoet and A. Karssen (Z. physikal. Chem., 1932, **B**, 15, 414—415).—Polemical against Zintl and Harder (A., 1931, 1358). R. Cuthill.

Crystal structure of lithium hydride. E. Zintl and A. Harder (Z. physikal. Chem., 1932, **B**, 15, 416).—A reply to Bijvoet and Karssen (cf. preceding abstract). R. Cuthill.

Complexity of arsenic trioxide. I. A. Smits and E. Beljaars (Proc. K. Akad. Wetensch. Amsterdam, 1931, 34, 1141—1155).—The v. p. of As_2O_3 has been determined over the temp. range 240—380°. Below 200° the octahedral β-modification is stable and above 200° the monoclinic α-form. On prolonged keeping the β-form passes into a hitherto undescribed γ-form. The triple points are as follows: S_α–*L*–*G* 312·3° and 66·1 mm.; S_β–*L*–*G* 272·1° and 26·1 mm.; S_γ–*L*–*G* 289·6° and 40·7 mm. The α-modification on distillation yields a distillate with a higher v. p. and a residue with a lower v. p. than before distillation. It is concluded that the α-form is a mixed crystal phase in internal equilibrium. J. W. Smith.

***X*-Ray investigations of a sub-sulphide of cobalt used as a catalyst for the hydrogenation of phenol.** V. Caglioti and G. Roberti (Gazzetta, 1932, 62, 19—29).—CoS has a hexagonal structure: *a* 3·38, *c* 5·20, *c*/*a* 1·54, and Co_4S_3 a face-centred cubic structure, *a* 9·91. Both these sulphides catalyse the hydrogenation of aromatic rings containing substituent groups. The structure of Co_4S_3 is analogous to that of bornite, which appears to be Cu_3FeS_3.
O. J. Walker.

Dimensions of the atoms and univalent ions in crystal lattices. G. Natta (Mem. R. Accad. d'Italia, 1931, 2, [Chim., 3], 31 pp.).—Solid HCl, HBr, and HI have been examined by the powder method. The face-centred cubic form of HCl has *a* 5·435±0·01 Å. at the transition temp., −175°; 4 mols. in unit cell; *d* 1·49. HBr also is dimorphous; at −170° the face-centred cubic lattice has *a* 5·76±0·02 Å.; 4 mols. in unit cell; *d* 2·80. At temp. below −173° a form of lower symmetry, probably pseudo-tetragonal, is formed; *a* 5·60±0·02Å., *c*/*a* 1·08; 4 mols. in unit cell. At −170° HI crystallises in the tetragonal system, with *c*/*a* 1·075, 4 mols. in unit cell; *d* 3·46. The radii of the Cl, Br, and I ions are 1·92, 2·04, and 2·21 Å., respectively, and derived vals. are given for the radii of F′ and CN′ and of the positive ions in various halides. H. F. Gillbe.

***X*-Ray examination of the oxides of lead.** J. A. Darbyshire (J.C.S., 1932, 211—219).—Lattice consts. determined were: PbO (red), tetragonal (*a* 3·968, *c* 5·011 Å.); PbO (yellow), orthorhombic (*a* 5·459, *b* 4·723, *c* 5·859 Å.); PbO_2, tetragonal (*a* 4·931, *c* 3·367 Å.). No definite suboxide of Pb was obtained. Pb_2O_3 prepared by two methods was amorphous. Pb_3O_4 had a characteristic structure, not examined in detail. *X*-Ray methods may be used for examining commercial samples of Pb oxides.
H. J. Emeléus.

Polymorphism of lead monoxide. M. P. Applebey and H. M. Powell (J.C.S., 1931, 2821—2829).—Crystallographic measurements of the red form of PbO are given. The densities, solubilities in NaOH solutions of concn. up to 20*N* at 84° and at 20°, and microscopical examination of various preps. of PbO show no definite evidence for a black modification. The black, green, and purple forms of PbO which have been described are due to the presence of Pb; the red and yellow forms turn black on exposure to light or heat only in the presence of a trace of alkali. J. W. Smith.

Crystal structure of lithium hydroxide. T. Ernst (Naturwiss., 1932, 20, 124).—LiOH crystals are tetragonal: *a* 3·55, *c* 4·34 Å.; 2 mols. in unit cell; parameter, *u*=0·20. W. R. Angus.

Lattice constants of certain compounds of the spinel type. H. Hauptmann and J. Novák (Z. physikal. Chem., 1932, **B**, 15, 365—372).—Ga_2MgO_4, Al_2MgO_4, and Al_2ZnO_4 have face-centred cubic lattices and the spinel structure, and the vals. of a_ω are 8·279±0·006, 8·059±0·004, and 8·093±0·004 Å., respectively. R. Cuthill.

Orientation of crystals deposited on cleavage plates of mica or chlorite. L. Royer (Compt. rend., 1932, 194, 620—621). C. A. Silberrad.

Alternation in long-chain compounds. New *X*-ray data for long-chain ethyl and methyl esters and iodides and a preliminary thermal examination of the esters. T. Malkin (J.C.S., 1931, 2796—2805; cf. A., 1931, 290).—*X*-Ray crystallographic measurements have been made on the Me and Et esters of the higher fatty acids. Two cryst. forms of Et esters exist, one being stable only over a small temp. range immediately below the m. p. Only Me esters of odd fatty acids exist in two forms. Me esters crystallise in layers of double mols. and Et esters in layers of single mols. It is suggested that this accounts for the slightly higher m. p. of the former. The theory of alternation is discussed and it is suggested that the essential feature of an alternating series is that the zig-zag C chain is tilted with respect to the terminal planes. J. W. Smith.

Crystalline carbon tetraiodide. O. Hassel and H. Kringstad (Teknisk Ukeblad, 1931, 78, 230; Chem. Zentr., 1931, ii, 2117).—The length of the side of the smallest possible unit cube is 9·14 Å.
A. A. Eldridge.

Crystal forms of orthoform. A. Kofler and A. Mayrhofer (Mikrochem., 1932, 10, 460—466).—Orthoform exists in anhyd. tetragonal and hydrated monoclinic forms. In the micro-m. p. apparatus the former melts sharply at 142°, whilst the latter either liquefies or becomes cloudy, owing to dehydration, at 52—60°. H. F. Gillbe.

***X*-Ray examination of β-methylxyloside.** E. G. Cox (J.C.S., 1932, 138—142).—β-Methylxyloside is monoclinic sphenoidal (*a* 7·82, *b* 6·89, *c* 7·74 Å.; 2 mols. in unit cell; space-group C_2^2). The probable mol. structure suggested resembles that of α-xylose.
H. J. Emeléus.

Dimorphism of normal saturated fatty dicarboxylic acids as a function of temperature.

F. D. LA TOUR (Compt. rend., 1932, **194**, 622—623).—β-Glutaric acid, monoclinic, is obtained on evaporating an EtOH solution; its unit cell has *a* 10·06, *b* 8·47, *c* 17·4 Å., β 132° 35′, and contains 4 mols. The α (unstable) form is monoclinic, and has *a* 10·34, *b* 5·08, *c* 32·9 Å., β 129° 0′, with 8 mols. in the unit cell; transition temp. 74—75°. *a* (in Å.) for the β and α forms, and the transition temp. of acids $C_nH_{2n-2}O_4$, for $n=11$, 13, 15, and 17 are respectively 11·3, 12·8, 91°; 13·35, 14·6, ?; 15·05, 16·8, ?; 17·1, 19·2, 103°. (Cf. A., 1929, 126; 1931, 1036.) C. A. SILBERRAD.

Molecular association, apparent symmetry of the benzene ring, structure of the nitro-group in crystalline *m*-dinitrobenzene, and valencies of nitrogen in some organic compounds. S. B. HENDRICKS and G. E. HILBERT (J. Amer. Chem. Soc., 1931, **53**, 4280—4290).—The unit cell of *m*-dinitrobenzene contains 4 mols. and has *a* 13·27, *b* 14·06, *c* 3·820 Å.; the space-group is *Pbnm* (V_h^{16}). The min. mol. symmetry is a plane of symmetry which contains the N, C, and H atoms of a mol. The compound is associated along the *c* axis. The crystallographic equivalence of the O atoms of a NO_2 group indicates N^V. N is probably quinquevalent in many compounds in which it is joined to at least two O atoms, and tervalent in the nitrones, nitrenes, azoxy- and nitroso-compounds, which are free radicals chemically similar to some aldehydes and ketones. Evidence is given in support of the inner NH_4 salt structure of NMe_3 oxide. A. L. HENNE (*c*).

***X*-Ray investigation of the crystals of *o*-azotoluene.** M. PRASAD and K. V. DESAI (Phil. Mag., 1932, [vii], **13**, 600—603).—The crystals belong to the monoclinic prismatic class, with 4 mols. per unit cell; *a* 13·93, *b* 6·604, *c* 14·55 Å., space-group C_{2h}^5. The structure is compared with that of azobenzene. H. J. EMELÉUS.

Structure of dianthracene. J. HENGSTENBERG and J. PALACIOS (Anal. Fís. Quím., 1932, **30**, 5—11).—The rhombic crystals of dianthracene have *a* 8·18, *b* 12·15, and *c* 18·75 Å., with 8 anthracene groups in the unit cell; space-group V_h^{15}. The mol. structure is discussed; it is probable that the two anthracene mols. are linked at the 9 and 9′ positions. H. F. GILLBE.

***X*-Ray examination of *d*-mannitol and *d*-mannose.** G. W. MCCREA (Proc. Roy. Soc. Edin., 1932, **51**, 190—197).—The orthorhombic bisphenoidal crystals of the β-form of *d*-mannitol have *a* 8·66, *b* 16·58, *c* 5·50 Å.; 4 mols. in unit cell; space-group Q_4. The measurements confirm Irvine and Steele's conclusion of an asymmetric configuration. The α-form of *d*-mannose has *a* 5·53, *b* 17·66, *c* 7·59 Å.; 4 mols. in unit cell; space-group Q_4. The configuration has not been established, but is probably of the pyran ring type. H. F. GILLBE.

Crystal structures of vitamin-*D* and related compounds. J. D. BERNAL (Nature, 1932, **129**, 277—278).—Ergosterol, α-dihydroergosterol (and EtOH), calciferol, pyrocalciferol-calciferol, lumisterol, and cholesterol have *a* 9·75, 30·8, 20·8, 20·2, 20·3, and 16·4, respectively; *b* 7·4, 7·4, 7·15, 7·35, 7·25, and —, respectively; *c* 39·1, 43·1, 38·5, 40·0, 20·4 Å., and —, respectively; β 65°, 53°, 68°, 63°, 60°, and —, respectively. The respective space-groups are $C_2^2-P2_1$, C_2^3-C2, $C_2^2-P2_1$, C_2^3-C2, $C_2^2-P2_1$, and C_1^1-P1, and the no. of mols. per unit cell, 4, 12, 8, 8, 4, and —. From the similarities of properties of the crystals and the simple relation between their unit cells it is concluded that the unit cell of the calciferol-pyrocalciferol contains 4 mols. of each kind showing that calciferol is probably a simple substance structurally. Formulæ are discussed. L. S. THEOBALD.

Dependence of permeability of iron wires on high-frequency fields. M. WIEN (Physikal. Z., 1932, **33**, 173—175). A. J. MEE.

Measurement of magnetic saturation [of iron]. E. GEROLD (Arch. Eisenhüttenw., 1931—1932, **5**, 267—268).

Magneto-resistance and magneto-caloric effects in iron and Heusler alloys. H. H. POTTER (Phil. Mag., 1932, [vii], **13**, 233—248; cf. A., 1931, 1116).—Measurements made give further evidence of the direct proportionality of the magneto-resistance change to the change in magnetic energy, but the proportionality factor varies considerably for different substances. N. M. BLIGH.

Magneto-strain and magneto-resistance. L. W. MCKEEHAN (Physical Rev., 1932, [ii], **39**, 368—371).—A survey. N. M. BLIGH.

Magnetisation of single crystals. F. BITTER (Physical Rev., 1932, [ii], **39**, 371—375; cf. A., 1931, 1117).—Experimental data are shown to be in satisfactory agreement with theory. N. M. BLIGH.

Barkhausen effect: orientation of magnetisation in elementary domains. R. M. BOZORTH (Physical Rev., 1932, [ii], **39**, 353—356). N. M. BLIGH.

Propagation of large Barkhausen discontinuities. K. J. SIXTUS and L. TONKS (Physical Rev., 1932, [ii], **39**, 357—358).—A formula for the time of penetration for a large travelling Barkhausen discontinuity is discussed. N. M. BLIGH.

Hall effect, particularly in weak fields. M. CANTONE and E. BOSSA (Mem. R. Accad. d'Italia, 1930, **2**, [Fis., 1], 31 pp.).—Measurements of the effect as a function of the field strength have been made with Fe, steel, Ni, Bi, Te, Sb, Cu, and many other diamagnetic and ferromagnetic metals and alloys. H. F. GILLBE.

Hull magneton. L. PINCHERLE (Atti R. Accad. Lincei, 1931, [vi], **14**, 290—293). O. J. WALKER.

Lattice distortion and hardness of heat-treated tungsten magnet steels. W. A. WOOD (Phil. Mag., 1932, [vii], **13**, 355—360).—The decrease in magnetic quality and hardness on heating W steels to 900° is due to the disappearance of lattice distortion (indicated by a broadening of the lines of the *X*-ray spectrum). The distortion reappears on heating to 1250°. H. J. EMELÉUS.

Supposed allotropy of lead. W. EDA (Sci. Rep. Tôhoku, 1931, **20**, 715—725).—No discontinuities occur in the differential thermal curve, the electrical resistance curve, and the hardness curve of single-crystal Pb between 20° and 300°. The hardness of polycryst. Pb quenched from different temp. shows an abrupt increase at 200°, but, as this change does not occur in single crystals, it is probably a secondary effect due to the state of aggregation of the smaller crystals and is not, therefore, a sign of an allotropic transformation. A. R. Powell.

Polish on metals. J. T. Randall and H. P. Rooksby (Nature, 1932, 129, 280—281).—A discussion (cf. this vol., 219). L. S. Theobald.

Determination of mol. wt. of dissolved substances by means of dynamic measurement of the lowering of vapour pressure. E. Bovalini (Atti R. Ist. Veneto Sci., 1930—1931, 90, 7—21; Chem. Zentr., 1931, ii, 2105—2106).—Vals. for $CO(NH_2)_2$, NaCl, H_3BO_3, mannitol, and galactose in H_2O, anethole in C_6H_6, and for $CO(NH_2)_2$ and succinic acid in EtOH have been determined. Practically normal vals. were obtained for $CO(NH_2)_2$, boric acid (as HBO_2), and NaCl (conc.) in H_2O, anethole in C_6H_6, and $CO(NH_2)_2$ in EtOH. A. A. Eldridge.

Difference in the effect of magnetic and electric fields on the conductivity of heat in gases. H. Senftleben (Physikal. Z., 1932, 33, 177—178).—Both a magnetic field and an electric field affect the conductivity of heat in gases, but the magnetic field decreases, whilst the electric field increases, the conductivity. If streaming takes place, the electric effect disappears, whilst the magnetic is unaffected. The magnetic effect is thus a pure heat conductivity effect, whilst the electric field probably gives rise to association of the gas mols. It is the later dissociation of these that causes the apparent increase in conductivity. A. J. Mee.

Resistance of lead and tin to high-frequency currents at superconducting temperatures. J. C. McLennan (Trans. Roy. Soc. Canada, 1931, [iii], 25, III, 191—193).—Pb shows a change to superconductivity at a lower temp. with alternating currents than with direct. With currents of frequencies 1·1—$1·6\times10^7$ per sec. a similar result was found for Sn. A. J. Mee.

Electrical conductivity of ruthenium, ruthenium carbide, and tungsten carbide. J. C. McLennan, J. F. Allen, and J. O. Wilhelm (Trans. Roy. Soc. Canada, 1931, [iii], 25, III, 13—25).—Specimens of impure Ru have been found to be superconducting, whereas pure Ru is not. The superconductivity is due to the presence of both W and C, in the form W_2C. A. J. Mee.

[Velocity of sound in carbon dioxide.] O. Heil (Z. Physik, 1932, 74, 31—33).—The discrepancy between Kneser's estimate of collisions per sec. (A., 1931, 553) and that from extinction of resonance spectra is due to neglect of the efficiency of each collision. A. B. D. Cassie.

M. p. of iridium. H. von Wartenberg, H. Werth, and H. J. Reusch (Z. Elektrochem., 1932, 38, 50).—Two differently prepared samples of Ir gave m. p. 2435±15° and 2440±15°, respectively. The accuracy of measurement at these temp. is about 25°. A few % of Os or Ru raise the m. p. several hundred degrees. M. S. Burr.

F. p. of the two forms of methylene iodide. H. W. Stone (J. Amer. Chem. Soc., 1932, 54, 112—114).—When liquid CH_2I_2 is immersed in an air-bath surrounded by ice water an unstable form with f. p. 5·54° separates. A stable form with f. p. 6·01° is obtained by immersing directly in the cooling bath. L. Kelley (c).

Specific heats of the diatomic gases. P. S. H. Henry (Nature, 1932, 129, 200—201).—A discussion. L. S. Theobald.

Specific heat of magnesium and aluminium oxides at high temperatures. G. B. Wilkes (J. Amer. Ceram. Soc., 1932, 15, 72—77).—Sp. heats of pure Al_2O_3 and MgO were determined up to 1700° and 1800°, respectively. The apparatus consisted of a vertical carbon tube furnace and a special calorimeter. Errors are discussed; an accuracy of at least 0·5% is claimed. J. A. Sugden.

Heat capacities at low temperatures of sulphides of copper and lead. C. T. Anderson (J. Amer. Chem. Soc., 1932, 54, 107—111; cf. A., 1931, 552).—The heat capacities of Cu_2S, CuS, and PbS were measured at 55—300° abs. From these and auxiliary data the following vals. were calc. for these substances, respectively, at 298·1° abs.: entropy, $S°$, 28·9, 15·9, 21·9; heat content change on formation from the elements, $\Delta H°$, −19,000, −11,600, −20,600; free energy of formation, $\Delta F°$, −20,640, −11,720, −20,200. F. D. Rossini (c).

Quantum dynamical correction for the equation of state of real gases. H. Margenau (Proc. Nat. Acad. Sci., 1932, 18, 56—62).—Deviations from the perfect gas law arise from forces due to the interaction of rapid electronic motions within the mols. Calculations of the second virial coeff. agree well with experimental vals. except for H_2 and He. This lack of agreement may be due to the existence of zero point energy associated with the vibration of mols. in quantised collision states which might render ineffective the attractive van der Waals forces. A mathematical investigation of this phenomenon and its effect on the equation of state are given. W. R. Angus.

Theory of equations of state. T. S. Wheeler (Phil. Mag., 1932, [vii], 13, 604—615).—A general expression for the work of dilution of a system of charged particles in thermal equilibrium is deduced from thermodynamic and dimensional considerations. H. J. Emeléus.

Influence of air on properties of organic solvents. J. Horiuti (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 17, 257—264).—The effect of dissolved air on d and the v. p. is discussed. R. Cuthill.

Density and molecular state of vapours of tellurium dibromide, tellurium tetrabromide, and selenium dioxide. D. M. Yost and J. B. Hatcher (J. Amer. Chem. Soc., 1932, 54, 151—155; cf. A., 1931, 294, 1117).—The v. d. of $TeBr_2$ and $TeBr_4$ were determined at 440—1000°. Above 750° $TeBr_2$ is appreciably dissociated into Te and Br_2. At 432° $TeBr_4$ is more than 90% decomposed into $TeBr_2$ and Br_2, and at 600° dissociation is complete, but the $TeBr_2$ formed does not dissociate appreciably into Te and Br_2 below 1000°. The v. d. of SeO_2 is normal at

360—500°, and the yellow colour of the vapour is unexplained. L. KELLEY (*c*).

Carbonyl selenide. I. Preparation and physical properties. T. G. PEARSON and P. L. ROBINSON (J.C.S., 1932, 652—660).—*Carbonyl selenide*, COSe, is prepared by passing CO over heated Se. It is a colourless evil-smelling gas condensing to a colourless mobile liquid, b. p. −22·9±0·2° at 725 mm. and crit. temp. 121·1±0·2°. It freezes to a snow-white cryst. solid, m. p. −122·1±0·5°. V. d. agrees with the formula COSe, which is also confirmed by analysis, d_4^{21} is 1·812 for liquid under its own v. p. The coeff. of expansion is 0·001756 between 4·1° and 21·1°. γ at 4·1° is 19·32±0·1 dynes per cm. with temp. coeff. 0·156 between 4·1° and 21·6°. The observed parachor is 126·6 (calc. 133·7). M. S. BURR.

Physical properties of carbonyl sulphide. T. G. PEARSON, P. L. ROBINSON, and J. TROTTER (J.C.S., 1932, 660—661).—The carbonyl sulphide was prepared by passing CO over heated S, drying by distillation over P_2O_5, and fractionating. V. d. is 0·002668, giving mol. wt. 59·74 (calc. for COS, 60); *d* of liquid at 0° is 1·073, coeff. of expansion (0—32·2°) 0·002710, and γ at 2·3° 13·00 dynes per cm. with temp. coeff. 0·1626. The Eötvös–Ramsay–Shields const. is 2·02, indicating absence of association. Parachor 111·1 (calc. 119·4). M. S. BURR.

Two different liquid states. M. WOLFKE and J. MAZUR (Z. Physik, 1932, 74, 110—127).—Temp. variation of the dielectric const., density measurements, and curves of rate of heating all indicate two distinct liquid states for CS_2, $PhNO_2$, and Et_2O.

A. B. D. CASSIE.

Physical properties of nitrobenzene in the neighbourhood of the m. p. N. B. MASSY, F. L. WARREN, and J. H. WOLFENDEN (J.C.S., 1932, 91—95).—The viscosity, density, and heating rate of $PhNO_2$ were measured from 6° to 14°. No evidence was found of reported discontinuities in physical properties at 9·8° (cf. A., 1931, 148, 741, 893).

H. J. EMELÉUS.

[Physical properties of methyl bromide, dichloroethylene, and methylamine.] R. PLANK [with A. W. HSIA, L. VAHL, W. BÜCHE, H. STAKELBECK, and W. H. SCHREIBER (Z. ges. Kälte-Ind., 1931, 38, 97—101; Chem. Zentr., 1931, ii, 2130).—MeBr: $\log$ v. p.$=10{\cdot}3344-1375{\cdot}625/T-1{\cdot}11078\log T+8{\cdot}559\times10^{-4}T$; b. p. 3·2°; f. p. −93°; crit. temp. 194°, d^0 1·731. *s*-$C_2H_2Cl_2$: b. p. 48·46°; $\log$ v. p.$=11{\cdot}23645-1702{\cdot}5468/T-1{\cdot}25137\log T+0{\cdot}00023807T$; *as*-$C_2H_2Cl_2$: b. p. 59·75°; $\log$ v. p.$=11{\cdot}4651-1711{\cdot}9275/T-1{\cdot}4394\log T+0{\cdot}000569T$. NH_2Me: sp. heat 15°, 0·765 kg.-cal. per kg. (°C). Thermal properties of the system NH_2Me–metallic chlorides, viscosities of CO_2, NH_3, and SO_2 at −20° to 20° or 31°, and the thermal conductivities of H_2O, CO_2, NH_3, and SO_2 at 20° are recorded.

A. A. ELDRIDGE.

Determination of isotherms for hydrogen between 0° and 100° up to 1000 atmospheres. A. MICHELS, G. P. NIJHOFF, and A. J. J. GERVER (Ann. Physik, 1932, [v], 12, 562—568).—The temp. used were approx. 0°, 25°, 50°, 75°, and 100°. Interpolated vals. were obtained for other temp. and pressures, and the virial coeff. was calc. A. J. MEE.

Possibilities in relativistic thermodynamics for irreversible processes without exhaustion of free energy. R. C. TOLMAN (Physical Rev., 1932, [ii], 39, 320—336).—Theoretical. N. M. BLIGH.

Density and surface tension of liquid hydrogen fluoride. J. H. SIMONS and J. W. BOUKNIGHT (J. Amer. Chem. Soc., 1932, 54, 129—135).—For liquid HF between −75° and +5° $d=1{\cdot}0020-0{\cdot}0022625t+0{\cdot}000003125t^2$. The surface tension from −80° to +19° may be represented by $\gamma=40{\cdot}7[1-(T/503{\cdot}2)]^{1{\cdot}78}$. γ and its temp. coeff. suggest that the liquid is polymerised. A. L. HENNE (*c*).

Effect of intensive drying on the rate of distillation and on the vapour pressure of ethyl bromide. J. W. SMITH (J.C.S., 1931, 2573—2583).—After intensive drying over P_2O_5, the rate of non-ebullitional distillation of EtBr between bulbs at const. temp. in an evacuated and sealed apparatus is retarded considerably. The v. p., however, remains unaltered and no difference could be detected between head and tail fractions after distillation. Ebullition occurs with more difficulty in the dried liquid. It is suggested that the internal equilibrium in a liquid is not disturbed by the intensive drying, but that the effects observed are due to some form of superheating probably induced by the removal of nuclei during the P_2O_5 treatment. J. W. SMITH.

High-frequency stroboscopy. J. A. STRONG (Nature, 1932, 129, 203—204).—Density changes in a quartz crystal can be observed stroboscopically using the principle previously described (this vol., 115). L. S. THEOBALD.

Physical constants. W. HERZ (Z. anorg. Chem., 1932, 203, 271—276).—Numerical relations between surface tension, viscosity, and temp. are discussed. Vols. of alkali halide mols. are calc. from refractive indices of their solutions, and vals. so obtained are compared with those derived by other methods.

F. L. USHER.

Viscosity of organic fluorine compounds. F. SWARTS (J. Chim. phys., 1931, 28, 622—650).—Determinations of viscosity over the range 20—60° are recorded for *n*-$C_5H_{11}F$, *n*-$C_7H_{15}F$, $CHF_2{\cdot}CHCl_2$, $CHCl_2{\cdot}CHFCl$, $CF_2Cl{\cdot}CFCl_2$, $CH_2Br{\cdot}CHF_2$, $CH_2F{\cdot}CH_2{\cdot}OH$, $CHF_2{\cdot}CH_2{\cdot}OH$, $CF_3{\cdot}CHMe{\cdot}OH$, $CF_3{\cdot}CMe_2{\cdot}OH$, $CH_2F{\cdot}CH_2{\cdot}OAc$, $CHF_2{\cdot}CH_2{\cdot}OAc$, $CF_3{\cdot}CHMe{\cdot}OAc$, $CH_2F{\cdot}CO_2Et$, $CHF_2{\cdot}CO_2Et$, $CF_3{\cdot}CO_2Et$, $CF_3{\cdot}CO_2H$, $CHF_2{\cdot}CO_2H$, CF_3Ac, PhF, 1:3- and 1:4-$C_6H_4F_2$, *o*-, *m*-, and *p*-C_6H_4MeF, $CPhF_3$, *o*-, *m*-, and *p*-$C_6H_4F{\cdot}NO_2$, *o*-, *m*-, and *p*-$C_6H_4F{\cdot}NH_2$, 1:2:5-$C_6H_3F_2{\cdot}NH_2$, *o*-, *m*-, and *p*-$C_6H_4F{\cdot}OEt$, and trifluoromethyl*cyclo*hexane. The data are discussed in relation to those for related compounds not containing F and are compared with vals. obtained for b. p., *n*, and heat of combustion. No simple, additive rule is found. $CF_2Cl{\cdot}CFCl_2$, obtained by acting on C_2Cl_2 with SbF_3 in presence of $SbCl_5$, has b. p. 47·4°, f. p. −36·4°, d^0 1·6200.

E. S. HEDGES.

Necessity of using absolute viscosity coefficients or coefficients of absolute kinematic vis-

cosity as practical measure of viscosity. P. Woog (Ann. Office Nat. combust. liq., 1930, 5, 805—829; Chem. Zentr., 1932, ii, 1114).—A comparison of theoretical and practical data. L. S. Theobald.

Allotropy of white tin and the equilibrium diagram of the system tin–cadmium. Y. Matuyama (Sci. Rep. Tôhoku, 1931, 20, 649—680).—Measurements of the electrical resistance, thermal expansion, and thermoelectric power of Sn and thermal and *X*-ray analysis of Sn between 20° and the m. p. failed to show the existence of a transformation point. The eutectic point at the Sn end of the Cd–Sn system occurs at 5% Cd and 181·7° and the eutectoid point at 4·3% Cd and 130°. A. R. Powell.

Equilibrium diagram of the iron–zirconium system. R. Vogel and W. Tonn (Arch. Eisenhüttenw., 1931—1932, 5, 387—389).—Fe and Zr combine readily with considerable evolution of heat when the metals are heated together in an atm. of A, forming the compound Fe_3Zr_2, m. p. 1640°. This compound forms a eutectic with Zr at 88% Zr and 1350° and a eutectic with γ-Fe at 16% Zr and 1330°. The solubility of Zr in δ-Fe is 7% and this solid solution decomposes at 1335° into saturated γ-Fe with 0·7% Zr and liquid; hence alloys with up to 7% Zr have a "second m. p." The presence of Zr in δ-Fe lowers the $\delta \longrightarrow \gamma$ transformation of Fe linearly with increasing Zr content from 1400° to 1335°. The solubility of Zr in α-Fe is 0·3% and the $\gamma \longrightarrow \alpha$ transformation is thereby lowered from 900° to 835°; Zr has no effect on the magnetic transformation point of Fe. The transformation point of Zr is raised by addition of Fe from 862° to 1000° with 5% Fe, after which it remains const. The solubility of Fe in α-Zr is about 10% and in β-Zr about 5%. A. R. Powell.

***X*-Ray experiments on the solubility of silver in copper.** P. Wiest (Z. Physik, 1932, 74, 225—253).—Precision measurements were made of lattice consts. Solubility is greater in the single crystal, and the diffusion process proceeds more slowly. Deposition of Ag from supersaturated solutions was also studied. A. B. D. Cassie.

Hall effect and other physical properties of the copper–cadmium series of alloys. W. Richards and E. J. Evans (Phil. Mag., 1932, [vii], 13, 201—225).—The electrical resistivities, temp. coeffs. of resistance, thermoelectric powers, Hall coeffs., and the sp. heats and densities of carefully annealed Cu–Cd alloys have been determined. Discontinuities in the electrical property–composition curves indicate the compounds $CuCd_3$, Cu_2Cd_3, Cu_4Cd_3, and possibly Cu_2Cd. The Hall coeff.–composition curves follow generally the phase changes. N. M. Bligh.

Segregation of cementite from austenite. R. F. Mehl, C. S. Barrett, and D. W. Smith (Nature, 1932, 129, 313—314).—Results differing from those of Hanemann and Schröder (this vol., 220) have been obtained. L. S. Theobald.

Density of mixtures of ethyl alcohol with petroleum distillation products. B. Karpiński (Przemysł Chem., 1932, 16, 1—4).—The densities of mixtures of EtOH with gasoline, benzine, or paraffin oil are less than those calc. from the mixture rule, the greatest deviations being for mixtures containing 40—60% of EtOH. The deviation increases with diminishing *d* of the hydrocarbon. R. Truszkowski.

Vapour pressures of binary mixtures. A. W. Porter (Trans. Faraday Soc., 1932, 28, 95—97; cf. A., 1928, 710).—Polemical. A formula used by Bancroft (this vol., 117) is a special case of Margules' general equation and is not applicable to dil. solutions. J. G. A. Griffiths.

Binary azeotropic mixtures. W. Swientosławski [with J. Just, L. Wajcenblitt, I. Wuttke, and P. Wojtczak] (Rocz. Chem., 1932, 12, 48—57).—C_6H_6 and AcOEt do not form azeotropic mixtures. The b. p. for CS_2–$COMe_2$ (33 mol.-% $COMe_2$) is 39·27°/760 mm., for C_6H_6–EtOH 67·93°, and for PhMe–EtOH 76·83°. R. Truszkowski.

Partial pressure isotherms. II. S. C. Lee (J. Physical Chem., 1931, 35, 3558—3582; cf. this vol., 117).—The isotherms for binary mixtures of C_6H_6 with MeOH and with $Pr^{\alpha}OH$ were determined at 40°. The abnormality of the curves obtained is attributed to the tendency of the mixtures to separate into two layers. G. M. Murphy (*c*).

The fluidity mixture law. E. C. Bingham and D. F. Brown (J. Rheology, 1932, 3, 95—112).—Batschinski's formula is used to derive a "volume-corrected fluidity" which should be a linear function of vol. concn. for an ideal solution. New density and fluidity data are given for mixtures of C_6H_6 with Et_2O and $COMe_2$. C. W. Davies.

Fluidities of non-aqueous mixtures. E. C. Bingham and H. E. Rogers (J. Rheology, 1932, 3, 113—120).—The equation of Bingham and Brown (cf. preceding abstract) is compared with available data. Where fluidity curves show minima due to compound formation, the max. deviation from the linear graph (and not the position of the min.) occurs at the correct mol. ratio and is independent of temp. C. W. Davies.

Surface tensions of mixtures of *n*-propyl alcohol and benzene. R. C. Brown (Phil. Mag., 1932, [vii], 13, 578—584).—The surface tension–composition curve shows a reversal of curvature at approx. 7% PrOH. A min. in the viscosity–composition curve occurs in the same region (cf. J.C.S., 1905, 87, 11). The formation of complex mols. $3C_6H_6,2PrOH$ is suggested. H. J. Emeléus.

System iron–mercury and the solubility of nickel in mercury. E. Palmaer (Z. Elektrochem., 1932, 38, 70—76).—A val. of about 0·00007% has been found for the solubility of Fe in Hg by stirring the latter with an amalgamated Fe wire, shaking the Hg with an acid solution of Hg_2SO_4 in presence of excess of the salt, pptg. Hg with HCl, and determining Fe colorimetrically by NH_4CNS. The solubility does not change appreciably between 20° and 211°. When Fe is deposited electrolytically in presence of Hg, crystals of "Fe amalgam" are deposited. These, however, have been shown to be crystals of pure Fe in suspension. The solubility of Ni in Hg, determined by stirring Hg with an amalgamated Ni wire, is

approx. 0·00014% at 20°. The method of separating Ni is the same as for Fe, Ni being subsequently determined colorimetrically by dimethylglyoxime and aq. Br.
M. S. Burr.

Velocity of crystallisation of sucrose. G. J. F. Breedveld and H. J. Waterman (Rec. trav. chim., 1923, **51**, 239—247).—A method of measuring the velocity of crystallisation of sucrose from a supersaturated solution, giving reproducible results, has been devised. $P_2^{\frac{1}{3}}-P_1^{\frac{1}{3}}=\frac{1}{3}\alpha kt$, where P_1 is the wt. of the crystal at the beginning, P_2 at the end of the time t, α the velocity of crystallisation in mg. per sq. m. per min., and k a coeff. depending on the kind of crystal. For sucrose $k=4{\cdot}12$. The supersaturation coeff. has been plotted against α and the results have been compared with those of Kucharenko (Planter Sugar Mfr., 1928).
M. S. Burr.

Behaviour of formic, acetic, propionic, butyric, and *iso*butyric acids on extraction from aqueous solution with light petroleum. J. Grossfeld and A. Miermeister (Z. anal. Chem., 1932, **87**, 241—262).—The constancy of the relation $c_1/\sqrt{c_2}$ (c_1 and c_2 are concn. in H_2O and light petroleum, respectively), previously observed for acids of higher at. wt. (A., 1931, 1270), is not maintained in the series examined, except for higher concn. of *n*- and *iso*-butyric acids. In general it diminishes as concn. diminishes. The ratio c_1/c_2 increases to a max. with diminishing concn., except for HCO_2H, where it diminishes. The % of acid extracted by equal vols. of light petroleum from solutions of different concn. is tabulated. The solubility of HCO_2H and AcOH in light petroleum is extremely small.
M. S. Burr.

Adsorption of gases by solids. H. S. Taylor (Trans. Faraday Soc., 1932, **28**, 131—138).—A general statement of the present position and a reply to criticisms of the author's theory of activated adsorption (A., 1931, 421).
J. G. A. Griffiths.

Adsorption of gases by solids. Experimental methods. E. K. Rideal (Trans. Faraday Soc., 1932, **28**, 139—147).—Methods of investigating the formation and nature of surface phases are summarised.
J. G. A. Griffiths.

Pressure measurements for investigating mutual behaviour of adsorbed hydrogen atoms. M. C. Johnson (Trans. Faraday Soc., 1932, **28**, 162—165).—See A., 1931, 1006; 1930, 1385, 1084, 525.
J. G. A. Griffiths.

Adsorption of saturated vapours by porous substances. Experimental methods. F. G. Tryhorn and W. F. Wyatt (Trans. Faraday Soc., 1932, **28**, 158—161).—Mainly a summary of methods previously described (cf. A., 1928, 118, etc.).
J. G. A. Griffiths.

Criticism of experimental evidence for activated adsorption. L. J. Burrage (Trans. Faraday Soc., 1932, **28**, 192—194).—Unless surfaces are perfectly clean, fictitious vals. of the energy of activation of the adsorption process are obtained from velocity measurements. Traces of foreign gases cannot be entirely removed by evacuation alone, but are best removed by flushing out with gas at high temp. "Cleaning up" effects may well account for some of the phenomena attributed to activated adsorption.
J. G. A. Griffiths.

Sorption of gases by glass. F. P. Burt (Trans. Faraday Soc., 1932, **28**, 179—184).—The sorption of NH_3 at const. pressures between 100 and 800 mm. has been investigated over long periods. The plot of log. sorption velocity against log. time affords two straight lines united by a short curve, and a general relation between sorption, time, pressure, and temp. is found. During desorption, the sorption halts at a higher val. than the corresponding point on the sorption curve, possibly owing to a balance between slow desorption and slow continued sorption. It is recommended that in density determinations the glass vessel be exposed for a long time to the gas at the max. pressure to be used.
J. G. A. Griffiths.

Adsorption of gases and vapours on plane surfaces. C. E. H. Bawn (J. Amer. Chem. Soc., 1932, **54**, 72—86).—The adsorption of CO, O_2, and A on mica at 90° and 193° abs. and at pressures from 1×10^{-4} to 2×10^{-2} cm. has been measured. At 90° the adsorption of CO and O_2 follows Langmuir's formula, but no simple equation will represent the adsorption of A. The isotherms at 193° are rectilinear up to 8×10^{-3} cm., but at higher pressures follow Langmuir's equation, which is also valid for the adsorption of $COMe_2$ at room temp. In no case does the adsorbed layer exceed one mol. in thickness.
Chemical Abstracts (*c*).

Thermionics in the study of adsorption of vapours and gases. J. A. Becker (Trans. Faraday Soc., 1932, **28**, 148—158).—Examples of previous work (*e.g.*, A., 1929, 756; 1930, 127) demonstrate the utility of thermionic emission phenomena in the study of evaporation, migration, and diffusion at surfaces.
J. G. A. Griffiths.

Vapour-pressure isotherms and submicroscopical structure of active carbon. II. P. Kubelka and M. Müller (Kolloid-Z., 1932, **58**, 189—197).—Experiments previously reported (A., 1931, 794) have been extended to other vapours, some new forms of activated C, and also SiO_2 gel. In all cases the equilibrium conditions indicate capillary condensation. The structure relations previously described for C do not hold for SiO_2 gel, but whether the difference is qual. or quant. is not clear.
E. S. Hedges.

Microtome method for determination of absolute amount of adsorption. J. W. McBain and C. W. Humphreys (J. Physical Chem., 1932, **36**, 300—311).—A method of determining the amount of adsorption at an air–H_2O interface is described. The surface of the solution, which is contained in a shallow Ag trough and is in equilibrium with the gas phase above it, is caused to assume a convex form by paraffining the ends of the trough. By means of a rapidly-moving microtome blade a layer of uniform thickness (0·05—0·1 mm.) is cut off from a known area of the surface of the solution and collected in a cylinder on which the blade is mounted, and its concn. is compared with that of the bulk of the solution by means of an interferometer. The results obtained with solutions of *p*-toluidine, PhOH, and hydrocinnamic acid indicate, when compared with results obtained by the bubble method (A., 1927, 1022; 1930, 152), that the ideal conditions of the experiment are almost realised in the new method, and that Gibbs' equation is a limiting law. S. LENHER (c).

Desorption methods for measurements to 2° absolute. K. MENDELSSOHN (Z. Physik, 1931, **73**, 482—501).—An apparatus is described by means of which a temp. of 1·6° abs. may be attained by desorption from charcoal. A. B. D. CASSIE.

Behaviour of adsorbed atoms. J. CHARITON, N. SEMENOV, and A. SCHALNIKOV (Trans. Faraday Soc., 1932, **28**, 169—176).—When the temp. of the surface in contact with Cd vapour of fixed density is raised above the supposed "crit." val., a deposit of Cd appears if sufficient time is allowed. This time increases with rise of temp. Such deposits, unlike those obtained below the "crit. temp.," are irregular. The discrepancy between the theory of Semenov (A., 1930, 851) and the absence of a "crit. temp." is attributed to the inhomogeneity of the surface, condensation occurring at the most active points from which the deposits grow. Approx. calculations show that the elementary displacement of an adsorbed atom is many times greater than the interat. distances of the adsorbent and it is suggested that impurities make the surface energetically smooth. Mols. from the gas phase impinging on adsorbed mols. have little effect on the establishment of the surface equilibrium provided the surface density is not large. J. G. A. GRIFFITHS.

Mixture isotherms at active points. H. DOHSE and H. MARK (Trans. Faraday Soc., 1932, **28**, 165—169).—Mixture isotherms for $Pr^{\beta}OH$ and H_2O on active points of bauxite are computed from the velocities of the unretarded and retarded dehydrations of $Pr^{\beta}OH$ on bauxite (A., 1929, 1231). J. G. A. GRIFFITHS.

Inner adsorption in crystalline salts. IV. D. BALAREV [with S. SOTIROV and B. SREBROV] (Kolloid-Beih., 1932, **34**, 441—461).—The observed inclusion of impurities in cryst. $MgNH_4PO_4$,aq., $ZnCO_3$, $CdCO_3$, and $CaCO_3$ is in accordance with the principles of inner adsorption formerly described for $BaSO_4$ etc. (A., 1930, 684). The hygroscopicity of Al_2O_3, CuO, MoO_3, and WO_3 is traced to their fine capillary structure and is considered from the same point of view. Further evidence is adduced to support the view that crystals have a mosaic structure (cf. A., 1929, 263), which can provide adsorbent surfaces. E. S. HEDGES.

Heats of adsorption of oxygen on nickel and copper catalysts. W. W. RUSSELL and O. C. BACON (J. Amer. Chem. Soc., 1932, **54**, 54—71).—The extent and heat of adsorption on promoted, unpromoted, supported, and unsupported catalysts have been measured. The approx. mol. heats of adsorption on Ni and Cu, each promoted with ThO_2, are 98,000 and 82,000 g.-cal., respectively. The adsorption by both metals is irreversible, but a catalytically active surface can be produced by the adsorption of O_2 at 0° followed by heating at some suitable temp., which presumably converts the adsorbate into stable oxide. The variation in the catalytic hydrogenating activity of a Cu catalyst with the extent and heat of O_2 adsorption suggests a relation between these properties. CHEMICAL ABSTRACTS (c).

Selective adsorption by activated charcoal from solutions containing two organic acids. C. OCKRENT (J.C.S., 1932, 613—630; cf. A., 1930, 1514).—Using activated ash-free sugar charcoal as adsorbent, adsorption isotherms (25°) of BzOH, o-$OH{\cdot}C_6H_4{\cdot}CO_2H$, o-$C_6H_4Me{\cdot}CO_2H$, $CH_2Cl{\cdot}CO_2H$, AcOH, HCO_2H, and $CCl_3{\cdot}CO_2H$ in aq. solution have been determined. Adsorption at equiv. concns. decreases in the order given. Adsorption from solutions containing pairs of the above acids is not proportional to their individual adsorptions, but the more adsorbable acid is selectively (in one case exclusively) adsorbed. Langmuir's theory applied to adsorption of two solutes is not valid without modification. Hydrolytic adsorption from salts of weak org. acids has been confirmed. F. L. USHER.

Adsorption of dyes from aqueous solution by Japanese acid clay. Y. TANAKA, T. KUWATA, and S. FURUTA (J. Fac. Eng. Tokyo, 1932, **20**, 53—64).—The adsorption of basic and acid dyes from aq. solution by Japanese acid clay in its natural state, after activation by elimination of acid-sol. Al and Fe, and after neutralisation, has been studied. Adsorption of basic substances is a result of the residual affinity of SiO_2 mols. oriented on the surface of the clay, which attract the OH groups of the H_2O and thus cause the formation of a new and active surface; salt formation then occurs at the outer surface. Acid dyes are adsorbed by replacement of the $H^{\cdot}$ of the electrical double layer by the cation of the dye; if the free acid is insol. it is pptd. on the clay, but if it is sol. no adsorption occurs. Activation of the clay is due to the greater SiO_2 surface exposed on removal of Al_2O_3 and Fe_2O_3. Basic dyes are adsorbed to a greater extent by the neutralised clay than by the acid clay, as the alkali liberated from the clay is free to combine with the anion of the dye; the adsorption of acid dyes is correspondingly reduced by neutralisation of the clay. H. F. GILLBE.

Influence of the solubility of the adsorbate on the adsorption of electrolytes. (MLLE.) L. DE BROUCKÈRE (Bull. Soc. chim. Belg., 1931, **40**, 737—740; cf. A., 1929, 757).—Previous work is extended to TlCl. The adsorption of chlorides on $BaSO_4$ increases with diminishing solubility of the chloride. C. W. DAVIES.

Adsorption of organic materials by the silver halides. S. E. SHEPPARD, R. H. LAMBERT, and R. L. KEENAN (J. Physical Chem., 1932, **36**, 174—184).—In the adsorption of pinacyanol by AgBr at p_H 6·8, 1·69 Br^- are necessary for 1 dye mol. Pinacyanol is adsorbed in an alkaline medium with an excess of Br^-. Acid dyes, such as dichlorofluorescein, are adsorbed by AgBr in an acid medium with an excess of Ag^+. Gelatin is also adsorbed, and even after boiling with H_2O for many hrs. a unimol. layer still remains. A 10% solution of H_2SO_4 alters the grains, but does not remove all the adsorbate. S. LENHER (c).

Thickness of adsorbed films on mercury. H. Cassel (Trans. Faraday Soc., 1932, **28**, 177—179; cf. A., 1931, 1119, 1120).—The adsorption of CCl_4 on Hg at 11° has been investigated by an improved method. The surface density corresponds with a unimol. film when the first layer is saturated. The density increases to 3·6 times this val. at the v. p. of CCl_4 in bulk. The adsorption follows Henry's law over a considerable range.
J. G. A. Griffiths.

Unimolecular films. Solid–liquid interface and sedimentation and flocculation of powders in liquids. W. D. Harkins and D. M. Gans (J. Physical Chem., 1932, **36**, 86—97).—A unimol. film of oleic acid on the surface of a fine powder suspended in a very dry, non-polar liquid deflocculates the powder, which settles to one quarter the vol. it would occupy in absence of the acid. The addition of very small amounts of H_2O to the C_6H_6 solution of the acid inhibits deflocculation. The extent of flocculation and of settling is not a simple function of the wettability of the powder by the liquid; the composition of the org. dispersing medium has a marked influence on the rate of settling. An adsorption method for the determination of the area of a fine powder is described. F. Urban (*c*).

Comparison of methods for determination of area of adsorbed molecules in interfacial films. F. E. Bartell and G. L. Mack (J. Physical Chem., 1932, **36**, 65—85).—The interfacial tension between H_2O and binary mixtures of $PhNO_2$ with C_6H_6, PhMe, PhEt, and PhBu, and of $NPhMe_2$ with C_6H_6 has been determined. The average mol. areas calc. from these data by Langmuir's max. adsorption method, the mixture rule method of Mathews and Stamm, and by a modified mixture rule method are: $PhNO_2$, 30·6, 32·1, and 21·8; $NPhMe_2$, 35·5, 41·5, and $26{\cdot}6\times10^{-16}$ sq. cm., respectively. The most satisfactory agreement with the mixture rule is obtained by using vol. compositions.
F. Urban (*c*).

Unimolecular films. Liquid–liquid interface and stability of emulsions. E. K. Fischer and W. D. Harkins (J. Physical Chem., 1932, **36**, 98—110).—Evidence is adduced showing that in general the stability of an emulsion increases as the emulsifying film changes from an expanded to a condensed unimol. film. Distribution curves for the variation of interfacial area with diameter in aq. emulsions of paraffin oil and C_6H_6 produced by Na oleate, and a size distribution curve for oil are reproduced. Soap films are unimol. F. Urban (*c*).

Thin lamellæ and their physical properties. H. Devaux (Kolloid-Z., 1932, **58**, 129—143).—A summary of published work. E. S. Hedges.

Coloured stratifications. A. Marcelin (J. Chim. phys., 1931, **28**, 605—621).—A summary and discussion of published work on the interference colours produced by very thin plates of certain org. crystals (cf. A., 1930, 1111, 1366). E. S. Hedges.

Influence of particle size on the heat of wetting of powdered adsorbents. F. Krczil (Kolloid-Z., 1932, **58**, 183—189).—A calorimeter for determining heat of wetting is described. Different absorbents (including C and SiO_2) were separated into fractions of different particle size by sedimentation and the heats of wetting of the fractions by EtOH and C_6H_6 were determined. The vals. obtained were independent of the particle size. E. S. Hedges.

Inversion of order of heats of wetting by pretreatment of the powder to be wetted. B. Iljin and S. Vassiliev (Z. physikal. Chem., 1932, **158**, 365—368; cf. A., 1915, i, 933).—The heat of wetting of a sample of Florida earth by aq. MeOH was found to decrease with the MeOH concn., but changed in the opposite direction when the earth was first dried at 120° or 350°. R. Cuthill.

Drainage of a vertical wetted plate, the shape of the profile, and thickness of the film. J. Satterly and L. H. Collingwood (Trans. Roy. Soc. Canada, 1931, [iii], **25**, III, 215—225).—The mathematical solution of this problem by Jeffreys has been studied experimentally, and the calc. relations between the time, distance from the top of the wetted portion, and the thickness of the film have been confirmed by observations with glycerol and olive oil. The film has a parabolic outline near the top of the wetted portion, but the outline changes with time.
A. J. Mee.

Theory of flotation. Wo. Ostwald (Kolloid Z., 1932, **58**, 179—183).—Flotation depends on the formation of a three-phase system (solid–liquid–gas). The components of such a system cannot meet in a plane, but only at an edge. The flotation of a solid is determined by the formation of rings of the bounding edges. An ideal flotation agent will be "triphilic," possessing a metal-affine group, a hydrophilic group, and a capillary active group. The xanthates have such a structure. E. S. Hedges.

Surface tensions and interfacial tensions with an application to the problem of the plate ridge. J. Satterly and L. H. Collingwood (Trans. Roy. Soc. Canada, 1931, [iii], **25**, III, 205—214).—The surface tensions and interfacial tensions of H_2O with a number of org. liquids have been found. There is a linear relation between the work of adhesion and the interfacial tension with H_2O. Interfacial tensions increase with rise of temp., the increase probably being connected with increased mol. orientation at the surface. No definite connexion has been found between the wt. of the "plate ridge" and the interfacial tensions and viscosities of liquids.
A. J. Mee.

Surface tension of soap solutions. P. L. du Noüy (Nature, 1932, **129**, 278—279).—A criticism (cf. this vol., 224). L. S. Theobald.

Capillary activity in aqueous solution. H. Mills (J.C.S., 1932, 419—430; cf. A., 1931, 1007).—The relation between surface tension and concn. has been determined with greater accuracy than heretofore for aq. solutions of $C_5H_{11}{\cdot}OH$, $BuCO_2H$, $C_5H_{11}{\cdot}CO_2H$, and $C_8H_{17}{\cdot}CO_2H$. Inflexions on the σ–c curves are observed in each case. The "coeff. of adsorption," denoted by the ratio (surface concn./bulk concn.) at the point of inflexion, is approx. const. over a wide range of concn. The inflexions are considered to be due to attainment of saturation in the surface layer and subsequent accumulation there of a conjugate solution. The limitations of Gibbs' equation are explained in accordance with the theory. The rate of adsorption of $C_8H_{17}\cdot CO_2H$ is proportional to the square of the concn. F. L. Usher.

Theory of hydrotropic solutions. II. Production of molecular compounds. A. von Kúthy (Biochem. Z., 1932, **244**, 308—318; cf. A., 1931, 1122).—As regards the solvent power and surface tension of solutions of their Na salts, cholic, dehydrocholic, deoxycholic, glycocholic, and taurocholic acids differ only quantitatively, not qualitatively. No cryst. mol. compounds can be obtained from many such acids; it seems that those which yield cryst. compounds are structurally related to 3 : 7-dihydroxycholanic acid. It is possible that there is a connexion between power to form mol. compounds (not necessarily crystallisable) and hydrotropy. W. McCartney.

Electrocapillarity. IV. Effect of salts on electrocapillary curves of solutions containing surface-active substances. J. A. V. Butler and A. Wightman (J. Physical Chem., 1931, **35**, 3293—3302; cf. A., 1931, 162).—The effect of inorg. salts on the electrocapillary curves of solutions containing EtOH, PhOH, and Na salicylate has been investigated. The adsorption curves for EtOH and PhOH become more symmetrical as the salt concn. is lowered. Br′ and I′ greatly reduce the adsorption of these solutes in the regions in which the ions themselves are adsorbed. In solutions containing Cl′, NO_3', and SO_4'' the surface tension lowering caused by the org. substances is increased by increasing the salt concn. in the region in which the salt is negatively adsorbed, and decreased in the region in which the salt is positively adsorbed. As the inorg. salt concn. falls the max. of the adsorption curve for Na salicylate moves towards positive potentials and its magnitude increases. H. M. Stark (*c*).

Types of binary osmotic systems. F. A. H. Schreinemakers (Rec. trav. chim., 1932, **51**, 218—232).—The different types of binary osmotic systems are classified and the influence of the composition and previous history of the membrane is discussed. M. S. Burr.

Experimental study of negative osmosis. A. Grollmann and K. Söllner (Trans. Amer. Electrochem. Soc., 1932, **61**, 81—88).—With membranes of MgO or Mg silicate, deposited in the walls of a porous pot, interposed between an aq. solution and H_2O or a solution of different concn., a flow of liquid sometimes occurs in a direction opposite to that of normal osmosis. When such a cell is filled with H_2O and immersed in 0·1*N*-$LiNO_3$, the entry of solution produces pressures as high as 300 mm. of H_2O. Such pressures rise to a max. in an hr. or two and then decrease again. The passage of solute through the membrane was shown by analysis, and in several cases the rate of passage of solution through the membrane was measured directly. H. J. T. Ellingham.

Experimental verification of a new theory concerning the mechanism of anomalous osmosis. A. Grollmann and K. Söllner (Trans. Amer. Electrochem. Soc., 1932, **61**, 89—99; cf. preceding abstract).—Anomalous (including negative) osmosis is attributed to electroendosmotic flow of solution through the larger pores in the membrane brought about by the p. d. developed at the smaller pores. Negative osmosis may occur if the less mobile ion of the solute forms the outer portion of the double layer on the membrane surface. This theory is supported by measurements of the pressures developed in cells devised to act as large-scale models of the conditions in a membrane with pores of differing sizes. H. J. T. Ellingham.

Membrane equilibrium and ion distribution. III. Dynamics of membrane permeability in relation to ion distribution. S. K. Liu (Kolloid-Z., 1932, 58, 144—155).—A general thermodynamical theory of membrane equilibrium and ion distribution for both diffusible and non-diffusible ions is worked out. The Donnan equilibrium is regarded as a special case, and the present theory reduces to the same form when it is assumed that the non-diffusible ion concn. can be neglected. E. S. Hedges.

Ionic equilibrium of sodium cellulose xanthate across a semipermeable membrane. T. Sugita (J. Cellulose Inst. Tokyo, 1932, 8, 3—11).—Measurements have been made of the conductivity of viscose solutions separated from a NaOH solution by a parchment-paper membrane, and of the p.d. between the two solutions; the results indicate that a membrane equilibrium is set up. The decomp. of Na cellulose xanthate is a process of direct hydrolysis. H. F. Gillbe.

Dependence of base exchange in permutits on the nature of the anions. II. E. Ungerer (Z. Pflanz. Düng., 1932, **23A**, 353—362; cf. A., 1931, 163).—In aq. suspension the adsorption of hydrated cations by permutits is increased by anions in the order of the lyotropic series, $\frac{1}{4}Fe(CN)_6'''' > OAc' > \frac{1}{2}CrO_4'' > SO_4'' > Cl' = NO_3' > ClO_3' > I' > CNS'$. In EtOH suspensions this effect is not observed. Anions have little or no effect on feebly-hydrated cations, *e.g.*, $Ba^{\cdot\cdot}$, $Ag^{\cdot}$, and their action in other cases is ascribed to a dehydrating effect. A. G. Pollard.

Mosaic membranes. K. Söllner (Biochem. Z., 1932, 244, 370—381; A., 1930, 688).—When solutions of an electrolyte of different concns. are separated by a membrane which is permeable to one of the ions only, the resistance of the solutions can be calc. because closed currents must flow in the system. The strength of the current and the amount of electrolyte which passes through the membrane in unit time can also be calc. Membranes which in certain regions are permeable to anions and in others to cations permit the passage of electrolytes in a precisely predictable manner. If a mosaic membrane of this kind is selective to one ion and also slightly permeable to the other, equalisation of the concns. of the solutions takes place. W. McCartney.

Explanation of some anomalies in the f. p. of fatty acids in benzene and nitrobenzene solution. A. Boutaric and M. Roy (J. Pharm. Chim., 1932, [viii], **15**, 161—166).—The fatty acids are associated in C_6H_6 and $PhNO_2$ solutions. A. J. Mee.

Ebullioscopic study of molecular equilibria of pyrocatechol in solutions of chlorides of calcium and barium. (Mlle.) O. Hun (Compt. rend., 1932, **194**, 716—718; cf. A., 1930, 689).—Results with solutions of $CaCl_2$ and $BaCl_2$ are of the same order as those with KCl and NaCl, association in aq. $BaCl_2$ being slightly greater than in aq. $CaCl_2$.
C. A. Silberrad.

Apparent volume of salts in solution. II. Interpretation. A. F. Scott (J. Physical Chem., 1931, **35**, 3379—3396; cf. A., 1931, 1122).—Assuming that as the concn. of the solution increases there is a continuous transition from the dissolved to the cryst. state on the part of the solute, the vol. of the solution in the limiting state may be taken as equal to V, the mol. vol. of the solid salt in the crit. disruptive state, *i.e.*, that state in which the ions are so far apart that the net cohesive force is a max. The val. of ϕ/V, where ϕ is the apparent mol. vol. of the solute in the crit. disruptive state, obtained by extrapolation of apparent mol. vol.–concn. data, is about 0·64 for the alkali halides. J. Balozian (*c*).

Physico-chemical properties of specific polysaccharides. M. Heidelberger and F. E. Kendall (J. Biol. Chem., 1932, **95**, 127—142).—The polysaccharide of type III pneumococcus (A., 1927, 77, 1114) yields a highly-ionised Na salt characterised by a mobile negative ion of very high valency. Aq. solutions do not behave normally with respect to viscosity, the ratio sp. viscosity/concn. increasing to a max. with increasing dilution. This deviation and also that from the square root conductivity relation at high dilutions are explained by increasing dissociation and an orientation of the highly-charged polycarboxylate ion at high dilutions. Such phenomena occur to a smaller degree with the type I polysaccharide. The viscosity effects of both type II polysaccharide and sp. gum arabic (A., 1929, 1201; 1930, 66) decrease with the relative no. of CO_2H groups in the mol. F. O. Howitt.

Theory of the electrification of aërosols. H. S. Patterson (Phil. Mag., 1932, [vii], **13**, 736; cf. this vol., 120).—A correction. H. J. Emeléus.

Ultrasonic measurements of the compressibility of solutions and of solid particles in suspension. C. R. Randall (Bur. Stand. J. Res., 1932, **8**, 79—99).—An ultrasonic interferometer is described. The apparatus has been used to determine ultrasonic velocities in H_2O and aq. sugar solutions at different concns. and temp. and from these data the compressibilities have been calc. Similar measurements were made with aq. suspensions of pyrex glass, containing particles $<2\ \mu$. The velocity decreases with increasing concn. of the suspension. E. S. Hedges.

Preparation and properties of hydrated beryllium oxide sols. W. H. Madson and F. C. Krauskopf (J. Physical Chem., 1931, **35**, 3237—3258).—BeO sols were prepared by igniting $BeCl_2$, then adding H_2O and dialysing, the disperse phase being a hydrated oxide containing $<0·5$ mol. of H_2O per mol. of BeO. Flocculation vals., which followed the Schulze–Hardy rule, decreased as the time of dialysis increased up to 12—24 hr., subsequently remaining fairly const. The concn. and $[H^{\cdot}]$ of the sol varied similarly with the time of dialysis. The lyotropic series obtained from the flocculation vals. were: $Fe(CN)_6'''' < Fe(CN)_6''' < H_2PO_4' < AsO_4''' < SO_4'' < CrO_4'' < OAc' < CCl_3{\cdot}CO_2' < CHCl_2{\cdot}CO_2' < CH_2Cl{\cdot}CO_2' < Cl,'$ and $Na^{\cdot} < K^{\cdot} < NH_4^{\cdot} < Mg^{\cdot\cdot}$. H. M. Stark (*c*).

Use of electrodialysed water for the preparation of gold sols by Zsigmondy's method. I. Guerrero and R. Wernicke (Anales Farm. Bioquim., 1931, **2**, 35—39; Chem. Zentr., 1931, ii, 1112).—Good colloidal Au solutions can be obtained with H_2O electrodialysed between parchment paper or cellophane membranes. Collodion membranes are unsuitable. The content of electrolytes and org. matter increases during dialysis owing to contact with the membrane. Suitable H_2O can also be obtained by simple contact with cellophane or parchment paper at higher temp. L. S. Theobald.

Particle size and constitution of colloidal ferric oxide. I. J. B. Nichols, E. O. Kraemer, and E. D. Bailey (J. Physical Chem., 1932, **36**, 326—339).—The particle-size distribution curve of an undialysed Fe_2O_3 sol prepared by hydrolysis of $FeCl_3$ was determined by the ultracentrifuge method. Dilution did not affect the curve. Digestion favoured dehydration and growth of cryst. hæmatite, the rate of growth increasing with the Fe_2O_3 concn. A negative sol produced with the aid of K citrate gave nearly the same curve as the above sol. The intermicellar liquid contained a semi-colloidal fraction of a dispersity approaching that of $FeCl_3$, in addition to primary and secondary portions observed in the ultracentrifuge. F. Urban (*c*).

Water relationships in colloids. II. "Bound" water in colloids. D. R. Briggs (J. Physical Chem., 1932, **36**, 367—386; cf. A., 1931, 1231).—Bound H_2O is defined as that portion of the H_2O in a system containing colloid and crystalloid which is associated with the colloid and those ions which form part of the colloid complex. It varies with the activity of the H_2O in the system in a manner consonant with the v.-p. isotherm. In a system in which colloids and crystalloids are in equilibrium the amount of H_2O associated with or bound by a given wt. of any of the non-aq. components will always be the same for a given H_2O activity, provided that these components do not react with each other. Some of the methods which have been used for determining bound H_2O are interpreted on these lines. F. Saunders (*c*).

Emulsions. III. Microscopical observations on the system xylene–phenol–sodium oleate–water. J. Weichherz (Kolloid-Z., 1932, **58**, 214—215; cf. A., 1929, 1379).—Photomicrographs are reproduced to demonstrate the existence of two regions of homogeneity as the H_2O content is increased. E. S. Hedges.

Systematology of celluloses based on their viscosities in solution. H. Fikentscher (Cellulosechem., 1932, **13**, 58—64).—An empirical equation is given expressing the viscosity, k, of a colloid in terms of the relative viscosity, concn., and two consts. k is calc. for a no. of colloids dissolved

in various solvents and is found to be fairly const. in each solvent, although there are some discrepancies in the vals. of *k* for the same colloid in different solvents.
J. L. D'Silva.

Alternating current effects on colloidal systems. M. Shikata and H. Hukuwatari (J. Soc. Chem. Ind. Japan, 1932, 35, 25—27B).—The stability of certain (unquoted) colloidal systems and the adsorptive power of charcoal are not affected by a high-tension alternating field, which, however, modifies the Liesegang ring formation obtained with aq. NH_3 and $MgCl_2$ in gelatin, increases the viscosity and rate of evaporation of gelatin solutions, and retards the vol. contraction occurring when photographic gelatin is hydrated with H_2O or H_2O–EtOH solutions. N. H. Hartshorne.

Emulsions and surface tension. K. C. Chang (Trans. Sci. Soc. China, 1931, 7, 17—23).—Liquid–liquid emulsions are divided into 2 groups: (1) the interfacial film is part of either the oil or the water phase, (2) the emulsifying agent exists as a third phase between the two liquid phases. In the first group Antonov's rule holds. Measurements were made by the capillary rise method. Chemical Abstracts.

Solid-phase relations in the dissolution of cellulose acetate. Wo. Ostwald and H. Ortloff (Kolloid-Z., 1932, 58, 215—225).—The solubility of cellulose acetate in EtOAc, Et acetoglycollate, MeOBz, Me phthalate, diacetone alcohol, *cyclo*hexanone, and $CH_2Ph\cdot OH$ at 25° varies with the amount of solid phase used. The curves connecting solubility with the amount of solid phase do not show a pronounced max., as is observed in adsorption or dissolution peptisation, but are linear, convex, or concave, according to the solvent. The solid-phase rule also holds in certain binary mixtures of the above solvents, in which case the curves are concave to the axis representing the amount of solid phase. The solid-phase relation is ascribed to the mixed nature of cellulose acetate. E. S. Hedges.

Viscosimetric investigations on the reaction of cellulose with concentrated zinc chloride solutions. K. Letters (Kolloid-Z., 1932, 58, 229—239).—The dispersion of different forms of cellulose in conc. $ZnCl_2$ solutions has been followed by a viscosimetric method. All the curves obtained are complex in form and are believed to indicate swelling, disintegration, and hydrolysis. A reversible swelling region occurs between 55 and 63% $ZnCl_2$, varying with the structure of the cellulose. In pure $ZnCl_2$ solutions swelling begins at 40°, whilst in the technical solutions containing 0·3*M*-$CaCl_2$ swelling begins at about 60°. The temp. variation of viscosity in two different solutions gives a means of characterising samples of cellulose. E. S. Hedges.

Coagulation. G. Wiegner (Kolloid-Z., 1932, 58, 157—168).—A lecture on published work.
E. S. Hedges.

Slow coagulation of sols. H. J. C. Tendeloo (Chem. Weekblad, 1932, 29, 151—153).—A survey of recent work. The simple theory of Smoluchowski is inadequate to account for the phenomenon of slow coagulation, possibly because of a gradual change of the charge on the particles. The form of the particles and the forces of attraction, which are of little significance in rapid coagulation, may also be of importance. H. F. Gillbe.

Dispersoid chemistry of kaolin earths. E. von Boguslavski (Kolloid-Beih., 1932, 34, 373—440).—Numerous experiments on the coagulation and sedimentation of kaolin suspensions, particularly under the influence of electrolytes, are described and discussed in relation to other work. All the observed phenomena are compatible with reversible surface reactions, which frequently involve the exchange-adsorption of ions. The formation of an insol. compound is not a necessary condition for exchange adsorption at the surface of kaolin particles. Addition of alkalis, particularly those having univalent cations, increases the stability of the suspensions, a considerable dispersing effect being observed when the concn. of alkali is 1—10 milliequiv. per litre. At higher concns. the alkali has a coagulating influence, increasing in the order $NH_4OH<LiOH<KOH<Ba(OH)_2 = Ca(OH)_2$. Since the same order holds for the dispersing influence, both effects are ascribed to the adsorbability and degree of dissociation of the alkali. $(NH_4)_2C_2O_4$ also has a dispersing effect on kaolin suspensions. E. S. Hedges.

Flocculation of colloidal solutions. II. Flocculation of negatively- and positively-charged sols by electrolytes; normal and irregular series. A. Lottermoser and K. May (Kolloid-Z., 1932, 58, 168—179).—The flocculation of a mastic sol by electrolytes is independent of the concn. of the sol. Irregular series are observed with $FeCl_3$, $AlCl_3$, $Th(NO_3)_4$, $TiCl_3$, $TlCl_3$, $ZrCl_4$, and $SnCl_4$, but p_H measurements show that the phenomenon is not caused by the hydrolysis products of these salts. The electrolyte coagulation of $Fe(OH)_3$ sols is independent of the sol concn. only in dil. sols. Irregular series are observed with $K_4Fe(CN)_6$, K_2HPO_4, Na_2WO_4, $(NH_4)_2MoO_4$, NaH_2PO_4, Na_2HPO_4, Na_3PO_4, Na_3AsO_4, $Na_3V_3O_9$, $(NH_4)_3V_3O_9$, and $Na_4P_2O_7$. Irregular series are observed in the flocculation of positively- and negatively-charged sols of AgI by $AgNO_3$ or KI and by the salts mentioned above.
E. S. Hedges.

Periodic precipitation. J. N. Friend and R. H. Vallance (Nature, 1932, 129, 205).—Morse's results (A., 1930, 1117) support the authors' view (J.C.S., 1922, 121, 472) that the main effect of the gel is to retard the release of supersaturation and thus to increase the relative effect of diffusion.
L. S. Theobald.

Choice of covering liquid in the exact measurement of cataphoretic migration velocity by the moving boundary method. J. N. Mukherjee (Kolloid-Z., 1932, 58, 155—157).—The covering liquid layer in electrophoretic measurements should have the same conductivity as the sol. This is not fulfilled when the ultrafiltrate is used as the covering liquid, except when the sol contains relatively large quantities of free electrolyte. E. S. Hedges.

Electrophoresis of agar–gold sols. E. B. R. Prideaux and F. O. Howitt (Trans. Faraday Soc., 1932, 28, 79—83).—Agar is a Ca sulphuric ester of a hemicellulose, the cyclic structure of which is responsible for its capacity to gelate. The electrophoretic velocity of dialysed gelatin-free commercial agar (0·1%) with 0·02% of Au sol in 0·03*N*-acetate buffers is increased slightly by raising the p_H from 2·6 to 8·3 (cf. A., 1930, 568). The velocity is uniformly less than that of colloidal Au (cf. A., 1929, 27) and the results are such as would be expected for a colloid the negative charge of which is due to a form of partial ionisation in which the Ca ions remain bound near the surface as long as the cyclic structure due to co-ordination persists. The absence of amphoteric characteristics and the suitability of agar as a support in investigations of ionic diffusion in dil. acid or alkali are emphasised.

J. G. A. Griffiths.

Streaming potential determinations on glass capillaries of various sizes. H. L. White, F. Urban, and E. T. Krick (J. Physical Chem., 1932, **36**, 120—129).—The streaming potential in a pyrex capillary through which 0·0005*M*-KCl is flowing under 60 cm. pressure is the same for capillaries of diameter 60—110 μ, but with diameters between 4·5 and 40 μ lower potentials are observed. Time–potential curves for an 83 μ capillary are reproduced.

Frank Urban (*c*).

Coherent expanded aërogels. S. S. Kistler (J. Physical Chem., 1932, **36**, 52—64; cf. A., 1931, 683).—Aërogels can be obtained by the successive displacement of the liquid in a gel by other liquids, each of which is completely miscible with the preceding one and the last of which has a low crit. temp. so that it may be displaced by a gas. Aërogels of SiO_2, Al_2O_3, WO_3, Fe_2O_3, SnO_2, Ni tartrate, cellulose and its nitrate, gelatin, agar, and ovalbumin were made by removal of H_2O from the normal gels.

A. L. Kibler (*c*).

Coacervation (separation) of mixtures of concentrated gum arabic and gelatin sols. H. G. B. de Jong and J. Lens (Kolloid-Z., 1932, **58**, 209—214).—The coacervation of mixtures of gum arabic and gelatin sols has no relation to the discharge of oppositely-charged sols, but is due to the desolvation of one of the colloids by the other. This view is supported by the fact that the effect of adding neutral salts is in accordance with the lyotropic series. The biological significance of this phenomenon is discussed.

E. S. Hedges.

Effect of surface-active substances on gelatin. I. Swelling. II. Gel–sol transformation. III. Optical activity. A. von Kúthy (Biochem. Z. 1932, **244**, 319—330, 331—336, 337—341).—I. The extent to which surface-active substances are adsorbed by gelatin can be taken as a measure of their effect on its swelling. In so far as certain hydrotropic substances occupy a special position in this connexion it is due to the great extent to which they are adsorbed; even at relatively low concns. they cause considerable swelling.

II. With certain exceptions those substances which cause swelling of gelatin also stimulate the transformation of gelatin gel into sol, whilst those which hinder the swelling act in the opposite way.

III. Since, in general (exceptions are numerous), substances which cause swelling and sol formation in gelatin likewise reduce its optical rotation and those which cause shrinkage and gel formation increase it, it is assumed that the factor common to the three processes is the transformation of the gelatin from the *A* into the *B* form. W. McCartney.

Rhythmic splitting of silicic acid gels. E. C. H. Davies (J. Physical Chem., 1931, 35, 3618—3630).—Silicic acid gels cast in glass tubes split rhythmically whenever there is sufficient contraction, and the initial split occurs along some line other than the inside circumference of the tube or one of its diameters. The best conditions for rhythmic splitting are realised in tilted narrow tubes, open at the top, and not covered with an aq. solution. If L_0 is the wave-length of the rhythmic split and *D* the diameter of the tube, then $L_0=4{\cdot}76D$, approx. Thus L_0 is about 1·5 times as great as for a true sine curve. Between 25° and 60°, L_0 decreases very slightly as the temp. rises, but the rate of splitting increases rapidly, especially in tubes of large *D*. The angle at which the tube is inclined does not affect the val. of L_0. F. L. Browne (*c*).

Base exchange in permutit and surface adsorption by silica gel. I. R. Haas (Chem.-Ztg., 1931, **55**, 975—976).—The base-exchange properties of permutit are attributed to ionic diffusion and to the reduction of the negative properties of the SiO_2 groups by the Al present. The impossibility of removing Ca from apophyllite by treatment with solutions of Na or K salts is, on the other hand, due to the close proximity of numerous negative SiO_2 complexes. Removal of Ca and Mg from solutions of their salts by certain varieties of SiO_2 gel is purely a surface adsorption phenomenon due to the highly disperse nature of the gel. A. R. Powell.

Cryolysis of lyophilic colloids. X. Mechanism of enzyme action. O. M. von Ranke-Abonyi and F. F. Nord (Kolloid-Z., 1932, 58, 198—208).—Freezing and subsequent thawing of solutions of albumin, gelatin, or gum arabic produces an increase in the surface tension, viscosity, electrical conductivity, and electrophoretic migration velocity, indicating an irreversible physical change, which is probably connected with an increase of sp. surface. The increased activity of zymase solutions after freezing and thawing is probably due to the same cause.

E. S. Hedges.

Cryolysis of lyophilic colloids, and its bearing on the mechanism of enzyme action. F. F. Nord and O. M. von Ranke-Abonyi (Science, 1932, 75, 54—55).—The surface tensions of solutions of ovalbumin, gelatin, gum arabic, and Na oleate are decreased by freezing at different temp. The viscosity is increased with ovalbumin, decreased with gelatin or gum arabic, and unaffected with Na oleate. The electrical conductivity of 0·01% solutions is increased, whilst that of solutions above 0·1% is decreased. The cataphoretic mobility of the colloidal particles of gelatin or ovalbumin is doubled by freezing. Lyophilic colloids may thus undergo aggregation as well as disaggregation after freezing. L. S. Theobald.

Swelling of collagen fibres. A. von Kúthy (Biochem. Z., 1932, 244, 342—346).—Below certain threshold vals. (which correspond with high concns. of the substance involved) collagen fibres do not swell under the influence of surface-active substances. Above these vals. considerable swelling occurs. In dil. AcOH swelling proceeds normally. It is inferred that the swelling in acids proceeds in an entirely anomalous manner or that the fibres are enveloped in a semi-permeable membrane through which acids but not the surface-active substances can pass. When the concn. of the latter attains a certain val. permeation occurs in accordance with theories previously discussed or because the membrane is destroyed. Other factors are also involved. W. McCartney.

Physical chemistry of the proteins. X. Solubility of hæmoglobin in solutions of chlorides and sulphates of varying concentration. A. A. Green (J. Biol. Chem., 1932, **95**, 47—66).—The solubilities of horse carboxyhæmoglobin in aq. solutions of NaCl, KCl, Na_2SO_4, K_2SO_4, $MgSO_4$, and $(NH_4)_2SO_4$ have been determined. The compound behaves as a globulin exhibiting a max. solubility in sulphates with increasing salt concns., the solvent power of sulphates being much less than that of the chlorides. In all cases the activity coeffs. found agree approx. with those calc. from a simplified Debye–Hückel equation, whilst the solubilities at 25° and at p_H 6·6 agree with the empirical equation $\log S = 1{\cdot}30 + 1{\cdot}6\sqrt{C} - k_0C$, where k_0 is a const. varying with the electrolyte. F. O. Howitt.

Physical chemistry of starch and bread-making. VIII. To what extent do substances related to native starch undergo gelatinisation and retrogradation ? M. Samec and J. R. Katz [with J. C. Derksen]. **IX. The *X*-ray spectrum of α-diamylose closely corresponds with that of certain starch preparations.** J. R. Katz and J. C. Derksen. **X. Heating effects only limit gelatinisation. Significance of this fact in appraisement of methods of determining gelatinisation temperature.** J. R. Katz (Z. physikal. Chem., 1932, **158**, 321—336, 337—345, 346—354; cf. B., 1931, 1069).—VIII. *X*-Ray examination shows that sol. starch, erythrogranulose, erythroamylose, and amylodextrin undergo retrogradation from an α to a β form. These substances do not gelatinise when heated with H_2O, although gelatinised starch consists of the α form. In 10% solution glycogen does not undergo retrogradation. The behaviour of dextrin depends on the extent to which degradation has occurred.

IX. The resemblance of the *X*-ray diagrams of α-diamylose I and II to the sharp *V*-spectrum of certain starch preps. is so pronounced as to afford strong support to the theory that starch is a polymerised α-diamylose (A., 1921, i, 310).

X. When starch is heated with a little H_2O at 100° or with a large excess of H_2O at lower temp., gelatinisation proceeds up to a point and then ceases. In investigating gelatinisation it is therefore preferable to work at a const. temp. rather than at a slowly rising temp. R. Cuthill.

Photophoresis, electro- and magneto-photophoresis. M. Reiss (Physikal. Z., 1932, **33**, 185—202).—A summary of recent work on the movement of sub-microscopic particles in a beam of light, and the effect of an electric and magnetic field on the movement. A. J. Mee.

Thermal dissociation of arsenic di- and trisulphides. E. V. Britzke, A. F. Kapustinski, and L. F. Tschentzova (J. Chem. Ind. Russ., 1931, **8**, No. 19, 1—7).—The densities of realgar vapour at 760—1080°, and of orpiment vapour at 820—1150°, show that the former contains As_2S_2, As_4, As_2, and S_2, whilst the latter contains As_2S_3 in addition. The heat of formation of As_2S_2 from As and rhombic S is 19·2 g.-cal. R. Truszkowski.

Variation of the affinity constants of substituted organic acids. A. Eucken (Angew. Chem., 1932, **45**, 203—208).—A lecture. H. F. Gillbe.

Association of strong electrolytes. J. Zirkler (Z. Physik, 1932, **73**, 707—708).—A verification of Nernst's method for determining the degree of association of strong electrolytes from conductivity data. A. B. D. Cassie.

Iodine equilibrium in aqueous solutions. A. Urmánczy (Magyar Chem. Fol., 1931, **37**, 164—173; Chem. Zentr., 1931, ii, 2410).—The solubility of I in 0·025*N*-KI, 0·5—3·0*N*-KNO_3, 0·5—7·5*N*-$NaNO_3$, 0·5—8·7*N*-$LiNO_3$, 0·5—1·37*N*-K_2SO_4, 0·25—3·5*N*-Na_2SO_4, 0·5—5·0*N*-Li_2SO_4, 0·5—4·0*N*-KCl, 0·5—5·0*N*-NaCl, and 0·5—13·5*N*-LiCl was determined. A new view of salting-out action is put forward; the dissociation consts. of I_2Cl', Br_3', and I_2Br' have been calc., the difficulties of calculation of the thermodynamic equilibrium consts. discussed, and the activity of I and the activity ratio I_3/I considered. A. A. Eldridge.

Bromine–bromide–tribromide equilibrium. R. O. Griffith, A. McKeown, and A. G. Winn (Trans. Faraday Soc., 1932, **28**, 101—107).—The equilibrium const. $K = [Br_2][Br'] / [Br_3']$ has been determined at 16·5° and 21·5° from partition experiments with free Br at concns. $<0{\cdot}01M$ and HBr, NaBr, KBr, and LiBr at concns. between 0·03 and 0·75*N*. Under these conditions, Br_5' formation is negligible. With NaBr, KBr, and LiBr, *K* increases with ionic strength, μ, and in some cases passes through a max. LiBr has the largest and KBr the smallest salt effect. HBr depresses *K* (cf. A., 1928, 841). When correction is made for the activity coeff. of Br, $K = 0{\cdot}0568$ at 21·5°. Contrary to Lewis and Randall, the activity coeff. of Br_3' is approx. 16% greater than that of Br′ when $\mu = 0{\cdot}5$ and Na˙ is the cation. J. G. A. Griffiths.

Physico-chemical study of solution of magnesium citrate. M. Oakley and J. C. Krantz, jun. (J. Amer. Pharm. Assoc., 1932, **21**, 132—135).—The p_H vals. of citric acid solutions have been determined. The threshold acid taste for the acid is at about 0·02%, p_H 3·16. The p_H changes occurring when pure MgO is added to citric acid solution indicate that when equiv. amounts are present, the solution contains $MgHC_6H_5O_7$ and $Mg_3(C_6H_5O_7)_2$. E. H. Sharples.

Statistical mechanics of dilute and of perfect solutions. E. A. Guggenheim (Proc. Roy. Soc., 1932, **A**, **135**, 181—192).—Mathematical. Using the two characteristic functions ψ and ϕ of Planck and the partition functions described by Fowler certain laws of dil. solutions are derived.

L. L. Bircumshaw.

Equilibrium diagrams. L. Grenet (Aciers speciaux, Métaux, Alliages, 1931, 6, 2—10; Chem. Zentr., 1931, ii, 2266).—A discussion of 1- and 2-component systems. L. S. Theobald.

Physico-chemical applications of thermodynamics to systems in motion. (Mlle.) Y. Dupont (Bull. Acad. roy. Belg., 1932, [v], 18, 83—94).—Theoretical. De Donder's theory of affinity is applied mathematically to the distribution of a solute in a centrifugal field (cf. A., 1931, 694), and to the distribution of suspended particles in a gravitational field. C. W. Gibby.

Reciprocal relations in irreversible processes. II. L. Onsager (Physical Rev., 1931, [ii], 38, 2265—2279; cf. A., 1931, 546).—Theoretical.

N. M. Bligh.

Thermodynamics applied to the iron–carbon system. F. H. Jeffery (Trans. Faraday Soc., 1932, 28, 98—100; cf. this vol., 15).—Polemical. The methods and conclusions of Chu-Phay (this vol., 15) are criticised. J. G. A. Griffiths.

Determination of free energy of ferrous hydroxide from measurements of electromotive force. M. Randall and M. Frandsen (J. Amer. Chem. Soc., 1932, 54, 40—46).—The e.m.f. of the cell $Fe|Fe(OH)_2(s)$, $Ba(OH)_2$ $0{\cdot}05M$, $HgO(s)|Hg$, is $0{\cdot}973 \pm 0{\cdot}005$ volt at 25°. The calc. free energy of formation of $Fe(OH)_2$ is $-115{,}400$ g.-cal. and that of the reaction $Fe(s)+2H_2O(l)=Fe(OH)_2(s)+H_2$ is -2280 g.-cal. L. P. Hall (c).

[Determination of] activity coefficients of salts in acetic acid solutions from solubility measurements. R. P. Seward and C. H. Hamblet (J. Amer. Chem. Soc., 1932, 54, 554—563).—The solubility of $KClO_4$ in glacial AcOH in the presence of NH_4ClO_4, $NaNO_3$, and NaBr, and that of KNO_3 in the presence of NH_4Cl and NH_4NO_3 at 25° agrees, if a large enough ionic diameter is assumed, with the results calc. from the original Debye–Hückel theory, but better agreement is obtained with Gronwall, La Mer, and Sandved's theory. The properties of salt solutions cannot be explained solely in terms of the dielectric const. of the solvent.

G. M. Murphy (c).

Formation of metal halides, especially silver bromide, from the viewpoint of Nernst's heat theorem. A. Eucken, K. Clusius, and H. Woitinek (Z. anorg. Chem., 1931, 203, 39—56).—Measurements of the sp. heat of Ag and of AgBr at low temp. and electrometric determination of the reaction entropy have given results in accordance with Nernst's heat theorem. The reported apparent deviations from the theory are criticised.

E. S. Hedges.

Water content of saturated air at temperatures up to 100°. J. H. Awbery (Proc. Physical Soc., 1932, 44, 143—150).—The H_2O content has been determined by absorption and weighing between 29° and 94° with a probable accuracy of 2%.

C. W. Gibby.

Vapour pressure of water over aqueous solutions of chlorides of the alkaline-earth metals. I. Experimental, with critical discussion of vapour-pressure data. II. Deviations from Raoult's law, as indicated by the molecular lowering of vapour pressure and van 't Hoff coefficients; with theoretical discussion. III. Correlation with other physical properties of the solutions. J. R. I. Hepburn (J.C.S., 1932, 550—566, 566—575, 575—582).—I. V. p. of solutions of the chlorides of Ca, Sr, and Ba over the concn. range $0{\cdot}2N$ to saturation have been measured at 25° by the dew-point method previously described (A., 1928, 1190). Data from other sources are critically discussed. Attention is directed to an error in the data of certain workers due to the use of Regnault's tables for the v. p. of H_2O.

II. The author's results, in agreement with those of several other workers, show that the mol. lowering of v. p. or the van 't Hoff coeff. has a min. val. at a concn. between 0·1 and $0{\cdot}5N$, for all three salts. For $CaCl_2$ and $BaCl_2$ there is also a max. at concns. approaching saturation. The existence of a min. is attributed to the opposing effects of dissociation of polymeric H_2O mols., and co-ordination of monomeric H_2O by the ions.

III. A review of the existing data for f. p. lowering, viscosity, and differential heat of dilution shows the existence of a close correlation between these properties and v. p. lowering, in respect of concn. No corresponding abnormalities are found in the sp. gr. of the solutions. F. L. Usher.

Vapour pressures of saturated aqueous solutions of certain salts. H. W. Foote, B. Saxton, and J. K. Dixon (J. Amer. Chem. Soc., 1932, 54, 563—568).—The v. p. at 0—25° of saturated solutions of NaCl, KCl, CsCl, K_2SO_4, and Na_2SO_4 have been determined by a new static method; the differences between the observed and calc. vals. of the temp. coeff. are within the limits of experimental error.

G. M. Murphy (c).

Effect of solvent on activity of acids: vapour pressure of hydrogen chloride in glacial acetic acid solutions. W. H. Rodebush and R. H. Ewart (J. Amer. Chem. Soc., 1932, 54, 419—423).—The v. p. at 24·8° of HCl over solutions in which the mol. fraction of the solute is 0·00242—0·0208 has been determined. Comparison with v. p. over aq. solutions shows that the relative activity of HCl in an AcOH solution is 10^5 times as great as in an aq. solution in which its molar fraction is the same. The effect of the solvent on the activity of dissolved acids is discussed. G. M. Murphy (c).

Equilibria between water and chlorides of potassium and sodium from −23° to 190°. E. Korneo and H. Krombach (Compt. rend., 1932, 194, 714—716).—The composition of solutions saturated simultaneously with respect to the two salts has been determined between −22·9° and 189·6°. The presence of KCl lowers the transition point $NaCl \rightarrow NaCl{,}2H_2O$ to −2·3°, and the eutectic point to −22·9°. The solubility of NaCl is a min. at 105°. (Cf. B., 1930, 507.) C. A. Silberrad.

Freezing of solutions as a method of investigation in pure chemistry. VII. Crystal–liquid equilibria in malic–tartaric mixtures. J. Timmermans and M. Dumont (Bull. Soc. chim. Belg., 1931, 40, 689—709; cf. A., 1931, 676).—Mixtures of two optically active substances have been examined by cryoscopic and solubility measurements. *l*-Malic acid gives a eutectic with *l*-tartaric acid, but forms a compound with *d*-tartaric acid. Similar results are obtained with the acid NH_4 salts, so that in each case the *d*-compounds have similar configurations. Only eutectics are found, however, in mixtures of *d*-tartaric acid with *d*- or *l*-chlorosuccinic acid, and of NH_4 *l*-malate with NH_4 *d*- or *l*-chlorosuccinate.
C. W. Davies.

Phase study of the system ammonia–hydrogen sulphide. L. Schleflan and C. R. McCrosky (J. Amer. Chem. Soc., 1932, 54, 193—202).—The v. p. and m. p. of mixtures of NH_3 and H_2S have been determined. The v. p.–composition diagram at 0° shows two regions of const. pressure, one of which represents the dissociation pressure of NH_4HS (80 mm. at 0°) and the other the pressure at which the solid compound is in equilibrium with solution and vapour at the same temp. The m.-p. data reveal the existence of NH_4HS, $(NH_4)_2S$, and a eutectic mixture of 95% NH_3 and 5% H_2S. Cryst. $(NH_4)_2S$ does not exist above −18°, at which temp. it decomposes into cryst. NH_4HS and melt. Probably only NH_4HS is stable above 0°. E. S. Hedges.

Thermal analysis of the systems phenylhydrazine–acetic acid. N. A. Trifonov and S. I. Tscherbov (Bull. Inst. rec. biol. Perm, 1929, 6, 313—318).—The m.-p. diagram shows an equimol. compound, m. p. 61·5°. R. Truszkowski.

Conductivity, surface tension, viscosity, and m. p. of certain binary systems. N. A. Trifonov [with K. I. Samarina, V. F. Ust-Katschkincev, P. M. Salnikova, A. I. Melnikova, E. N. Kobeleva, A. T. Chelesova, E. P. Teluschkin, R. W. Merzlin, M. S. Pronina, A. I. Mogilnikov, A. N. Popov, N. A. Vasilieva, C. S. Avrutova, and M. A. Vorsina] (Bull. Inst. rec. biol. Perm, 1931, 7, 343—406).—The conductivity curves for mixtures of allylthiocarbimide with piperidine, *o*-toluidine, or NH_2Ph exhibit 2 maxima, with a sharp min. at 50 mol.-%; for mixtures of H_2O with pyridine, piperidine, PhOH, or chloral, and of AcOH with NHPhEt or $NPhEt_2$ the curves have only one max. in the vicinity of the AcOH or H_2O axis. The surface tension isotherms for the system PhOH–piperidine have a max. at 75 mol.-% PhOH, for $SnCl_4$–AcOEt at 33·3 mol.-% $SnCl_4$, and for $SnCl_4$–PhOH 2 maxima, at 5 and 70—80 mol.-% $SnCl_4$; for the systems C_3H_5NCS–*o*- or *p*-toluidine, or $NHPh_2$ the max. is at 50 mol.-%, at which point C_3H_5NCS–NHPhMe, NHPhEt, $NHPh_2$, or piperidine, PhNCS–NHPhMe, and Ac_2O–H_2O exhibit minima, whilst for C_3H_5NCS–$NPhEt_2$ or $NPhMe_2$, PhNCS–$NPhMe_2$, H_2O–chloral or pyridine, PhOH–$NHPh_2$ or *o*-toluidine, AcOH–pyridine, *o*-toluidine, quinoline, NHPhMe, or $NPhMe_2$, and EtOH–piperidine no well-defined maxima or minima are observed. The viscosity isotherms for C_3H_5NCS–*o*- or *p*-toluidine, and PhNCS–NPhHMe, NHPhEt, or $NPhEt_2$ have a max. at 50 mol.-%, at which point AcOH–$NHPh{\cdot}NH_2$ has a min.; for AcOH–*o*-toluidine max. viscosity occurs at 72 mol.-% AcOH, whilst the isotherm for EtOH–piperidine is concave over its entire length. The fusion diagrams for *p*-toluidine–cinnamic acid, $NHPh_2$–AcOH, $NPhMe_2$–BzOH, $CO(NH_2)_2$–BzOH or cinnamic acid, benzoquinone–C_6H_6, $C_{10}H_8$, $PhNO_2$, or BzOH, and bromocamphor–PhOH, resorcinol, or BzOH indicate the absence of compound formation. Equimol. compounds are formed by *p*-toluidine–AcOH, m. p. 42°, $CHPh_2{\cdot}CO_2H$, m. p. 54·5°, or salicylic acid, m. p. 83°; NH_2Ph–salicylic acid, m. p. 73°, $CO(NH_2)_2$–quinol, m. p. 131·5°, or resorcinol, m. p. 101°, benzoquinone–*p*-nitrophenol, m. p. 62·8°, 2 : 4-dinitrophenol, transition point 70·8°, picric acid, m. p. 76—77°, or salicylic acid, transition point 93° at 38 mol.-% benzoquinone, and bromocamphor–resorcinol, m. p. 48°. The following compounds are also recorded: $C_6H_4O_2,2PhOH$, m. p. 69·4°, and $C_6H_4O_2,2OH{\cdot}C_6H_4{\cdot}OMe$, m. p. 61°. The eutectic mixture of *o*- and *p*-toluidine (−33°) contains 12·5 mol.-% of the *p*-isomeride.
R. Truszkowski.

Application of thermopiles to the measurement of the temperature in the dehydration and explosion of certain metal picrates. T. Tucholski (Rocz. Chem., 1932, 12, 58—66).—When cryst. Na, K, Pb, Ca, and Cu picrates are slowly heated, their temp. is lower than that of the surrounding atm., owing to evaporation of H_2O of crystallisation. When all the H_2O has been expelled, the two temp. are for a short interval equal, after which the temp. of the picrates rises above that of the environment, owing to thermal decomp., followed by explosion. The temp. of the environment and of the dry picrate at the moment of explosion are respectively 318° and 324·4° for Na, 333·1° and 338·8° for K, 260·6° and 267·8° for Pb, 318·3° and 325·8° for Ca, and 281·8° and 286·2° for Cu picrates. R. Truszkowski.

System sodium metasilicate–sodium fluoride. H. S. Booth and B. A. Starrs (J. Physical Chem., 1931, 35, 3553—3557).—Thermal analysis shows the system to be of the one-eutectic type. The eutectic point is 913±2°, the liquid phase containing 28·5±1·0% NaF. Tentative data for the system Na disilicate–NaF are given. A. L. Henne (*c*).

System Fe–C–O. E. Jänecke (Z. anorg. Chem., 1932, 204, 257—290).—A comprehensive survey of recent work, with an extensive bibliography. The author's diagram has been somewhat modified, and the equilibria at various pressures and temp. have been calc. The heat of formation of cementite is −6·5 kg.-cal., and that of pearlite −2·77 kg.-cal. Contrary to previous views, there is a max. pressure in the univariant system Fe–austenite–FeO–gas at 820°. The equilibria in the Fe–C–O system between 500° and 1000° and 0·2 and 5 atm. are represented by a three-dimensional model. H. F. Gillbe.

Recent investigations of the equilibrium of systems involved in the production of steel. F. Sauerwald [with W. Hummitzsch] (Arch. Eisenhüttenw., 1931—1932, 5, 355—366).—A crit. review of recent work on the systems Fe–O, Fe–FeO–CaO, Fe–O–C, Fe–Si–O, and Fe–MnO, and of equilibria involving P and S in the steel bath is followed by a tabulated summary of the equilibrium consts. obtained by the various workers. A. R. Powell.

Equilibria in the systems silica, lime, and alumina with carbon. R. Brunner (Z. Elektrochem., 1932, 38, 55—68).—Pressure–temp. relations have been investigated in the systems SiO_2–C, CaO–C, and Al_2O_3–C. In the first system a quintuple point has been found at 525 mm. and 1570° where the phases SiO_2, $(SiC)_2O$, SiC, C, and CO co-exist. A pressure–temp. curve for CO formation is obtained below the CaO–CaC_2 eutectic at approx. 1640°. In the system Al_2O_3–C equilibria for both carbide and metal formation are obtained. The pressure–temp. curves for these intersect to give a quintuple point at 1·5 mm. and 2013°. In all three systems sublimates are formed by combination of metal and CO in the gaseous phase. M. S. Burr.

Phase boundaries in the systems silica and alumina with carbon. E. Baur (Z. Elektrochem., 1932, 38, 69—70).—Phase diagrams have been constructed from the data in the preceding abstract. M. S. Burr.

System Na_2O–B_2O_3–H_2O. Isotherms at 35°, 20°, and 0° and polythermal diagram. U. Sborgi (Gazzetta, 1932, 62, 3—14; cf. A., 1930, 1122).—The limits of existence between 90° and the cryohydric temp. of the ternary compounds, 1 : 5 : 10, 1 : 2 : 10, 1 : 2 : 5, 1 : 1 : 8, 1 : 1 : 4, 1 : 1 : 1, 2 : 1 : 1 (the figures representing the no. of mols. of Na_2O, B_2O_3, and H_2O) and of H_3BO_3 and NaOH have been derived. O. J. Walker.

[System sodium sulphate–aluminium sulphate–water.] J. T. Dobbins and R. M. Byrd (J. Physical Chem., 1931, 35, 3673—3676).—Application of the residue method shows the existence at 25° of $Na_2SO_4,10H_2O$, $Al_2(SO_4)_3,18H_2O$, and $Na_2SO_4,Al_2(SO_4)_3,24H_2O$. The efflorescent double salt may be obtained by evaporation at 25° of solutions between 5% Na_2SO_4, 26% $Al_2(SO_4)_3$, and 19% Na_2SO_4, 8% $Al_2(SO_4)_3$. G. M. Murphy (*c*).

Ternary systems. XI. Magnesium iodate–sodium iodate–water. XII. Sodium iodate–potassium iodate–water. XIII. Potassium iodate–potassium chloride–water. XIV. Potassium iodate–potassium sulphate–water. A. E. Hill and J. E. Ricci (J. Amer. Chem. Soc., 1931, 53, 4305—4315; cf. A., 1931, 568).—The systems were investigated at 5°, 25°, and 50°, but no double salts were found. A method of algebraic extrapolation of tie-lines suitable for testing the composition of the solid phases and the precision of the solubility determinations is described. The existence of colloidal constituents in $NaIO_3$ and KIO_3 solutions may explain the length of time necessary to reach equilibrium in these systems. G. M. Murphy (*c*).

Ternary systems. XV. Potassium iodate–potassium nitrate–water. XVI. Calcium iodate–sodium iodate–water. A. E. Hill and S. F. Brown (J. Amer. Chem. Soc., 1931, 53, 4316—4320; cf. preceding abstract).—The system KIO_3–$NaNO_3$–H_2O was investigated at 5°, 25°, and 50·4°, but no compound formation was observed. The solubility of $Ca(IO_3)_2$ was determined at 5—90°, and a transition from $Ca(IO_3)_2,H_2O$ to $Ca(IO_3)_2$ found at 57·5°. The system $Ca(IO_3)_2$–$NaIO_3$–H_2O was investigated at 25°. G. M. Murphy (*c*).

Ternary system potassium permanganate–potassium fluoborate–water. R. C. Ray and K. K. Chatterji (J.C.S., 1932, 384—386).—The composition of the liquid and solid phases at 25° has been determined. Within certain limits orthorhombic bipyramidal crystals of a double *salt*, $KBF_4,6KMnO_4$, are formed. F. L. Usher.

System calcium oxide–sucrose–water. W. Reinders and D. W. van Gelder (Rec. trav. chim., 1932, 51, 253—259).—Above concns. of 30, 35, and 40% sucrose, respectively, the stable solid phase at 12°, 25°, and 45° is no longer $Ca(OH)_2$, but a saccharate of unknown composition. By dissolving finely-divided CaO in dil. sucrose solution a supersaturated solution is formed which deposits at first a metastable disaccharate at lower temp. or trisaccharate at higher temp. The proportion of Ca in this gradually increases, however, until only $Ca(OH)_2$ is left as the stable phase. M. S. Burr.

Heat of dissociation of oxygen. A. K. Dutta (Nature, 1932, 129, 317).—SO_3 vapour shows continuous absorption with a long wave-length limit at 3300 Å. corresponding with 86·7 kg.-cal. Assuming that the reaction due to light is $SO_3+86{\cdot}7=SO_2+O$ (atomic) the calc. heat of dissociation of O_2 is 128 kg.-cal. L. S. Theobald.

Thermochemistry of thallium. W. A. Roth and A. Meichsner (Z. Elektrochem., 1932, 38, 87—93).—The heat of formation of Tl_2O, determined by dissolving Tl and Tl_2O in H_2SO_4 under the same conditions, is $43{\cdot}2_2$ kg.-cal. at 20° and const. pressure. The heat of dissolution of the metal is derived from e.m.f. as well as thermochemical data. Measurements of the heat of dissolution of Tl_2O and TlOH in H_2O give $3{\cdot}3_6$ kg.-cal. as the heat of hydration of Tl_2O. Other data obtained are: $[Tl]+\frac{1}{2}(O_2)+\frac{1}{2}(H_2)=[TlOH]+57{\cdot}4_6$ kg.-cal.; $[Tl]+\frac{1}{2}(Cl_2)=[TlCl]+50{\cdot}3_5$ kg.-cal.; $2[TlOH]+H_2SO_4$ (pure)$=[Tl_2SO_4]+2H_2O+50{\cdot}8_3$ kg.-cal.; $[Tl_2O]+SO_3=[Tl_2SO_4]+75{\cdot}4_1$ kg.-cal.; $2[Tl]+[S]$rhomb.$+2(O_2)=[Tl_2SO_4]+223{\cdot}2_3$ kg.-cal.; $[TlOH]+(HCl)=[TlCl]+H_2O+38{\cdot}2_4$ kg.-cal. The solubility of TlCl in H_2O and aq. HCl of different concn. has been measured at 20°. Heats of dissolution in mixed solvents, chiefly dil. H_2SO_4, have been determined for different concns. of Tl_2O, TlOH, TlCl, Tl_2SO_4, $ZnSO_4,1{\cdot}08H_2O$, Zn, and Tl. M. S. Burr.

Affinity and heat effect of hydrogenation of double linkings between carbon atoms. W. Hiltner (Z. physikal. Chem., 1932, 158, 398—410).—Oxidation–reduction potential measurements yield vals. for the affinity of the hydrogenation of liquid esters of cinnamic and crotonic acids which are inconsistent among themselves and with vals. deduced from heat effect data. This discrepancy is probably connected with the catalytic activity of the electrodes and the formation of absorbed films. R. Cuthill.

Heats of combustion of methyl and ethyl alcohols. F. D. Rossini (Bur. Stand. J. Res., 1932, 8, 119—139).—The alcohol vapours were burned in a stream of purified air in a reaction vessel in the calorimeter. The heat of combustion, in international kilojoules per g.-mol., is 763·68±0·20 for MeOH vapour at 25° and 1407·50±0·40 for EtOH vapour at 32·50°. Combining these data with the heats of vaporisation the following vals. are obtained for the heat of combustion in the liquid state at 25° : MeOH 173·61±0·05, EtOH 326·61±0·10 kg.-cal. (15°) per g.-mol. A rapid and accurate determination of the ratio C/H in a volatile org. liquid can be made by saturating a stream of inert gas with the vapour of the liquid and passing the mixture over hot CuO.

E. S. Hedges.

Application of calorimetry to pyrroles. P. Rothemund and H. Beyer.—See this vol., 280.

Calorimetry. II. Influence of amorphous silicic acid on the heats of combustion of fatty oils. III. Heat of combustion of rubber. H. Endoh (J. Soc. Chem. Ind. Japan, 1932, **35**, 3—4B, 4—7B; cf. *ibid.*, 1928, **31**, 186B).—II. Addition of pptd. silicic acid lowers the observed heats of combustion of BzOH and olive oil, and raises those of bean oil and whale oil.

III. The heats of combustion of Para rubber, smoked sheet, and pale crêpe are 10,761·0, 10,680·4, and 10,681·6 g.-cal., respectively. Mechanical treatment thus appears to reduce the heat of combustion. The results of previous workers are criticised.

N. H. Hartshorne.

High-frequency conductivity of electrolytes by a calorimetric method. A. Deubner (Physikal. Z., 1932, **33**, 223—227).—Two calorimetric methods are described for comparing the high-frequency conductivities of electrolytes which conduct equally at low frequencies. The accuracy of the methods is high. A. J. Mee.

Dissociation constants of organic acids. V. Mobility of the hydrogen ion at 18° and at 25°. G. H. Jeffery and A. I. Vogel (J.C.S., 1932, 400—415; cf. A., 1931, 1012).—Conductivities of HIO_3, HCl, and $PhSO_3H$ have been measured in cells of SiO_2 at 25° and at concns. between 10^{-2} and $10^{-4}N$. Equations representing the relation between Λ and concn. are given. The mean val. for the mobility of the H ion at 25° is 349·0 or 348·0±0·7, the alternative depending on the choice of the cation transport no. for KCl. From measurements on HIO_3 at 18° the mobility is calc. to be 314·1 or 313·4 at 18°. The plot of Λ against $\sqrt{}$concn. is parabolic in the case of all three acids, the curvature being very slight only for $PhSO_3H$. F. L. Usher.

Conductivity of solutions of aniline hydrohalides in aniline. M. Hłasko and E. Michalski (Rocz. Chem., 1932, **12**, 35—47).—The mol. conductivity of HF, HCl, HBr, and HI dissolved in NH_2Ph has been measured at 25°. The conductivity and the degree of dissociation increase with the at. wt. of the halogen present. λ_v has a min. val. in all cases for $0·02N$ solutions; for NH_2Ph,HI the λ_v–concn. curve shows a max. at $0·6N$. The val. of the concn. giving min. λ_v is given by Walden's formula : $C_{\text{min.}}=(\varepsilon/K)^3$. The above solutions contain only undissociated mols. at concns. below $0·02N$; association occurs at higher concn.

R. Truszkowski.

Transference number of lithium chloride as a function of the concentration. G. Jones and B. C. Bradshaw (J. Amer. Chem. Soc., 1932, **54**, 138—150).—Transference nos. for LiCl measured at 25° by the Hittorf method over the range 0·023—$2·95N$ agree with the equation $t=[1·3337/(1+0·03605\sqrt{c})]-1$. These results do not agree with previous vals. obtained by the e.m.f. method (A., 1920, ii, 466), but if the latter data are interpreted by the method of Jones and Dole (A., 1929, 767) the discrepancy is less. M. Dole (*c*).

Limiting law for transference numbers. M. Dole (J. Physical Chem., 1931, **35**, 3647—3648).—The expression for the change of transference no. with change of ionic concn. derived by means of the Debye–Hückel conductivity equation is similar to empirical equations previously published (A., 1925, ii, 398; 1929, 767). M. Dole (*c*).

Potential of lead electrode. W. R. Carmody (J. Amer. Chem. Soc., 1932, **54**, 210).—The electrolyte may be passed over a Pb amalgam electrode without affecting its potential, but the potential of a AgCl electrode may be changed by 6 mv. by passing a solution over it. If the results of Randall and Cann (A., 1930, 422) are corrected accordingly, the val. 0·1263 volt is obtained for the potential of the Pb electrode. M. Dole (*c*).

Standard electrode potential of iron, and activity coefficient of ferrous chloride. M. Randall and M. Frandsen (J. Amer. Chem. Soc., 1932, **54**, 47—54; cf. A., 1926, 803).—From e.m.f. measurements with the cell $Fe|0·1M$-$FeCl_2$, HgCl|Hg, the single electrode potential of Fe at 25° has been found to be 0·4402 volt, and the free energy of formation of the $Fe^{\cdot\cdot}$ ion —20,310 g.-cal. Activity coeffs. of $FeCl_2$ have been calc. from existing data.

L. P. Hall (*c*).

Measurement of electromotive force in dilute aqueous solutions. II. Silver chloride electrode. W. R. Carmody (J. Amer. Chem. Soc., 1932, **54**, 188—192; cf. A., 1929, 1391).—The e.m.f. of the cell $Pt,H_2(g)|HCl, AgCl(s)|Ag(s)$ was measured at concns. below $0·01M$ at 25°. The standard electrode potential for AgCl obtained by extrapolation is —0·2223 volt, the val. calc. from f.-p. measurements being —0·2221 volt. M. Dole (*c*).

Measurement of glass electrode potentials by a valve electrometer. G. D. Greville and N. F. Maclagan (J.C.S., 1932, 720—721; cf. A., 1931, 801).—A reply to a criticism by Morton (this vol., 24).

F. L. Usher.

Glass electrode studies : cupric hydroxy-acid complexes. C. Morton (Trans. Faraday Soc., 1932, **28**, 84—88).—Erroneous results are obtained with the H_2 electrode (A., 1930, 49). Electrometric titration, with the glass electrode, of $CuSO_4$ in excess of Na tartrate, citrate, malate, and salicylate affords two inflexions in the neutralisation curves; the first corresponds with the formation of the basic complexes $Cu_8(OH)_{10}(C_4H_4O_6)_3$, $Cu(OH)_3C_6H_5O_7$,

$Cu_2(OH)_2C_4H_4O_5$, and $Cu(OH)(OH{\cdot}C_6H_4{\cdot}CO_2)$, respectively, and the second inflexion with complete alkaline decomp. into highly-basic hydrosols, of which only the salicylate is decomposed by boiling. [$Cu^{\cdot\cdot}$], determined by means of the Cu electrode, decreases at first slowly and then rapidly as the neutral point is approached and the point of inflexion coincides with the first inflexion in the corresponding p_H curve. Whereas in acid solutions all the Cu can be removed by dialysis, none can be removed from slightly alkaline solutions.

The neutralisation curves of $CuSO_4$ in excess of Na glycerate, lactate, glycollate, and mandelate have only one inflexion, and a blue basic ppt. appears during each titration. It is probable that no stable complexes are formed, and that the inflexion corresponds with the formation of basic sulphate. To the peptising properties of these OH-acid anions is attributed the absence of pptn. in alkaline solution in the presence of large excess of the Na salt.

J. G. A. GRIFFITHS.

Elimination of liquid contact potentials with potassium chloride and ammonium chloride. G. M. KLINE, M. R. MEACHAM, and S. F. ACREE (Bur. Stand. J. Res., 1932, **8**, 101—110).—The results obtained with 4·1*N*-KCl as eliminator are within the accuracy of routine experimental errors and its general use is recommended for annulling contact potentials between (*a*) HCl and especially org. salts and buffers on the one hand and (*b*) KCl or Na H phthalate solutions used in standard electrodes. An approx. isoelectric eliminator, such as $3N$-KCl+N-KNO_3 should be used for solutions with p_H vals. between 3 and 10.

E. S. HEDGES.

Potentiometric investigation of electrolytic dissociation. I. Cadmium halides. H. L. RILEY and V. GALLAFENT (J.C.S., 1932, 514—523).—The concn. of $Cd^{\cdot\cdot}$ ions in solutions of CdX_2 (X=Cl, Br, or I) has been determined by potentiometric titration using a suitable concn. cell, and the concn. of the several mol. and ionic species present has been calc. by means of a mass-action relationship. The significance of the results is discussed.

F. L. USHER.

Five new oxidation–reduction indicators. M. LETORT (Compt. rend., 1932, **194**, 711—714).—E–p_H curves, where E is the normal oxidation–reduction potential for the p_H considered, are given for Nile-blue 2B (p_H 3·85—7·80), new-methylene-blue (3·85—8·50), Capri-blue (3·85—8·50), solid-cotton-blue (2·95—8·10), and muscarine DH (3·85—7·80), using 0·1*M* buffer solutions, $TiCl_3$ and $Na_2S_2O_4$ as reducers, and a H_2 electrode. The curves of the three indicators last named lie between those of the indophenols and cresyl-blue.

C. A. SILBERRAD.

Electrostatic potentials at the phase boundary electrolyte–unattackable electrode, and the physical chemistry of the flotation process. B. KAMIENSKI (Z. physikal. Chem., 1932, **158**, 441—444).—The potential of a Pt, galena, or graphite electrode in contact with aq. KCl becomes more negative on addition to the liquid phase of an emulsion of K xanthate and terpineol. This suggests that in the flotation process the adhesion of the sulphide particles to the oil is due to static phase-boundary potentials.

R. CUTHILL.

Sour taste of acids. F. B. KENRICK (Trans. Roy. Soc. Canada, 1931, [iii], **25**, III, 227—228).—The proportions of buffer solution required to bring the p_H of the various acids to 5 are approx. proportional to their sourness. The sourness can therefore be determined by titration with phosphate buffer to p_H 5. Threshold concns. for sour taste may be lowered by adding to the acids astringent or bitter substances.

A. J. MEE.

Electrolytic overvoltage and its dependence on the degree of curvature of the cathode. P. SEDERHOLM and C. BENEDICKS (Z. Elektrochem., 1932, **38**, 77—86).—The overvoltage of H_2 at polished electrodes of sharply defined curvature has been determined. Globules of Hg, Pt, pure Ag, and an alloy of Ag were employed. The overvoltage is given by $\varepsilon=k\log(a+b/r)$, where k is a const., a and b are consts. for a given metal, and r is the radius of curvature of the electrode, or $\varepsilon=k\log a+k\log(1+n/r)$, where $k\log a$ is the overvoltage at a plane surface and $n=b/a$ and is a const.

M. S. BURR.

Optical investigation of passivity of metals. I. Iron and steel. L. TRONSTAD (Z. physikal. Chem., 1932, **158**, 369—397).—A detailed account of experiments of which the principal results have already been reported (A., 1931, 301).

R. CUTHILL.

Theory of passivity. XIV. Passivity of nickel. W. J. MÜLLER, H. K. CAMERON, and W. MACHU (Monatsh., 1932, **59**, 73—92).—The natural oxide film on Ni is less easily attacked by H_2SO_4 than the corresponding film on Fe (A., 1931, 1238), so that the time of passivation is very short, and even in $15N$-H_2SO_4 a freshly-polished or cut Ni electrode has a current–time curve of the $1/i^2$ character (*loc. cit.*). At voltages below 1·5 volts coating passivity is due to a salt of $Ni^{\cdot\cdot}$. In *N*-acid the salt is not doubly-refracting and is obviously basic. When the concn. of acid is above 5*N* a strongly doubly-refracting layer appears, viz., $NiSO_4,7H_2O$. Above 2 volts chemical passivation sets in due to a porous super-oxide coating. This layer is very stable and is unaffected by contact with Zn, but the passivation time can be increased by brushing in a concn. of H_2SO_4 above 7*N*. Cathodic charging activates Ni. In all circumstances Ni becomes momentarily passive in Na_2SO_4. Cathodic charging with H_2, however, results in a finite time of passivation. The resistance to corrosion of Ni as compared with Fe is due to the greater stability of the natural oxide layer.

M. S. BURR.

Velocity coefficient of interchange reactions. H. PELZER and E. WIGNER (Z. physikal. Chem., 1932, B, **15**, 445—471).—Application of the methods of wave-mechanics shows that the essential condition which must be fulfilled for double decomps. such as $H+Cl_2\rightleftharpoons HCl+Cl$ to take place adiabatically as postulated by London (A., 1930, 1097) is that the lowest energy surface shall, in point of energy, be far removed from the others. By means of the theory an equation giving the abs. velocity coeff. of the transformation of para-H into normal H (cf. A., 1931, 688) has been derived. R. CUTHILL.

Rôle of surface adsorption in chain reactions. C. N. HINSHELWOOD (Trans. Faraday Soc., 1932, 28, 184—191).—The criteria for deciding whether reaction chains in a steady reaction originate and terminate in the gas phase or at the surface are examined. Various explanations (cf. recent papers) offered for the existence of " explosion limits " are discussed.
J. G. A. GRIFFITHS.

Oxidation of fuel vapours in air. E. W. J. MARDLES (Trans. Faraday Soc., 1932, 28, 69—79).—A discussion by others of the author's work (A., 1931, 1372). J. G. A. GRIFFITHS.

Oxidation of pentane and other hydrocarbons. I, II. L. M. PIDGEON and A. C. EGERTON (J.C.S., 1932, 661—676, 676—686).—I. The temp. at which reaction proceeds rapidly in C_5H_{12}–O_2 mixtures rises as the pressure falls and is lowest for a 50% mixture. The temp. is also lower in SiO_2 than in glass and is raised with increase of surface, but lowered by addition of N_2. Reaction velocity is affected more by change of C_5H_{12} concn. than of O_2 concn. The effect of temp. and pressure on reaction velocity has also been studied. The results indicate the existence of reaction chains. There is an induction period during which active centres accumulate. The chains are initiated in the gas and broken at the walls. The effect of temp., pressure, surface, and diluents on the period of induction is rather irregular.

II. In the slow combustion of C_6H_{14} the temp. at which oxidation becomes rapid and the influence of total pressure and concn. on the reaction have been investigated. The decrease in pressure observed in the case of C_6H_{14} is mainly due to formation of a condensable product, but in the case of amylene to the direct absorption of O_2. The influence of these compounds on the oxidation of C_5H_{12} has been observed. C_6H_{14}, which has a lower reaction temp. than C_5H_{12}, initiates reaction at a lower temp. in the latter than occurs with C_5H_{12}–O_2 mixtures alone. This is probably due to the active centres formed by the C_6H_{14} and is additional evidence for the chain reaction theory. Valeraldehyde has a still more marked effect, but amylene and H_2O are inactive, which may be regarded as evidence against the theory of dehydrogenation of the reacting mol. and the theory of hydroxylation, respectively. $PbEt_4$ acts as an inhibitor, but the Pb has to be oxidised before it can become effective. M. S. BURR.

Rate of rise of pressure in the combustion of some gas–oxygen mixtures. C. CAMPBELL, W. B. LITTLER, and C. WHITWORTH (J.C.S., 1932, 339—348).—The rates of rise of pressure, as determined by a diaphragm pressure-recording apparatus, when mixtures of O_2 with H_2, C_2H_4, CH_4, or CO are ignited in a steel explosion cylinder, are slower when there is an excess of either O_2 or combustible gas than when the proportions theoretically necessary for complete combustion are employed. In the latter case, except for $2CO+O_2$, the rate of rise is so rapid that measurement becomes impossible. The explosion wave in CH_4–O_2 mixtures travels most rapidly in the 50% mixture, corresponding with the reaction $CH_4+O_2 \rightarrow CO+H_2+H_2O$. In the 33% mixture the second O_2 is probably acting as a diluent. The rate of rise of pressure in moist CO–O_2 mixtures is increased by the addition of small amounts of other combustible gases. The effect for equal additions increases in the order H_2, C_2H_2, C_2H_4, CH_4, and C_5H_{12}. The limiting composition of gas mixtures for detonation, as determined by different observers, is in close agreement with the composition of the mixture reaching its max. pressure 0·04 sec. after the first sign of pressure rise, in the apparatus used. M. S. BURR.

Theory of gaseous explosions and oxidation of hydrogen sulphide. H. W. THOMPSON (J. Physical Chem., 1931, 35, 3639—3643).—The equation used by Taylor (A., 1931, 1240) is corrected to $\log P/T=A/T+B$, in accordance with Semenov's theory, and from this the heat of activation is calc. It is agreed that the oxidation of H_2S is a chain reaction.
J. E. AUSTIN (*c*).

Dissociation of ozone and mechanism of its thermal decomposition. O. R. WULF (J. Amer. Chem. Soc., 1932, 54, 156—160; cf. A., 1927, 631, 834, 943).—The mechanism of the thermal decomp. of O_3 is represented by $O_3 \rightleftharpoons O_2+O$, $O_3+O \rightarrow 2O_2$. The entropy of gaseous O_3 calc. from other entropies is $S_{298}=52\cdot6$. Using this val., the equilibrium const. for the first step of the mechanism has very nearly the requisite val., *i.e.*, the no. of collisions between O and O_3 corresponds approx. with the observed second-order rate. Since there are more than 10^4 more collisions than reactions between O_3 and O, the O_3 mol. probably requires activation before it will react with O atoms. For low rates and high total pressures, the reaction of O atoms with O_3 mols. is probably the principal cause of the thermal decomp. of O_3.
L. KELLEY (*c*).

Kinetics of the bromine–oxalate reaction. R. O. GRIFFITH, A. MCKEOWN, and A. G. WINN (Trans. Faraday Soc., 1932, 28, 107—126; cf. A., 1928, 715).—The kinetics of the reaction at 21·5°, 16·5°, and 11·5° between $M/600-M/300$-Br and $H_2C_2O_4$, neutral and acid oxalates, and mixtures of the latter, in the presence of 0—0·5N-bromides and HBr (total ionic strength, μ, is between 0·0 and 0·8) are in accord with the reactions (I) $H_2C_2O_4 \rightleftharpoons H^{\cdot}+HC_2O_4'$, (II) $Br_2+H_2O \rightleftharpoons H^{\cdot}+Br'+HOBr$, and (III) $HC_2O_4'+HOBr \rightarrow H_2O+2CO_2+Br'$ of which (III) determines the over-all rate. The second ionisation const. (k_2) of $H_2C_2O_4$ is computed to be 7×10^{-5} at $\mu=0$ and 21·5°, k_2 increases with ionic strength, NaBr having a slightly greater effect than KBr. The hydrolytic const. of Br_2 increases markedly with μ and for reaction (III) the bimol. velocity coeff. is 2×10^4 approx. (units: litres, g.-mol., min.) and the crit. increment 15,400 g.-cal. The abnormally high temp. coeff., 6 approx., of the net reaction is attributed to the combined effects of temp. on equilibrium (II) and reaction (III).
J. G. A. GRIFFITHS.

Velocities and heats of saponification of amides. E. CALVET (Compt. rend., 1932, 194, 610—612).—The heats, Q, and velocities of saponification at 17°, k_{17}, and 0°, k_0, and the temp. coeff., c, per 10° between 0° and 17°, of mono-, di-, and tri-chloroacetamide are respectively 23·2, 7·5, 1·952, 9000; 335, 136, 1·698, 10,100; 1110, 464, 1·67, 10,700. k_{17} and c are connected with Q by the relations $\log k_{17}=0·001005(Q-7600)$, and $\log c=0·0000476(15,200-Q)$, which also hold for the normal fatty amides with 2—4 C atoms (cf. A., 1929, 1389; 1931, 916). There is no appreciable hydrolysis of a chloroacetamide in aq. solution, nor in aq. NaOH of the Cl as compared with that of NH_2. C. A. SILBERRAD.

Velocity of decomposition of diazo-compounds in water. VII. E. YAMAMOTO (J. Soc. Chem. Ind. Japan, 1932, **35**, 11—13B; cf. A., 1930, 1529).—The decomp. velocities of *m*- and *p*-$SO_3H·C_6H_4·N_2Cl$ and 2-nitro-*p*-toluenediazonium chloride in H_2O have been measured at different temp. The decomp. is unimol. N. H. HARTSHORNE.

Rates of formation of the active reductants of several sugars. M. H. ROEPKE and J. M. ORT (J. Physical Chem., 1931, **35**, 3596—3611).—The rate of formation of the active reducing agents in slightly alkaline aq. solutions of glucose, mannose, galactose, fructose, maltose, and lactose has been determined by adding an excess of $K_3Fe(CN)_6$ and measuring its rate of reduction. At const. temp. and const. p_H the rate of reduction is const. The influence of p_H is represented by $\log V=1·116p_H+C$, where C is a const., except for galactose, in which case $\log V=0·86p_H+C$. Comparison of these results with the dissociation consts. of the sugars suggests that the active reducing agent is derived from the sugar ion; the influence of other electrolytes supports this view. A secondary effect of p_H, influencing galactose in one direction and the remaining sugars in the other direction, suggests that increasing p_H causes a shift in the equilibrium from the 1 : 5- to the less stable 1 : 4-oxide ring structure in the glucose series and in the reverse direction in galactose. The rate of formation of the active reducing agent from glucose is increased 100-fold by a rise in temp. of 22·5°, and increases linearly with concn. over the range 1—60%. The concn. relation may be due to an increase in the dissociation const. of glucose with increasing concn. The rate of formation is not influenced by the presence of $Fe(OH)_2$. The rates measured are believed to be the rates of formation of the 1 : 2-enediol forms for the aldoses studied and both the 1 : 2- and 2 : 3-enediols in the case of fructose. E. S. HEDGES.

Steric hindrance in the hydrolysis of benzylidene chloride. G. LOCK and F. ASINGER (Monatsh., 1932, **59**, 152—160).—By the substitution of a Cl atom in the *o*-position in $CHPhCl_2$ the velocity of hydrolysis of the side-chain is considerably reduced, and by substitution in both *o*-positions it is practically inhibited. The hydrolysing agents used were a mixture of equal proportions of $COMe_2$ and dil. aq. K_2CO_3, conc. H_2SO_4, and anhyd. $H_2C_2O_4$. M. S. BURR.

Kinetics of reaction between potassium persulphate and sodium thiophenoxide. T. B. DOUGLAS (J. Physical Chem., 1931, **35**, 3280—3285).—This stoicheiometrically termol. reaction is kinetically bimol. The velocity coeff. of the simple velocity equation varies with the OH′ concn. and the concn. of reactants, an anomaly which is ascribed to increased activation caused by complex ion formation. R. H. CHERRY (*c*).

Theory of the rate of dissolution of gas into liquid. S. MIYAMOTO (Bull. Chem. Soc. Japan, 1932, **7**, 8—17).—The rate of dissolution of O_2 in H_2O, and oxidation velocities in solution, are better explained by the author's theory (A., 1931, 437) than by the theory of diffusion from a saturated surface layer. C. W. DAVIES.

Kinetics of dissolution of readily soluble salts in water. K. JABŁCZYŃSKI and J. GUTMAN (Rocz. Chem., 1932, **12**, 9—22).—Spectrophotometric measurements of solutions in which crystals of coloured salts are being rotated indicate that the velocity of dissolution, K, is proportional to that of diffusion from the solid to the liquid phase. The temp. coeff. of the reaction is 1·44 for $CuSO_4,5H_2O$, 1·52 for $NiSO_4,7H_2O$, and 1·35 for $K_2Cr_2O_7$. The absorption of red light by aq. $CuSO_4$ is increased by addition of EtOH. The val. of K of salts in aq. EtOH is smaller than that in H_2O alone, owing to reduction in velocity of diffusion, and varies directly with the solubility of a given salt. R. TRUSZKOWSKI.

Kinetics of dissolution of substances in non-aqueous media. K. JABŁCZYŃSKI and A. WALCZAK (Rocz. Chem., 1932, **12**, 23—34).—Measurements of K of rotated cylinders of picric acid or azobenzene in EtOH, aq. EtOH, and EtOH–CCl_4 mixtures indicate that the process of dissolution proceeds according to the same laws as for solutes in H_2O (cf. preceding abstract). K varies directly with the CCl_4 content of the solvent (EtOH), and inversely with the H_2O content. The temp. coeff. of reaction is 1·08 for azobenzene, and 1·50 for picric acid in EtOH. R. TRUSZKOWSKI.

Thermal decomposition of nitrous oxide and its catalysis by nitric oxide. F. F. MUSGRAVE and C. N. HINSHELWOOD (Proc. Roy. Soc., 1932, **A**, **135**, 23—39).—The unimol. reaction, relatively important in the low-pressure decomp. of N_2O, is homogeneous. Its velocity coeff. falls at low pressures, the change belonging to the quasi-unimol. class. The abs. rate has the order of magnitude expected for activation in two square terms. It is suggested that the high- and low-pressure parts of the reaction necessitate the changes $2N_2O \rightarrow 2N_2+O_2$ and $N_2O \rightarrow N_2+O$, respectively. The formation of NO during the decomp. of N_2O has been investigated; it may be produced by the action of at. O on N_2O. NO exerts a catalytic action on the decomp. of N_2O, the rate being proportional to $[NO][N_2O]$. L. L. BIRCUMSHAW.

Sulphurous acid and its salts. X. Decomposition of sulphurous acid catalysed by iodide ions. F. FOERSTER and E. GRUNER (Z. anorg. Chem., 1932, **203**, 245—270; cf. A., 1923, ii, 853).—The rate of decomp. of aq. H_2SO_3 in presence of I′ has been studied at room temp., 100°, 125°, and 150°, with and without the addition of other substances. According to the relative amounts of positive and negative catalysts present, the velocity curves may be linear, concave to the time axis, or S-shaped. The net change, $3H_2SO_3 \rightarrow 2H_2SO_4 + S + H_2O$, is retarded by H˙, and accelerated by S_2O_3'', S, or I′. I′ forms complex ions with SO_2, notably $[I(SO_2)_4]'$, whereby the retarding influence of $H^{\cdot}$ is mitigated. It also promotes the formation of S_3O_6'', which is considered to be the intermediate product responsible for the autocatalysis. F. L. Usher.

Kinetics of a catalysed isomeric change in solution. R. C. Traill (Phil. Mag., 1932, [vii], 13, 225—233).—Data for the velocity of mutarotation of Be benzoylcamphor in CCl_4, and also in $CHCl_3$, catalysed by pyridine, EtOH, and *p*-cresol are analysed by the law of mass action, and give velocity coeffs. in agreement with those of Lewis' equation for a bimol. gaseous reaction. N. M. Bligh.

Catalytic decomposition of hydrogen peroxide by cadmium iodide. R. U. Gooding and J. H. Walton (J. Physical Chem., 1931, 35, 3612—3617).—$Cd^{\cdot\cdot}$ has no appreciable catalytic effect, the active agents being I', $CdI^{\cdot}$, and CdI_3'. I' decomposes H_2O_2 more than twice as fast as CdI_3', the rate of decomp. being in each case proportional to the concn. of the active ion. The kinetic data thus confirm the ionic complexity of aq. CdI_2 (cf. A., 1905, ii, 371). Addition of I causes a considerable diminution in the velocity coeff. if the concn. of CdI_2 is low, but in conc. solutions has very little effect. F. L. Browne (*c*).

Change of acidity produced by salts in sulphurous acid solutions at high temperature. E. Hägglund (Biochem. Z., 1932, 244, 278—283; cf. Kullgren, B., 1930, 984).—The rate of hydrolysis of starch by H_2SO_3 at 110° and 120° is greatly affected by the presence of salts, being lowered by $NaHSO_3$ or $NaSO_4$ and increased by NaCl or $NaNO_3$. There is a direct relation between the rate and the $[H^{\cdot}]$ of the solutions which depends on the nature and amount of salt present. The inversion of sucrose by H_2SO_3 is similarly affected by Na_2SO_4 and it is suggested that the influence of Na_2SO_4 in the sulphite pulp process is analogous. W. McCartney.

Heavy metal catalysts. I. Fission of starch by artificial peroxidase. T. Omori (J. Biochem. Japan, 1931, 14, 331—337).—H_2O_2 in presence of 0·01—0·002*M* Mn, Co, Ni, and especially V, Cu, and Fe salts exhibits an amylolytic activity which is accelerated by the presence of tyrosine, pyrocatechol, quinol, or *p*-cresol. The mechanism of such a fission, however, is not identical with that of diastatic action. F. O. Howitt.

Effect of change of medium on velocity of hydrolysis of ethyl orthoformate. H. S. Harned and N. N. T. Samaras (J. Amer. Chem. Soc., 1932, 54, 1—8).—The hydrolysis at const. p_H has been investigated, and the catalytic coeff. of the hydronium ion determined. The velocity coeff., k, in aq. solutions of MeOH, EtOH, $Pr^{\alpha}OH$, $Pr^{\beta}OH$, $Bu^{\alpha}OH$, $COMe_2$, and glycerol is given by $\log_e k_0 - \log_e k = 0{\cdot}07(D_1 - D)$, where k_0 is the velocity coeff. when the org. solvent is absent, and $(D_1 - D)$ the lowering of the dielectric const. caused by the org. solvent. In an aq. solution of glycine both k and D increase with the glycine concn., but not in a linear manner. S. Lenher (*c*).

Medium changes in homogeneous catalysis and an approach to their theoretical interpretation. H. S. Harned and N. N. T. Samaras (J. Amer. Chem. Soc., 1932, 54, 9—23).—In order to take account of the effect of the solvent medium in homogeneous catalysis the replacement of the kinetic factor, F, in the velocity equation $v = kc_A c_B \ldots F$ by $e^{-W/kT}$ is suggested, and approx. equations for W, which is related to the change in dielectric const. produced by a neutral substance, have been derived. For the hydrolysis of Et orthoformate (cf. preceding abstract) the theory leads to a relation between the change in dielectric const. and the change in velocity coeff. which agrees satisfactorily with the experimental data. The primary medium effect in the reaction of MeI with $Na_2S_2O_3$ and the transformations of substituted aminobenzenes also agrees with the theory. S. Lenher (*c*).

Inversion of sucrose. E. Toporescu (Compt. rend., 1932, 194, 724—726).—Since the inversion of sucrose by 0·25*N*-HCl in aq. solution at 25° is almost inhibited by addition of $CO(NH_2)_2$ (75 to 10 g. sucrose in 100 c.c.) it is suggested that the inversion is effected not by H ions but by depolymerised H_2O mols., the function of the acid being depolymerisation. J. W. Baker.

Mechanism of racemisation. A. N. Campbell and A. J. R. Campbell (Nature, 1932, 129, 281).—The sp. rotation of Na NH_4 tartrate decreases with an increase in concn. of added NaOH and eventually becomes strongly negative. The change in sign occurs with approx. 10*N*-NaOH. This is taken to show that racemisation by NaOH is accompanied, and probably conditioned, by complex formation. The usual view of racemisation is discussed in relation to these results, and the stereochemical conception of optical activity as a static phenomenon is considered to be not entirely satisfactory. L. S. Theobald.

Induced oxidation of glucose in presence of insulin acting as an inductor. H. L. Dube and N. R. Dhar (J. Physical Chem., 1932, 36, 444—448).—If air is passed at 25° through a solution of glucose containing insulin, the former is appreciably oxidised, and the oxidation is markedly accelerated by phosphates, $Ce(OH)_3$, and $Fe(OH)_2$. The insulin also is oxidised, but more slowly than when glucose is absent, so that the oxidation of the insulin must be assumed to induce the oxidation of the glucose, which is the probable explanation of the increased oxidation of glucose in the presence of insulin in the animal body. In presence of Na_2CO_3, which apparently inactivates insulin, there is no induced oxidation. F. Saunders (*c*).

Catalytically active surfaces. I. H. J. Prins (Chem. Weekblad, 1932, 29, 66—72).—A discussion of the conditions assumed to obtain at active surfaces. S. I. Levy.

Catalytically active surfaces. II. H. J. Prins (Chem. Weekblad, 1932, 29, 89—92).—A review. H. F. Gillbe.

Conversion of para-hydrogen into ortho-hydrogen over iron synthetic ammonia catalysts. P. H. Emmett and R. W. Harkness (J. Amer. Chem. Soc., 1932, 54, 403—404).—On passing a stream of para- and ortho-H in the ratio 49 : 51 over an NH_3 catalyst at −20° to 40° a considerable amount of the para form is converted into the ortho form, the approach to the equilibrium being the closer the higher is the temp. C. J. West (*c*).

Mechanism of the reaction $H_2+I_2 \longrightarrow 2HI$, and of similar reactions at boundary surfaces. H. Ekstein and M. Polanyi (Z. physikal. Chem., 1932, B, **15**, 334—341).—It is suggested that the atoms of the I_2 mol. first move apart, then attack the H_2 mol., one at each end, approaching it along its axis. Assuming that the energy required for the first step is equal to the heat of dissociation of I_2, the heat of activation of the second step, calc. by the method previously described (A., 1931, 688), is sufficiently small for the heat of activation of the reaction as a whole to agree satisfactorily with the observed val. An explanation of the intermediate formation in the catalysed wall reaction of hydrides on the catalyst surface is advanced. R. Cuthill.

Hydrogen–carbon dioxide reaction. E. H. Boomer and H. E. Morris (J. Amer. Chem. Soc., 1932, **54**, 407).—After passing over a Zn–Cu–Al catalyst at 325°, a mixture of 27% CO_2, 71% H_2, and 2% N_2 under 1700 lb. pressure contained 4% CO, suggesting that the first step in the synthesis of MeOH from CO_2 and H_2 involves the reduction of CO_2 and the nature of the catalyst determines the extent to which the resultant CO will be hydrogenated. As the activity of the catalyst decreases, the reaction giving MeOH is affected most; the same catalyst produced an appreciable amount of CO_2 from water-gas. C. J. West (*c*).

Thermal decomposition of ammonia on the surface of osmium. E. A. Arnold and R. E. Burk (J. Amer. Chem. Soc., 1932, **54**, 23—32).—The reaction at 288—367° is of zero order, and is retarded by the products in such a way that the free surface may be represented by the term (1 — concn. of products) in the velocity equation. The calc. energy of activation is 47,600 and 42,200 g.-cal. per mol. over the temp. range. S. Lenher (*c*).

Catalytic effect of alkali and alkaline-earth sulphides on reaction between phosphorus trichloride and sulphur. W. H. Woodstock and H. Adler (J. Amer. Chem. Soc., 1932, **54**, 464—467).—Small amounts of alkali sulphides, alkaline-earth sulphides, or similar substances catalyse the formation of $PSCl_3$ from PCl_3 and S at 150°. Chemical Abstracts (*c*).

Catalytic decomposition of hydrogen peroxide by platinum-black. A. Sieverts and H. Brüning (Z. anorg. Chem., 1932, **204**, 291—304).—The decomp. of H_2O_2 in presence of Pt-black is an approx. unimol. reaction; an initial rise of the velocity coeff. is ascribed to the increased activity of the catalyst during the early stages of the decomp., and a later slow fall to increasing poisoning or reduction of active surface of the Pt. The influence of stirring and of temp. on the reaction indicates that diffusion is the factor which determines the apparent velocity; the temp. coeff. falls from 1·66 at 25—35° to about 1·4 at 45—55°. Traces of NaOH accelerate the decomp., and larger quantities cause retardation. The velocity in presence of $0{\cdot}02N$-H_2SO_4 is a linear function of the activity of the catalyst ("catalytic concn."), and may therefore be employed as a measure of this quantity. O_2 adsorbed on the Pt-black is removed during the reaction; O-free Pt is at first inactive, but the reaction commences after a short time. Hydrated PtO is an active catalyst and is unchanged after the reaction. H. F. Gillbe.

Velocity of catalysed hydrogenation. II. A. Kailan and J. Kohberger (Monatsh., 1932, **59**, 16—43).—The velocity of hydrogenation of olive oil, oleic acid, and Et oleate has been investigated at 180°±5° and H_2 pressures of 360, 760, and 1160 mm. Hg, using as catalysts Ni on Al_2O_3 and Ni and Co both separately and together on kieselguhr. The velocity coeff. calc. for a unimol. reaction increases approx. as the power 1·5 of the H_2 pressure between 760 and 1160 mm. and approx. as the power 1 between 360 and 760 mm., whether the substance to be hydrogenated contains one double linking in the mol., *e.g.*, oleic acid and Et oleate, or three, *e.g.*, triolein in olive oil. The results contradict Thomas' theory of the reaction mechanism (A., 1920, ii, 169). The Ni–kieselguhr catalyst is far more active than Ni–Al_2O_3. Co and Ni on kieselguhr have about the same activity and are each more active than the mixed metals. The velocity of hydrogenation of Et oleate is greatest, but the difference is within the limits of experimental error. M. S. Burr.

Catalytic chlorination and bromination of gases rich in methane hydrocarbons. M. Zapan (Diss., Univ. Paris, 1930, 9—99).—CH_4, C_2H_6, coal gas, and petroleum gas were chlorinated with catalysts mounted on pumice treated with $FeCl_3$ or $CuCl_2$. $SbCl_5$, $TiCl_4$, and $SnCl_4$ were effective in that order. Bromination was effected in presence of $FeBr_3$. Yields of chlorination products up to 75% on the CH_4 in coal gas and 12—49% yields of brominated products are recorded. Chemical Abstracts.

Slow combustion of acetylene. R. Spence (J.C.S., 1932, 686—696).—At 320° wall activation predominates in the slow oxidation of C_2H_2, and increase in the relative amount of surface results in a shorter induction period and increased velocity of reaction. There is also an inhibiting effect in vessels <4 mm. diameter, but in vessels of diameter >6 mm. inhibition by the walls is small compared with inhibition by O_2. Wall inhibition can be brought into prominence again, however, by coating with KCl. This is probably due to a smaller efficiency of the KCl in catalysing the production of active centres. The results point to a branched chain mechanism, and a similar mechanism may be shown to operate in the slow oxidation of C_2H_4. M. S. Burr.

Effect of concentration of electrolyte on the formation of the anodic film on aluminium. S. Setoh and A. Miyata (Bull. Inst. Phys. Chem. Res. Tokyo, 1932, **11**, 319—382).—The formation of the anodic film on Al in 0·5—8·0% $H_2C_2O_4$ solutions at 0—60° has been examined, using a.c., d.c., and a.c. superimposed on d.c. The thickness of the active film is proportional to the p.d. it sustains, as shown by measurements of electrostatic capacity and counter-e.m.f., but does not increase indefinitely as the applied e.m.f. is increased. There is no definite thickness for the active layer and no crit. e.m.f. In general, the film is the thinner the higher is the temp., the greater the concn. of electrolyte, and the lower the c.d. The thinner film is more compact. At room temp. the current efficiency is greatest (about 80%) with 2—4% solutions of $H_2C_2O_4$, using 50—60 volts and 15 milliamp. per sq. cm. The apparent density of the film is nearly 3·0. E. S. Hedges.

Mixed borides of thorium and cerium. L. Andrieux (Compt. rend., 1932, **194**, 720—722; cf. A., 1930, 305).—By electrolysing between C electrodes mixtures in varying proportions of ThO_2 and CeO_2 in a bath of B_2O_3, MgO, and MgF_2 at 1150°, with a current of 25 amp. at 8 volts, a series of solid solutions of ThB_6 and CeB_6 is obtained. The relative amounts of Th and Ce in the product depend on those of ThO_2 and CeO_2 in the bath; that of B is approx. const. The amount of Ce is relatively greater than that of Th in accordance with the smaller heat of formation of CeO_2, but Th is never absent. C. A. Silberrad.

Relation between Kolbe's reaction and hydrogen-ion concentration. Mechanism of Kolbe's reaction. H. R. Matsuda (Bull. Chem. Soc. Japan, 1932, **7**, 18—27).—H_2O_2 is formed during electrolysis of KOAc and NH_4OAc; by comparison of the ratio $H_2O_2 : C_2H_6$ produced it is concluded that Ac_2O_2 is first formed at the anode. This may give H_2O_2 by way of the peracid, or may decompose to C_2H_6 and CO_2; the former is favoured by high p_H. C. W. Davies.

Reactions of hydrocarbons in the glow discharge. E. G. Linder and A. P. Davis (J. Physical Chem., 1931, **35**, 3649—3672).—The decomp. of 57 hydrocarbons in the glow discharge has been investigated under identical conditions. The rate of gas evolution per unit current increases with mol. wt., which is attributed to the fact that with increase in the no. of degrees of freedom the mol. may absorb energy in other ways than by ionising. The amount of insol. residue increases with decrease of the ratio H : C in the original hydrocarbon. Analyses of the gaseous products are given. A theory of chemical action in the glow discharge is advanced. G. M. Murphy (c).

Triatomic halogen molecules in photochemical reactions. G. K. Rollefson and H. Eyring (J. Amer. Chem. Soc., 1932, **54**, 170—177).—By using the quantum mechanical equation for the potential energy of systems of three atoms, it has been shown that for all the halogens mols. of the type X_3 are stable at room temp. with respect to the decomp. into X_2 and X. The significance of this fact in relation to the mechanism of the reactions of Cl_2 with H_2 and with CO, and to Senftleben and Germer's optical dissociation experiments on halogens (A., 1929, 1209) is discussed. Chemical Abstracts (c).

Reaction between hydrogen and oxygen under the influence of photochemically produced hydrogen atoms, and connexion with the "knallgas" reaction at higher temperatures. W. Frankenburger and H. Klinkhardt (Z. physikal. Chem., 1932, B, **15**, 421—444).—See A., 1931, 1136.

Hydrazine. Photochemical oxidation of hydrazine by ferricyanide. E. C. Gilbert (J. Physical Chem., 1931, **35**, 3631—3634; cf. A., 1929, 1017).—The rate of oxidation at 25° in a 0·2M-Na_2HPO_4 buffer solution is increased by about 10% by exposure to weak light, the effective radiation being that absorbed by the ferricyanide. G. M. Murphy (c).

Photochemical reaction between hydrogen and chlorine in presence of oxygen. M. Ritchie and R. W. G. Norrish (Nature, 1932, **129**, 243—244).—The presence of HCl markedly inhibits this reaction. The formula $\gamma_{HCl}=k_1/(O_2)([HCl]+k_2)$ represents the quantum efficiency for O_2 pressures from 10 to 350 mm., and for a ten-fold variation in intensity. The inhibiting action of HCl is sp. and there is no inert gas effect. The kinetics of the reaction are discussed. L. S. Theobald.

Temperature coefficient of photochemical formation of hydrogen chloride. E. Hertel (Z. physikal. Chem., 1932, B, **15**, 325—333).—The temp. coeff. of the formation of HCl from a mixture of H_2 and Cl_2 free from O_2 in light of wave-lengths lying in the visible portion of the continuous absorption spectrum of Cl_2 is 1·37±0·02 at 25—55°. If a considerable amount of O_2 is present, the val. is 1·12±0·02. If the amount of O_2 is sufficient to play a notable part in breaking the reaction chains but not sufficient to be solely responsible for this, the velocity coeff. will lie between these two limits, and this seems to have been the case in Lind and Livingston's experiments (A., 1930, 434). The temp. coeff. for a mixture free from O_2 exposed to light of wave-length greater than corresponds with the convergence point in the banded spectrum of Cl_2 is 1·48±0·04. R. Cuthill.

Action of light on mixtures of ozone and chlorine. II. Results with high ozone concentration. Discussion. A. J. Allmand and J. W. T. Spinks (J.C.S., 1932, 599—612).—The mist observed in a previous investigation (A., 1931, 1018) when a Cl_2–O_3 mixture is insolated contains $HClO_3$ and $HClO_4$ due to the intermediate formation of ClO_3 or Cl_2O_6 from ClO_2 and O_3. In experiments with a high concn. of O_3 and low Cl_2 the behaviour previously observed is accentuated. The quantum efficiency γ is far higher (max. 59) and shows a distinct temp. coeff. (approx. 1·5). There is a tendency to approx. to the $I^{1/2}$ law. The dark reaction is also greater. γ falls rapidly while much of the O_3 is still present. It is concluded that O_3 disappears by (*a*) a primary reaction, (*b*) an incipient chain reaction of one complete term in the gas phase, (*c*) a chain mechanism of which one constituent reaction, viz., $ClO_3+O_3 \rightarrow ClO_2+2O_2$, takes place on the surface of the cell. (*a*) gives $\gamma=2$ without dependence on O_3 concn., λ, or T. (*b*) can add a max. of 4 to the val. of γ and causes the divergence from $\gamma=2$ in dil. mixtures and the effect of λ. (*c*) is favoured by high concn. of O_3 and low concn. of Cl_2. It accounts for the $I^{1/2}$ relation and the dependence of γ on T, but independence of λ. This mechanism is in accord with most of the experimental observations such as the induction period, due to formation and decomp. of adsorbed ClO_3, the final rise of velocity, due to catalysis by Cl atoms of an adsorbed Cl_2O_6 layer, and the rapid fall of γ in conc. O_3, due to the fact that O_3 and Cl_2O_6 do not react as do O_3 and ClO_3 so as to continue the chain. The corresponding thermal reaction is briefly discussed. The temp. coeff. with conc. O_3 gives an activation energy of 7·4 kg.-cal., but this result has a qual. val. only. M. S. Burr.

Photosensitised decomposition of nitrogen trichloride. II. Effects of surface and inert gases, and the mechanism of reaction. J. G. A. Griffiths and R. G. W. Norrish (Proc. Roy. Soc., 1932, A, **135**, 69—83).—The photosensitised decomp. of NCl_3 by Cl_2 is a homogeneous change propagated by a chain mechanism. In a vessel washed with H_2O or heated to above 100° the quantum efficiency is abnormally high, but in a matured vessel the quantum efficiency is independent of the illuminated surface and of the total surface. The maturing of the surface is due to an invisible film of NH_4Cl. The quantum efficiency is depressed by inert gases to a limiting val. of about 2, according to the equation $\gamma=1/\{\Sigma(k_x[X])\}+2{\cdot}5$, where $\Sigma(k_x[X])$ refers to the sum of the effects of the various gaseous species present. A theory based on a chain reaction initiated by Cl atoms is developed and found to agree with the experimental results. L. L. Bircumshaw.

Optical sensitisation in photography. W. D. Bancroft, J. W. Ackerman, and C. A. Gallagher (J. Physical Chem., 1932, **36**, 154—173).—An optical sensitiser in photography is a coloured substance which is adsorbed by AgBr but does not form a colour screen by dissolving in gelatin, and is a strong enough reducing agent to form a latent image with AgBr when activated or reduced by light. It is probable that the AgBr is reduced by the activated dye and not by a reaction product. The optical sensitisation of aq. $FeCl_3$ and $AgNO_3$ with a no. of light-sensitive dyes was studied. Sensitisation was observed when Na eosinate was added to a mixed solution of ammoniacal CuO and $NHPh{\cdot}NH_2$ which was of such composition that it was bleached by light, but stable in the dark. S. Lenher (*c*).

Photochemical reaction of carbon monoxide with ammonia and with amines. H. J. Emeléus (Trans. Faraday Soc., 1932, **28**, 89—94; cf. A., 1931, 1251).—The apparent rate of photochemical decomp. of 3—30 cm. of NH_3 at 100—150° in the full radiation of the quartz–Hg vapour lamp is approx. doubled by the addition of 14—26 cm. of CO. Less than 5% of the NH_3 reacting affords N_2 and H_2, the principal primary product being $HCO{\cdot}NH_2$, which undergoes secondary changes. The mechanism of the reaction is discussed. Preliminary experiments indicate that NH_2Me and NH_2Et react with CO under similar conditions. J. G. A. Griffiths.

Photo-reduction of carbonic acid, hydrogen carbonates, and carbonates to formaldehyde. N. R. Dhar and A. Ram (Nature, 1932, **129**, 205).—H_2CO_3, carbonates, and H carbonates are reduced to CH_2O by Mg and Zn, the yield being greater in light than in the dark. HCO_2H could not be detected (cf. J.C.S., 1907, **91**, 687). The yield is increased by photosensitisers such as ZnO. 100 c.c. of a 10% solution of $KHCO_3$ and 1 g. of powdered Mg in the presence of ZnO give 0·0045 g. of CH_2O after 5·5 hrs.' exposure to sunlight. No reducing sugar is detectable. $FeCO_3$ also brings about photo-reduction of these substances. L. S. Theobald.

Photochemical polymerisation of acetylene. S. C. Lind and R. Livingston (J. Amer. Chem. Soc., 1932, **54**, 94—106).—When C_2H_2 is irradiated with light from a Hg arc in the absence of Hg vapour a yellow solid, apparently cuprene, but no H_2, is formed. At lower pressures the rate of polymerisation is proportional to the pressure, but at 65 cm. it approaches a const. val., indicating that the rate is directly proportional to the intensity of absorbed light, but otherwise independent of the pressure. The temp. coeff. for a C_2H_2 pressure of 10 cm. is 1·25. Wave-lengths longer than 2537 Å. are either not absorbed or photochemically ineffective. The quantum efficiency for an average wave-length of 2150 Å. is 9·2± 1·5, independent of the C_2H_2 pressure and of the radiation absorption. This val. is approx. equal to the average yield per ion. E. J. Rosenbaum (*c*).

Photochemical polymerisation of cyanogen. T. R. Hogness and L. Ts'ai (J. Amer. Chem. Soc., 1932, **54**, 123—129).—The absorption spectrum of C_2N_2 has a set of diffuse bands from 2200 Å. to the transmission limit of quartz, from which it is concluded that C_2N_2 dissociates into CN radicals, one of which may be excited. No fluorescence was observed. C_2N_2 at 1 atm. absorbs 8·8% of radiation of effective wave-length 2150 Å. The quantum efficiency of the polymerisation of C_2N_2 to paracyanogen is 3. This val. can be accounted for by a second reaction, $C_2N_2+CN \rightarrow (CN)_3$; the $(CN)_3$ could polymerise further to paracyanogen. E. J. Rosenbaum (*c*).

Photochemical decomposition of chloroform. D. G. Hill (J. Amer. Chem. Soc., 1932, **54**, 32—40).—The decomp. of $CHCl_3$ vapour by light in the far ultra-violet has been studied. 4 mols. of HCl but no Cl_2 are formed per quantum absorbed. The yield is proportional to the square of the pressure of added O_2. Chemical Abstracts (*c*).

Photochemical studies. XIII. Photochemical reaction between chlorine and benzene in the gaseous phase. C. E. Lane, jun., and W. A. Noyes, jun. (J. Amer. Chem. Soc., 1932, **54**, 161—169; cf. A., 1931, 442).—The rate of the reaction in light of wave-length 4500—6000 Å. is proportional to $[Cl_2]$. The first step is the production of PhCl. This soon condenses out on the walls and the succeeding reactions are chiefly those of addition, C_6H_6 hexachloride, one of the products found, probably representing the final stage in the addition of Cl to C_6H_6 dissolved in the PhCl on the walls.

W. E. Vaughan (*c*).

Reactions of chlorine with solid carbonates. I. Sodium carbonate. F. Ishikawa, T. Murooka, and H. Hagisawa. **II. Potassium carbonate.** F. Ishikawa and H. Hagisawa (Bull. Inst. Phys. Chem. Res. Tokyo, 1932, **11**, 284—296, 297—303).—I. The main reaction is $2Na_2CO_3+2Cl_2=4NaCl+2CO_2+O_2$. Na_2CO_3 prepared by heating $NaHCO_3$ at 350° reacts more easily with Cl_2 than that prepared at 500°. $NaClO_4$ is also formed, particularly with Na_2CO_3 prepared at 350°.

II. The reaction is similar to that with Na_2CO_3.

$KClO_4$ is also formed in small amount. The reaction of Cl_2 with Li_2CO_3 and $MgCO_3$ was also studied; no perchlorate was formed. E. S. Hedges.

Potassium dibromoiodide hydrate. G. H. Cheesman and J. H. Martin (J.C.S., 1932, 586—588).—The crystals obtained by slow evaporation of a saturated solution of $KIBr_2$ in H_2O over syrupy H_3PO_4 have the composition $KIBr_2,H_2O$. The dissociation pressure–temp. curves have been drawn for the monohydrate and the anhyd. salt, pressure for the former being much higher than for the latter. The hydrated salt melts at 59°, causing a slight break in the dissociation curve. M. S. Burr.

Reactivity of alloys and its dependence on fusion or transformations in the solid state. I. Interaction of copper–tin alloys and lime or quartz in oxygen. J. A. Hedvall and F. Ilander (Z. anorg. Chem., 1932, 203, 373—389; cf. A., 1926, 695).—Measurement of the quantity of O_2 absorbed by mixtures of CaO with CuSn or Cu_3Sn heated at temp. up to 750° are considered to support the author's view that chemical reactivity is enhanced during the breaking down of a crystal lattice. Similar experiments were performed with SiO_2. The effect observed does not depend on fusion. Cu–Sn alloys attack refractories containing CaO or SiO_2 at or above 400°. F. L. Usher.

Synthesis of calcium silicates. II. S. Nagai and K. Akiyama (J. Soc. Chem. Ind. Japan, 1932, 35, 8—10B; cf. B., 1932, 262).—On heating a mixture of $CaCO_3$ and SiO_2 in the mol. ratio of 2 : 1 for 1 hr. at various temp. the amount of combination increases with rise of temp., and the products are $3CaO,2SiO_2+2CaO,SiO_2$ from 900° to 1100°, $2CaO,SiO_2$ from 1200° to 1450°, and $2CaO,SiO_2+3CaO,SiO_2$ from 1500° to 1550°. The compressive strength of $2CaO,SiO_2$ cements is greater than that of CaO,SiO_2 cements, but both are poor compared with those of Ca aluminate cements. N. H. Hartshorne.

Ammoniates of zinc, copper, and manganese sulphates. O. R. Foz and L. Le Boucher (Anal. Fís. Quím., 1932, 30, 21—30).—Study of the decomp. pressure–temp. curves has confirmed the existence of $ZnSO_4,5NH_3$ and $CuSO_4,5NH_3$, but $MnSO_4,5NH_3$, described by Ephraim, does not appear to exist. $ZnSO_4$ forms also compounds containing 4, 3, 2, 1, and 0·5 mols. of NH_3; the v.-p. curves and heats of formation have been determined. $CuSO_4$ forms a tetra- and a di-ammoniate. H. F. Gillbe.

Homogeneous and heterogeneous complex salts in solution. III. G. Spacu and P. Spacu (Bul. Soc. Stiinte Cluj, 1931, 5, 473—487; Chem. Zentr., 1931, ii, 1118; cf. A., 1931, 1380).—The following *compounds* have been prepared:
$[CdI_2Br_2][Cu\,en_2]$, $[CuCl_2Br_2][Cu\,en_2]$,
$[CdCl_4][Cu\,en_2]$, $[BiCl_6][Co\,en_3],2H_2O$, $[CdCl_4][X]_2(^1_6)$,
$[CuCl_4][X]_2(^1_6)$, $[BiCl_6][X]_3(^1_6)$, $[HgBr_3][X](^1_6)$,
$[CdI_4][X]_2(^1_6)$, $[CdI_4][X]_2(^1_2)$, $[CdBr_4][X]_2(^1_6)$,
$[SnCl_6][X]_2(^1_6)$, $[SnCl_3][X](^1_6)$, $[HgI_3][Co\,en_2CO_3]$,
and $[AgI_2][Co\,en_2CO_3]$, where X is $Co\,en_2Cl_2$. The cation $[Co\,en_2Cl_2]^{\cdot}$ in the *cis*-form remains unchanged only in the compound $[CdI_4][X]_2(^1_2)$. In most other cases the *trans*-compound is preserved owing to the greater solubility of the *cis*-salts; the former are green and the latter violet in colour. The complex $[SnCl_4][X]_2$ could not be prepared. L. S. Theobald.

Boron hydrides. I. Preparation of diborane, bromodiborane, and pentaborane. H. I. Schlesinger and A. B. Burg (J. Amer. Chem. Soc., 1931, 53, 4321—4332).—If a mixture of BCl_3 and H_2 obtained by passing H_2 through liquid BCl_3 at −40° is subjected to the action of a high-tension electric discharge, about 25% of the BCl_3 undergoes reaction, the chief product, apparently *chlorodiborane*, B_2H_5Cl, being accompanied by much smaller amounts of B_2H_6. At 0°, however, B_2H_5Cl decomposes: $6B_2H_5Cl \rightleftharpoons 5B_2H_6+2BCl_3$. When B_2H_6 is heated at 120—130° in presence of a little HCl a considerable proportion is converted into B_5H_9. A good yield of B_2H_5Br is obtained by interaction of B_2H_6 and BBr_3. H. Stoertz (*c*).

Alkali aluminosilicates. IV. [with E. Hirsch]. **Action of alkali sulphide and polysulphide solutions on permutites. V. Relationship between sulphide permutites and ultramarines.** E. Gruner (Z. anorg. Chem., 1932, 204, 232—246, 247—256).—IV. Alkali and alkaline-earth permutites, when treated with alkali sulphide or polysulphide solution in presence of air, become blue; the blue substance is decolorised by H_2O, with liberation of H_2S and S. In absence of air only the polysulphides cause the appearance of the blue compound, whereas the sulphides react with formation of colourless compounds containing 2 atoms of S per 3 mols. of permutite; these sulphide permutites yield with H_2O H_2S but no S. The curve relating the quantity of S absorbed with the concn. of the sulphide solution resembles an ordinary adsorption isotherm. During the removal of S from the solution the p_H increases, presumably owing to the interchange of OH′ from the permutite and SH′ from the solution. This ionic exchange proceeds rapidly, but the subsequent oxidation is slow and has a velocity coeff. of 0·039 for $Na_2(Al_2Si_2H_4O_{10})$ and of 0·061 for $Na_2(Al_2Si_2H_4O_{10}),H_4SiO_4$.

V. The sulphide permutites are of the type $Na_6[Al_6Si_6H_{10}O_{28}(SH)_2]$; on oxidation the SH groups are converted into S_2 or S_2H groups, and by hydrolysis they are replaced by OH groups, yielding the original permutite. The polysulphide permutites probably exist in dynamic equilibrium with S and the monosulphide compound, in accordance with the theory of Hofmann and Biltz. The analogous Na polyselenide permutite is red and readily decomposes with liberation of Se. Faint blue colorations are produced by the action of alkali sulphide solutions on basic or amphoteric hydroxides, such as those of Al, Cr, Th, and Zr, but not with acidic hydroxides (Si, Ti). If the blue polysulphide permutites are prepared at temp. above about 200° they are of much greater stability and yield the same *X*-ray diagram as ultramarine. H. F. Gillbe.

Removal of free carbonic acid from water. J. Tillmans, P. Hirsch, and H. Lürmann.—See B., 1932, 242.

Persilicates. F. Krauss (Z. anorg. Chem., 1932, 204, 318—320).—*Na persilicate*, $Na_2SiO_3,2H_2O_2,H_2O$, has been prepared as a non-hygroscopic, stable, and very sol. powder by adding H_2O_2 to a solution of Na_2SiO_3 and evaporating to dryness in vac.

H. F. GILLBE.

Alkali salts of fluotitanic acid. IV. H. GINSBERG (Z. anorg. Chem., 1932, 204, 225—231).—Pure anhyd. Na_2TiF_6 has been prepared by pptn. with EtOH from its aq. solution. The solubilities and m. p. of all the alkali salts have been determined; the solubilities in EtOH are very small (0—0·01%). The thermal decomp. of these compounds is not normally a hydrolytic process, but it is accelerated by the presence of H_2O and of O_2, and becomes mainly hydrolytic when the atm. is saturated with H_2O. The TiF_4 evolved when the salts are heated at 600—660° (Li 430°) yields on the walls of the containing vessel a deposit of TiO_2. H. F. GILLBE.

Action of hydrocyanic acid on halides of ter- and quadri-valent metals. T. KARANTASSIS (Compt. rend., 1932, 194, 461).—$TiCl_4$ and HCN, cooled in ice and salt, combine to form $TiCl_4,2HCN$, which sublimes as yellow crystals at 70°. $SnCl_4$ and HCN form a very volatile white ppt. (cf. Annalen, 1850, 74, 85). $AlCl_3$ forms $AlCl_3,2HCN$ (cf. this vol., 132). No compounds are formed with SnI_4, SnI_2, $SnBr_4$, $SbCl_3$, $AsCl_3$, or $CrCl_3$. C. A. SILBERRAD.

Heteropoly-acids of germanium. II. A. BRUKL and B. HAHN (Monatsh., 1932, 59, 194—201).—12-Tungstogermanic acid (I), $H_8Ge(W_2O_7)_6$, is prepared +4, 15, and $22H_2O$ (cf. A., 1930, 1538). Electrometric titration of (I) with NaOH indicates only four readily replaceable H atoms, but a $Hg_8^{\cdot}$ *salt* ($+5H_2O$) can be prepared from (I) and $HgNO_3$. A K H *salt*, $3K_2O,2GeO_2,24WO_3,30H_2O$ (loses $17H_2O$ at 95—100°), is occasionally prepared. (I) (1 mol.) and K_2CO_3 (5·5 mols.) give the *salt*, $7K_2O,2GeO_2,20WO_3,24H_2O$ [corresponding *Ag* salt ($+6H_2O$)], convertible into the *guanidine* salt, $(CH_5N_3)_7,GeO_2,10WO_3,13H_2O$ (loses $8H_2O$ at 130°); the free (10-tungstogermanic) acid could not be isolated. (I) and K_2CO_3 (7·5 mols.) give a product containing Ge hydroxide; addition of NH_4NO_3 to a dil. solution affords the *salt*, $8NH_3,3K_2O,2GeO_2,20WO_3,17H_2O$. The existence of other tungstogermanic acids is not indicated.

H. BURTON.

Decomposition of nitrates and nitrites of metals with different valencies. II. Stannous nitrate. C. MONTEMARTINI and E. VERNAZZA (Ind. chim., 1931, 6, 632—638; Chem. Zentr., 1931, ii, 1117—1118; cf. A., 1931, 583).—$Sn(NO_3)_2$ has been prepared from $SnCl_2$ or $SnSO_4$ [from $Sn(OH)_2$ and H_2SO_4] and $Pb(NO_3)_2$, or from $Sn(OH)_2$ and HNO_3. $Sn^{\cdot\cdot}$ is determined using $KMnO_4$ in H_2SO_4 solution after addition of $Fe_2(SO_4)_3$ or Fe alum. Aq. $Sn(NO_3)_2$ solutions are completely stable at room temp. in an atm. of CO_2. Heating in a stream of CO_2 leads to the formation of $Sn(OH)_2$, basic nitrate, SnO_2, and $Sn(OH)_4$; whilst in contrast with $Fe(NO_3)_2$, NO, N_2O, and N_2 are evolved and NH_3 is formed in the solution. The decomp. is very rapid in its final stages, and is accelerated by the addition of HNO_3; the more conc. is the acid the greater is its effect.

L. S. THEOBALD.

Rhombic modification of lead chromate. F. QUITTNER, J. SAPGIR, and N. RASSUDOVA (Z. anorg. Chem., 1932, 204, 315—317).—Rhombic $PbCrO_4$ is obtained when $K_2Cr_2O_7$ solution is added to a neutral solution of a Pb salt at room temp., provided that the concn. of the Pb solution does not exceed 10% and that the product is dried at a temp. below 25°. The substance is of a brilliant yellow colour and is stable for about 1 month at room temp. When ground with linseed oil it darkens very rapidly. The Debye–Scherrer diagram closely resembles that of $PbSO_4$ (anglesite). H. F. GILLBE.

Mechanism of precipitation processes. VIII. Precipitations with lead and iodide ions. Z. KARAOGLANOV and B. SAGORTSCHEV (Z. anorg. Chem., 1932, 203, 390—400; cf. A., 1931, 1021).—When an aq. solution of $Pb(NO_3)_2$ is added to one of H_2SO_4 in presence of KI the resulting ppt. contains I which is gradually given up to the liquid. The ppt., initially white, becomes yellow. The process is expressed by: $2PbI^{\cdot}+SO_4''\rightarrow(PbI)_2SO_4$, followed by $(PbI)_2SO_4\rightarrow PbI_2+PbSO_4$. Similar results were obtained in presence of KCl and KBr, but not KCNS; or when $Na_2C_2O_4$ or $(NH_4)_2CrO_4$ is substituted for H_2SO_4.

F. L. USHER.

Ammonium thiosulphate. W. KLEMPT, F. BRODKORB, and H. ERLBACH.—See B., 1932, 179.

Anhydrous hydrazine. V. Hydrazinates of calcium trinitride. A. L. DRESSER and A. W. BROWNE (J. Amer. Chem. Soc., 1931, 53, 4235—4242).—*Ca azide dihydrazinate*, $Ca(N_3)_2,2N_2H_4$, prepared by crystallisation of $Ca(N_3)_2$ from anhyd. N_2H_4, is isomeric and possibly identical with the Ca derivative of either of the unknown compounds Δ^1-pentazine, $NH{:}N{\cdot}NH{\cdot}NH{\cdot}NH_2$, and Δ^2-pentazine, $NH_2{\cdot}NH{\cdot}N{:}N{\cdot}NH_2$. The *monohydrazinate*, $Ca(N_3)_2,N_2H_4$, was prepared by gradual dehydrazination of the solute. H. STOERTZ (*c*).

Absorption and evolution of hydrogen sulphide from solutions containing both sodium carbonate and arsenious oxide. H. A. J. PIETERS and J. SMEETS (Chem. Weekblad, 1932, 29, 73—74).—The presence of As_2O_3 enables a solution of Na_2CO_3 to take up more H_2S, but on regeneration the amount evolved is diminished. S. I. LEVY.

Structure of ultramarine. K. LESCHEWSKI and H. MÖLLER (Ber., 1932, 65, [*B*], 250—253; cf. A., 1931, 1380).—White ultramarine obtained from the blue compound and HCO_2Na or HCO_2K and "U blue 2," obtained by heating the white substance, are distinguished from the original material by higher alkali content. The total S content is unchanged, but combined S is doubled. Oxidation of white ultramarine or "U blue 2" with molten $NaClO_3$ or $NaNO_3$ regenerates ultramarine. In consequence of hydrolysis, formate ultramarine becomes pale blue when treated with boiling H_2O. The conversion of blue into pale pink ultramarine by boiling ethylene chlorohydrin is accompanied by great diminution of the Na content and not by removal of S. Fusion with NaCl restores the colour. A white ultramarine is obtained by this process from an original material with 7·9% S; this becomes coloured by molten or dissolved Na_2S but not by NaCl. H. WREN.

Salts of trithionic acid. C. G. Katraki (Praktika, 1929, 4, 120—123; Chem. Zentr., 1931, ii, 1116).—A solution of $Na_2S_2O_3$, containing an excess of NH_3, gives on warming and cooling with a conc. solution of $CuSO_4$ blue crystals of $Cu_2S_3O_6,Na_2S_2O_3,3NH_3$ which are insol. in EtOH and in $COMe_2$ and sparingly sol. in H_2O. NH_3 is evolved with cold H_2O and some $Cu(OH)_2$ formed. CuS is first formed on heating, and then NH_3 and SO_2 are evolved. $BaCl_2$ gives BaS_3O_6, and $AgNO_3$ forms Ag_2S on warming. The S is oxidised to H_2SO_4 with $KMnO_4$ or I, whilst reducing agents yield H_2S and SO_2.

L. S. Theobald.

Impurity and radical chains in the mechanism of the reaction of organic and enzymic processes. F. Haber and R. Willstätter (Ber., 1931, 64, [*B*], 2844—2856).—The primary action in the oxidation of H_2SO_3 by $Cu^{\cdot\cdot}$ is formulated: $SO_3''+Cu^{\cdot\cdot}+H_2O=\underset{\downarrow}{S}O_3H+Cu^{\cdot}+OH'$; it is succeeded by the chain reactions, $\underset{\downarrow}{S}O_3H+O_2+H_2O+SO_3''=2SO_4''+\underset{\downarrow}{O}H+2H^{\cdot}$ and $\underset{\downarrow}{O}H+SO_3''+H^{\cdot}=OH'+\underset{\downarrow}{S}O_3H$. The following cases involve the same principles as a consequence of which the contact substance (enzyme) suffers univalent reduction ($Fe^{\cdot\cdot\cdot}$ to $Fe^{\cdot\cdot}$) and the substrate univalent oxidation. The product of dehydrogenation is therefore a radical with a free valency which can occur at C or S. Schemes are proposed for the biological oxidation of EtOH and MeCHO. Since the radical produced by dehydrogenation of an aldehyde is identical with that formed by a so-called mutase, it depends on experimental conditions whether autoxidation or disproportionation occurs. The following cases are considered in detail: Cannizzaro's disproportionation of PhCHO; conversion of methylglyoxal into lactic acid in presence of an aldehyde-mutase; dehydrogenation of succinic acid by succinodehydrase; peroxidase and catalase action; catalytic hydrogenation.

H. Wren.

Reaction of violet solutions of chromium salts. II. C. Montemartini and E. Vernazza (Ind. chim., 1931, 6, 492—497; Chem. Zentr., 1931, ii, 1167—1168; cf. A., 1931, 1140).—With ZnO, $Zn(OH)_2$, $Zn(HCO_3)_2$, and $ZnCO_3$, green Cr salt solutions give ppts. the composition of which varies with conditions but is different from that of the pinkish-violet ppt. obtained with violet Cr solutions. The pptn. of violet solutions of $Cr(NO_3)_3$ and $CrCl_3$ with $Zn(NO_3)_2$ or $ZnCl_2$ and $KHCO_3$ in the absence of SO_4'' gives no definite compound, but the addition of 1 mol. of SO_4'' to 1 of Cr_2O_3 yields ppts. of $Cr_2O_3,4ZnO,SO_3$ which contain neither Cl' nor NO_3'. L. S. Theobald.

Characteristic reactions for violet solutions of chromium salts. V. C. Montemartini and E. Vernazza (Ind. chim., 1931, 6, 862—866; Chem. Zentr., 1931, ii, 2135).—In a sufficiently alkaline solution lilac ppts. of $Cr_2O_3,4ZnO,N_2O_5$ and $Cr_2O_3,4ZnO,Cl_2$ can be obtained. The group $Cr_2O_3,4ZnO$ is very stable; when the salts are boiled with alkali salts the anions are exchanged.

A. A. Eldridge.

Reactions of tungsten hexachloride. A. J. Cooper and W. Wardlaw (J.C.S., 1932, 635—637).—C_5H_5N reacts with a solution of WCl_6 in CCl_4 to give a green insol. *compound*, $(C_5H_6N)_2[WOCl_5,H_2O]$, instead of a co-ordination compound of the type WCl_6,xC_5H_5N. Attempts to produce the corresponding green quinoline compound resulted in a brown *compound* $(C_9H_8N)_8[W_3Cl_{17}]$, which may be a compound of the series $R_3W_2Cl_9$ associated with the co-ordination compound $(C_9H_8N)_5[WCl_8]$. A modification of Roscoe and Hill's method for the prep. of WCl_6 is described.

M. S. Burr.

Luminescent compounds. A. Schloemer (J. pr. Chem., 1932, [ii], 133, 51—59).—Details are given for the prep. of some luminescent tungstates, molybdates, vanadates, uranates, and silicates, and of a ZnS (containing NaCl, MgF_2, and Cu) as luminescent as the best commercial product. R. S. Cahn.

Reaction chains in oxidative processes. H. Kauffmann (Ber., 1932, 65, [*B*], 179—184; cf. Haber and Willstätter, this vol., 352).—Addition of H_2O_2 to a hypochlorite bleaching liquor causes immediate evolution of O_2 and enhanced bleaching activity during the change. The effect is judged by the time required for discharging the colour of orange II, suitability of period being obtained by regulated addition of NaOH. The dye is very resistant to alkaline H_2O_2. The effect is not attributable to nascent O, since enhanced bleaching activity is also observed after addition of N_2H_4, NH_3, NH_2OH, semicarbazide, carbamide, oxamide, succinimide, and veronal. The activator differs from a catalyst, since it is decomposed during the change. The primary radical is considered to be ClO obtained by discharge of ClO', the second radical OH. The processes may be summarised: $\underset{\downarrow}{ClO}+ClO'+OH'=2Cl'+O^2+OH\rightarrow$ and $\leftarrow OH+ClO'=\underset{\downarrow}{ClO}+OH'$. Activators are substances which cause the occurrence of OH in the bleaching liquor, their action depending on the union of the liberated OH with the dye, cellulose, or other substrate thus: $RH_2+\underset{\downarrow}{O}H=\underset{\downarrow}{R}H+H_2O$ and $\underset{\downarrow}{R}H+ClO'=R+Cl'+\underset{\downarrow}{O}H$. In absence of catalyst or activator, high activity of a bleaching liquor is attributed to hydrolytically formed HOCl in equilibrium with hypochlorite. The production of OH by this means is shown by the scheme $HOCl+ClO'=\underset{\downarrow}{Cl}O+Cl'+\underset{\downarrow}{O}H$. The equation further explains the lack of high oxidising power in ClO' or HOCl singly and their powerful action when in conjunction and also the repression of the activity of bleaching liquors by addition of alkali hydroxide.

H. Wren.

Bromine hydrate. I. W. H. Harris (J.C.S., 1932, 582—585).—Investigation of the system $KBr-Br_2-H_2O$ at 0°, for concns. of KBr below approx. 16%, indicates that one Br hydrate only, $Br_2,10H_2O$, exists at this temp. M. S. Burr.

Preparation and crystal form of pure iodic acid. A. Pérez-Vitoria and J. Garrido (Anal. Fís. Quím., 1932, 30, 12—20).—Details are given of the prep. of HIO_3 by oxidation of I with fuming HNO_3; hydrates of HIO_3 do not separate from a HNO_3 solution, whatever the concn. Crystallographic data are given. H. F. Gillbe.

Rhenium pentoxide. W. A. Roth and G. Becker (Ber., 1932, 65, [*B*], 373; cf. Briscoe and others, this vol., 32).—Formation of Re_2O_5 is observed during the combustion of Re to Re_2O_7 in the calorimetric bomb in presence of paraffin oil and O_2 under pressure. H. Wren.

Concentration, acids, and lithium salts of element 85. F. Allison, E. R. Bishop, and A. L. Sommer (J. Amer. Chem. Soc., 1932, 54, 616—620; cf. A., 1930, 1541).—The name "alabamine" and symbol Am are suggested for element 85. By the magneto-optic method its partial concn. from monazite sand was followed, its compounds were studied, and its at. wt. was found to be about 221. Minima for HAm, HAmO, $HAmO_2$, $HAmO_3$, and $HAmO_4$ and the Li salts were found. Am is oxidised in alkaline solution and more readily in acid. The peralabamates are the most stable of the compounds.
L. P. Hall (*c*.)

New type of complex platinum compounds. Ter- and quinque-valent platinum. IV. P. C. Rây and S. C. S. Gupta (Z. anorg. Chem., 1932, 203, 401—404; cf. A., 1931, 810).—A solution of $PtClEt_2S_2$ in $CHCl_3$ when boiled with Br gives the *compound* $PtBrEt_2S_2$ (I). If in the prep. of $PtClEt_2S_2$ the filtrate from the first crop of crystals is boiled with EtOH for several days, the *compound* $Pt_3Cl_2,3Et_2S_2$ is formed, and this, on treatment with Br, is converted into (I).
F. L. Usher.

Quantitative spectral determinations with gaseous mixtures. A. Gatterer (Physikal. Z., 1932, 33, 64—73).—A special form of gas burette for preparing mixtures is described. The spectral change with concn. of six binary systems was photographed and the intensity of blackening determined by a microphotometer. The intensity of blackening is proportional to log. concn. There are definite deviations from this for a few mixtures, but these can be explained. The application of the work to the quant. analysis of gaseous mixtures and org. elementary analysis is discussed. A. J. Mee.

Standards for acidimetry. G. Calcagni and M. Sturnajolo (Annali Chim. Appl., 1932, 22, 16—24).—Li_2CO_3, K_2CO_3, $CaCO_3$, $BaCO_3$, MgO, CaO, Na, K, and Mg may be used for standardising acid solutions. Some of these substances are simpler to use than Na_2CO_3 and the results are equally accurate.
O. F. Lubatti.

Micro-acidimetry. II. J. Mika (Mikrochem., 1932, 10, 384—396).—Error due to CO_2 may be compensated by using an indicator correction. The most satisfactory standard alkali solution (approx. 0·01*N*) is prepared by saturating a *M*-$CaCl_2$ solution with $Ca(OH)_2$, filtering, and adding 3·5 vols. of *M*-$CaCl_2$ solution. Standardisation is effected by titrating with a solution of 20 mg. of KIO_3,HIO_3 to p_H 4·8 (Me-red), using a citric acid–Na_2HPO_4 buffer solution for comparison. Details are given of vessels suitable for handling the solutions and for the titrations. H. F. Gillbe.

Micro-alkalimetry and -acidimetry. S. K. Tschirkov (Bull. Inst. rec. biol. Perm, 1931, 7, 427—441).—The wt. of acid used (*A*) in the titration of alkali is given by $A=V'f-0{\cdot}001MV([H^{\cdot}]-[OH'])$, where V' is the vol. of acid added, f is its titre, M its equiv. wt. in g., and V is the final vol. of the solution. Applying the above formula, and using solutions not more conc. than 0·01*N*, the experimental error is $\pm5\times10^{-7}$ g. R. Truszkowski.

Possibilities and limitations of potentiometric analysis. F. L. Hahn (Angew. Chem., 1932, 45, 77—80).—A discussion, especially of conditions which must be observed when titrating weak acids or weak bases. Certain factors, such as the degree of accuracy of the potential measurement necessary to obtain a result with a given limit of error, are dealt with in detail. H. F. Gillbe.

Determination of the end-point and the turning potential in potentiometric titration. F. L. Hahn (Z. anal. Chem., 1932, 87, 263—268).—In a potentiometric titration the region of most rapid potential change, and therefore the end-point of the titration, can be determined with considerable accuracy, but it is not possible to obtain a very exact val. for the true potential at the end-point. The turning potential determined by Knop (A., 1931, 1261) for the Fe-$KMnO_4$ titration cannot therefore be regarded as giving the true const. for this reaction, although the method gives a satisfactory val. for the point of equivalence. M. S. Burr.

Titration of hydrogen peroxide in presence of alkali oxalates. W. Fehre (Z. anal. Chem., 1932, 87, 180—185).—The solution is neutralised if acid, then excess of a 10% aq. solution of $BaCl_2$ is added in the cold. After 2 hr., in the course of which the BaC_2O_4 settles out, the clear liquor is titrated with $KMnO_4$. This procedure is recommended for the analysis of bleaching baths. R. Cuthill.

Electrometric determination of chlorides. I. Use of portable p_H apparatus. A. Itano. **II. Determination of chloride in soils.** A. Itano and A. Matsuura (Ber. Ohara Inst. Landw. Forsch., 1931, 5, 145—150, 171—176).—I. The authors' apparatus is applied to the determination of Cl' (cf. Best, A., 1930, 1124).

II. Results obtained agreed well with those of the direct (chromate) titration method, small discrepancies occurring only when the Cl' content was very low. The Cl' content of soils decreased as the source of irrigation was approached. A. G. Pollard.

Preparation of nephelometric test solutions. A. F. Scott and J. L. Moilliet (J. Amer. Chem. Soc., 1932, 54, 205—209; cf. A., 1920, ii, 633).—The formation of Ag halide suspensions by various different methods was studied. Variations in the turbidity originate apparently in the speed with which the precipitant is added to the saturated solution rather than in the rate of mixing; the more rapidly the precipitant is added, the weaker is the turbidity.
L. Kelley (*c*).

Winkler titration in methylene-blue media. G. Marsh (J. Biol. Chem., 1932, 95, 25—27).—In the iodometric titration of dissolved O_2 (A., 1889, 79) starch is replaceable by methylene-blue in a concn. of 0·00005*M*. Addition of $MnCl_2$ and NaOH+KI to an aq. solution of methylene-blue results in the formation of the leuco-compound, which regains its

original colour in about 2 min. This re-oxidation is due to the Mn, the reduction of the dye being completely reversed and hence introducing no error in the determination of dissolved O_2.
F. O. Howitt.

Sensitivity of lead paper towards hydrogen sulphide. H. Leroux (J. Usines Gaz, 1931, 55, 117—122; Chem. Zentr., 1931, ii, 1166).—Filter-paper strips moistened with 1% $Pb(OAc)_2$ solution were exposed for 15 min. to gases with different H_2S contents and a velocity of 105 litres per hr. The limiting detectable amounts were in H_2 0·10, town gas 0·15, N_2 0·60, and CO_2 3·50 g. H_2S per 100 cu. m. The sensitivity increases with the Arnold diffusion coeff.
L. S. Theobald.

Determination of nitrogen peroxide. E. J. B. Willey and S. G. Foord (Proc. Roy. Soc., 1932, A, 135, 166—181).—The method depends on the measurement of the light transmitted by a column of NO_2 by a K photo-cell. The apparatus, including an arrangement for amplifying the photo-electric current, is fully described. The Beer–Lambert law is shown to be applicable over a wide range of NO_2 concn. The conditions for max. sensitivity and max. accuracy of the method are discussed, and several applications suggested.
L. L. Bircumshaw.

Ronchèse's method. Application to the determination of ammonia in Kjeldahl determinations. V. Colobraro (Anales Farm. Bioquim., 1931, 2, 3—25; Chem. Zentr., 1931, ii, 1169).—$K_2C_2O_4$ or Hg is the catalyst and H_2SO_4 free from H_3PO_4 is used in the Kjeldahl method. The resulting liquid is made neutral to phenolphthalein with NaOH and aliquot parts are treated with excess of neutral 20% CH_2O solution. The acid liberated by the formation of $(CH_2)_6N_4$ from the NH_4 salts and CH_2O is titrated with 0·1*N*-NaOH. The no. of c.c. of 0·1*N*-NaOH used is multiplied by 0·001446. The Hg catalyst, if used, is removed by $Na_2S_2O_3$.
L. S. Theobald.

Micro-determination of phosphoric acid with strychnine molybdate. E. Rauterberg (Mikrochem., 1932, 10, 467—482).—Available methods are reviewed and an account is given of the photometric measurement of the turbulence produced. The reagent is prepared by dissolving 7·5 g. of MoO_3 in 60 c.c. of H_2SO_4 (*d* 1·785), cooling, and pouring into 900 c.c. of a solution containing 2 g. of strychnine sulphate. After boiling for 15 min. and cooling, the solution is diluted to 1000 c.c., and after a few days it is filtered. The reagent may be used for determining 2·5—40×10^{-6} g. of P_2O_5 in 15—20 c.c. of solution.
H. F. Gillbe.

Determination of boric acid. II. Determination of boric acid in natural and artificial silicates. E. Schulek and G. Vastagh (Z. anal. Chem., 1932, 87, 165—172).—In applying the distillation method for the determination of boric acid (A., 1931, 812) to silicates, a much greater amount than usual of the mixture of MeOH and H_2SO_4 must be added to the mixture to be distilled, and the concn. of H_2O must be kept within certain limits. Under these conditions SiO_2 does not begin to separate until near the end of the distillation, and then appears largely as a powder; errors due to adsorption of boric acid by gelatinous SiO_2 are thus avoided. With many silicates, particularly those containing Fe, the distillation must be repeated. Methods of procedure for both the macro- and the micro-determination are described.
R. Cuthill.

Colorimetric determination of silica, especially in water. A. Jolles (Angew. Chem., 1932, 45, 150).—A claim for priority (cf. this vol., 34).
H. F. Gillbe.

Colorimetric determination of silica, especially in water. O. Liebknecht (Angew. Chem., 1932, 45, 150).—A reply to Jolles (cf. preceding abstract).
H. F. Gillbe.

Rapid determination of carbon monoxide. P. Borinski and H. Murschhauser (Chem. Fabr., 1932, 41—42).—The apparatus described is fitted with an electrically-driven pump which forces the air to be analysed through an electrically heated tube containing I_2O_5 and then through a solution containing starch and a known quantity of $Na_2S_2O_3$. When the solution becomes blue the no. of strokes made by the pump is noted, and from this and the vol. of the pump cylinder is calc. the vol. of air which has passed through the apparatus. Results are accurate with air containing up to about 0·2% of CO, and with higher concns. the accuracy is sufficient for most purposes. The apparatus is portable, and determinations take but little time and may be carried out by persons without special training.
H. F. Gillbe.

Determination of traces of carbon dioxide. J. Lindner and N. Figala (Mikrochem., 1932, 10, 440—445).—Errors arise when using the method previously described (A., 1930, 1543) owing to occlusion of OH′ by the $BaCO_3$ ppt. In the modified method described the solution is heated for 10 min., after a preliminary end-point (phenolphthalein) has been obtained, and is then re-titrated. An apparatus for producing known quantities of CO_2 from Na_2CO_3 is described.
H. F. Gillbe.

Detection of traces of metals by physical development. G. Kögel (Mikrochem., 1932, 10, 452—455).—Paper coated with gelatin is treated with aq. NH_3 or dil. HCl, brought into contact with the metal, and immersed in 1% $AgNO_3$ solution for a few secs. The Ag which is thus liberated forms the nucleus for a further quantity liberated by development. The developer used is made by dissolving 4 g. of metol in 100 c.c. of 50% AcOH and diluting to 1500 c.c. Images may be produced also by reduction in a similar manner of $Cu_3[Fe(CN)_6]_2$, $FeFe(CN)_6$, $Pb_3[Fe(CN)_6]_2$, and $(UO_2)_3[Fe(CN)_6]_2$; suitable solutions are mentioned.
H. F. Gillbe.

Systematic detection of cations. G. Vortmann (Z. anal. Chem., 1932, 87, 190—196).—The material for analysis is fused with Na_2CO_3 and S, and the product treated with H_2O. The insol. material is boiled with NH_4Cl to dissolve Ca, Sr, and Mg, and then roasted to convert the sulphides into oxides. By fusion with $K_2S_2O_8$ followed by extraction with H_2O, Cu, Ag, Cd, Tl, Fe, Mn, Zn, Co, Ni, U, and Cr are brought into solution, whilst $BaSO_4$ and Pt remain in the residue. The aq. extract from the original melt may contain Al, Be, As, Sb, Sn, Mo, W, V, Se, Te, and Au; it is warmed with NH_4Cl and aq. NH_3 to ppt. Al and Be, and the sulphides pptd. on addition of acid are roasted and subjected to treatment with $K_2S_2O_8$ to separate As, Mo, and V (sol.) from W, Sb, and Sn. The detection of the individual metals after carrying out the above separation is largely by means of dry reactions. Iodide sublimates for the purpose of identifying metals of the H_2S group are obtained most readily by heating the substance for examination with KI in the microcosmic salt bead under a cool surface. R. CUTHILL.

Quantitative analysis of alloys by means of *X*-ray spectroscopy. C. E. EDDY and T. H. LABY (J. Physical Chem., 1931, **35**, 3635—3638; cf. A., 1931, 702).—Defects in technique, by the elimination of which trustworthy results can be obtained, are discussed. Data for alloys of elements of nearly equal at. no. are reproduced.
CHEMICAL ABSTRACTS (*c*).

Reactions of several metallic ions in the presence of organic acids. S. HAKOMORI (Sci. Rep. Tôhoku, 1931, **20**, 736—763).—The reactions of Mo, Ti, V, $Fe^{\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, Cr, Al, Cu, Ni, Co, $UO_2^{\cdot\cdot}$, Be, Pb, Zr, and Mn with NaOH in the presence of oxalic, succinic, malic, and citric acids have been investigated by conductivity measurements and by spectrographic, ultramicroscopic, and colorimetric observations. The results in many cases confirmed the formation of complex compounds. The yellow colour produced in MoO_3 solutions by H_2O_2 is intensified by addition of citric, tartaric, or succinic acid. A. R. POWELL.

Tests for element 87 (virginium) by the use of Allison's magneto-optic apparatus. J. L. McGHEE and M. LAWRENZ (J. Amer. Chem. Soc., 1932, **54**, 405—406; cf. A., 1931, 1348).—HCl solutions of samarskite, pollucite, and lepidolite and crude CsCl, all of which contain element 87, and solutions of $SnCl_4$ and $ReCl_2$, were examined. There are no corresponding minima for Re and Sn in sulphate solutions of these minerals. None of the minima attributed to ViCl was found in the solutions of $SnCl_4$ or $ReCl_2$.
C. J. WEST (*c*).

Peculiar adsorption and peptisation reaction of calcium oxalate. Colour detection of calcium in the presence of strontium. F. L. HAHN (Ber., 1932, **65**, [*B*], 207—209).—In the presence of an alkaline solution of 1 : 2 : 5 : 8-tetrahydroxyanthraquinone, CaO or $CaCO_3$ becomes at most pale pink, but blue to bluish-black if C_2O_4'' is added. Preformed and even coarsely cryst. CaC_2O_4 becomes cornflower-blue and partly peptised, since the supernatant liquid is dark blue. $CaCO_3$, $CaSO_4$, $Ca_2FeC_6N_6$, SrC_2O_4, and BaC_2O_4 do not give a similar reaction. Since the reaction involves the pptn. of CaC_2O_4, it is not more sensitive than this reaction, but is more distinctive and particularly useful for the detection of Ca in presence of much Sr. H. WREN.

Micro-analysis of glasses. IV. W. GEILMANN.—See B., 1932, 228.

Determination of radium in alkaline-earth sulphates. A. KARL (Compt. rend., 1932, **194**, 613—614).—An equimol. mixture of NaCl, KCl, and LiCl, m. p. 485°, dissolves 36% of $BaSO_4$, giving a product of m. p. 495°, quite limpid and emitting no vapours at 520—530°. The material containing Ra as $RaSO_4$ is fused ($\not>$36% of the whole) in such a mixture in pyrex glass, and the emanation determined by passing a current of air through the molten solution. C. A. SILBERRAD.

Error in ferrocyanide titration of zinc. B. PARK (J. Amer. Chem. Soc., 1932, **54**, 180—181).—A standard solution of $K_4Fe(CN)_6$ often contains a little ferricyanide, which, if H_2S is present in the solution to be titrated, will be reduced, thus increasing the pptg. power of the solution towards Zn.
W. T. HALL (*c*).

Acidimetric determination of lead salts. F. VIEBÖCK and C. BRECHER (Arch. Pharm., 1932, **270**, 109—114).—Two volumetric methods of determining Pb are described. R. S. CAHN.

Determination of mercuric oxide and "mercuric ammonium chloride." E. J. SCHORN and R. M. McCRONE (Pharm. J., 1932, **128**, 187—188).—Dissolution of HgO in aq. $Na_2S_2O_3$ instead of aq. KI gives a clearer end-point on titration with 0·1*N*-HCl. NH_2HgCl is more readily sol. in aq. KI than in aq. $Na_2S_2O_3$. Me-red is recommended as an indicator.
T. McLACHLAN.

Reduction of mercuric salts by hypophosphorous acid. JEAN (Bull. Soc. Pharm., Bordeaux, 1930, **68**, 239—243; Chem. Zentr., 1931, ii, 1168).—$Hg^{\cdot\cdot}$ salts are quantitatively reduced to Hg by H_3PO_2. Reduction with NaH_2PO_4 is quant. only when sufficient HCl is present to liberate the requisite amount of H_3PO_2. L. S. THEOBALD.

Sensitisation of the mercury iodide reaction for the detection of mercuric ions. G. DENIGÈS (Bull. Soc. Pharm. Bordeaux, 1930, **68**, 207—209; Chem. Zentr., 1931, ii, 1168).—Since the ppt. of HgI_2 is sol. in excess of KI, a solution of $HgI_2,2KI$ is used to replace KI in testing for $Hg^{\cdot\cdot}$ ions. This reagent is added to the $Hg^{\cdot\cdot}$ salt solution until a permanent red ppt., insol. in excess, is obtained. The reaction is $HgI_2,2KI+HgCl_2=2HgI_2+2KCl$.
L. S. THEOBALD.

Volumetric determination of the mercuric ion. J. BARCELÓ (Anal. Fís. Quím., 1932, **30**, 71—75).—The $Hg^{\cdot\cdot}$ is pptd. with a solution prepared by dissolving 4 g. of benzidine in 20 c.c. of warm 50% AcOH, pouring gradually into 1 litre of H_2O at 70°, and filtering after 24 hr. The pptd. complex is dissolved in dil. HCl, the benzidine is pptd. as sulphate by adding Na_2SO_4 solution, and the ppt. is titrated with 0·1*N*-Na_2CO_3 and phenolphthalein; 1 c.c. of 0·1*N*-Na_2CO_3 corresponds with 0·01002 g. of Hg. The error rarely exceeds 0·4%. H. F. GILLBE.

Spectral analysis by sensitive lines within the range of the glass spectrograph. II. W. KRAEMER (Z. Elektrochem., 1932, **38**, 51—53; cf. this vol., 35).—By the examination of W carbides containing rare earths and Mo, alloys of Ag, Au, and Ni, resistance wire of unknown composition, and brass, sensitive lines for the following elements and for one radical have been determined, using as control the A lines obtained in an air Geissler tube: Hg, Mg, Pb, Si, Hf, Ce, Th, Sm, Y, La, Dy, Nd, Pr, Tb, Er, Gd, Au, Ag, Mo, Zn, Cd, Mn, Ni, Co, As, Ca, Al, Fe, Cu, Ti, Zr, S, P, I, CN, H_2. M. S. Burr.

Determination of aluminium. Formation of lithium aluminate. J. T. Dobbins and J. P. Sanders (J. Amer. Chem. Soc., 1932, 54, 178—180).—To the solution containing about 0·1 g. Al in 100 c.c. are added a slight excess of 10% LiCl solution, and sufficient dil. aq. NH_3 to make slightly alkaline to phenolphthalein in the cold. After ignition, the ppt. has the formula $Li_4Al_{10}O_{17}$. W. T. Hall (c).

Volumetric determination of aluminium. F. Vieböck and C. Brecher (Arch. Pharm., 1932, 270, 114—124).—The Al solution is treated with Na NH_4 tartrate and $BaCl_2$ and forms a sol. complex Ba Al tartrate, which is neutral to phenolphthalein. Addition of KF liberates KOH equiv. to the Al present. This decomp. is not immediate, but requires several min.; excess of $Ba^{\cdot\cdot}$ is inhibitive and should be removed by K_2SO_4. The liberated KOH is treated with excess of $0{\cdot}1N$-H_2SO_4 and the excess is titrated back with $0{\cdot}1N$-KOH. Special notes are given on the analysis of certain pharmaceutical preps. containing Al. E. S. Hedges.

Use of *X*-rays in quantitative analysis. V. Caglioti and P. Agostini (Atti R. Accad. Lincei, 1931, [vi], 14, 301—305).—The ratios of the intensities of the Cu $K\alpha$ and $K\beta$ lines are measured before and after passing the *X*-ray beam through the sample to be analysed. The method has been tested for mixtures of Al_2O_3 containing up to 4% NiO. The ratio of the intensities of the two lines is proportional to the % NiO in the mixture. O. J. Walker.

Determination of zirconium in rocks. H. F. Harwood (Tidsskr. Kjemi Berg., 1932, 12, 23).—The rock powder is decomposed by repeated evaporation with $HClO_4$ and HF. The unattacked residue (which contains practically the whole of the zircon) is collected and fused with Na_2CO_3. The melt is extracted with H_2O, the solution filtered, the residue fused with $Na_2S_2O_7$, and the melt taken up with dil. H_2SO_4. The Zr in this solution is then pptd. as usual with Na_2HPO_4 after addition of H_2O_2. The original $HClO_4$ solution is also tested for Zr with Na_2HPO_4 and H_2O_2, any ppt. formed being added to the previous one. H. F. Harwood.

Quantitative separation of germanium and arsenic. H. J. Abrahams and J. H. Müller (J. Amer. Chem. Soc., 1932, 54, 86—94).—From a solution less than $0{\cdot}09N$ in respect of HCl or H_2SO_4, As^{III} can be pptd. completely as As_2S_3, but no GeS_2 separates until the acidity is increased. In mineral analysis, therefore, it is advisable to remove $AsCl_3$ and $GeCl_4$ by distillation, and then ppt. As_2S_3 from dil. acid solution containing NH_4 salt and ppt. GeS_2 in the filtrate after increasing the acidity. The mineral germanite probably has the composition $7CuS,FeS,GeS_2$. W. T. Hall (c).

Volumetric determination of vanadium and molybdenum (reducing activity of metallic copper). G. Scagliarini and P. Pratesi (Atti R. Accad. Lincei, 1931, [vi], 14, 298—300; cf. A., 1929, 532).—In presence of H_2SO_4 at the b. p. of the solution vanadates and molybdates are rapidly reduced by Cu to V^{III} and Mo^{V}, respectively, and the solution is then titrated with $KMnO_4$ as for Fe and U. O. J. Walker.

Analytical chemistry of tantalum, niobium, and their mineral associates. XXI. Quantitative separation of titanium from tantalum and niobium. W. R. Schoeller and C. Jahn (Analyst, 1932, 57, 72—78; cf. A., 1928, 1047; 1929, 902, 1160).—The oxalate–salicylate method for the separation of Ti from the earth acids has been perfected, and the H sulphate–tannin method is employed for the recovery of the last traces of earth acids from the bulk of the Ti. An almost quant. separation is achieved, less than 1 mg. of TiO_2 being left in the earth acids; this may be allowed to counteract unavoidable loss. Results are accurate to within 0·5%. The basis of the separation is due to the fact that the earth acids do not, whilst Ti does, form sol. salicylic acid complexes, and that the earth acids do not, whilst Ti does, form sol. sulphates, nitrates, and chlorides. Earlier attempts were unsuccessful owing to the formation of hydrolysis ppts.; this is overcome by the addition of tannin. T. McLachlan.

Cathode-ray tube in *X*-ray spectroscopic analysis of niobium and tantalum. G. R. Fonda (J. Amer. Chem. Soc., 1932, 54, 115—122).—A procedure for the determination of Nb and Ta by the cathode-ray method is described. There is an abs. error of about 2%, independent of the quantity of material analysed. R. H. Lambert (c).

Determination and separation of rare metals from other metals. XX. Determination of iridium and separation from platinum and other metals. L. Moser and H. Hackhofer. **XXI. Determination of rhodium and its separation from platinum and other metals.** L. Moser and H. Graber (Monatsh., 1932, 59, 44—60, 61—72).—XX. Ir is obtained as sol. Na_2IrCl_6 by heating with an equal wt. of NaCl in a stream of Cl_2 at 400°. It may be separated from Pt in aq. HCl by neutralising with Na_2CO_3, treating the boiling solution with $NaBrO_3$ and NaBr, and reducing the pptd. IrO_2,xH_2O in a stream of H_2. The metallic Ir is then weighed. The Pt solution is treated with HNO_3 to remove Br, decomposed with NH_4OAc, and the Pt reduced with $N_2H_4,2HCl$ and weighed. A similar method is used in the separation from Au. In the separation from Pd a large proportion of Pd is carried down by the IrO_2 ppt., owing to the induced pptn. observed with metals of the Pt group, and must be subsequently removed from metallic Ir by repeated treatment with aqua regia, which dissolves Pd but not Ir. Pd is determined by a method similar to that used for Pt. Cu is also pptd. with the Ir, but may be readily removed by treating the metallic mixture with aq. HNO_3. Cu is subsequently determined electrolytically. Ir is separated from Fe by treating the slightly acid solution of Na_2IrCl_6 and $FeCl_3$ with an excess of hot $H_2C_2O_4$ until sol. complexes are formed. H_2S is passed through and excess of aq. NH_3 added. FeS is pptd. and weighed after calcining in a stream of H_2 and H_2S. The Ir solution is evaporated and the resulting Ir_2S_3 reduced in H_2 and weighed. The solubility of IrO_2 in H_2O is $0{\cdot}1\times10^{-4}$ mol. per litre and in $0{\cdot}002N$-HCl, $0{\cdot}2\times10^{-5}$ mol. per litre.

XXI. The separation of Rh from Pt is difficult but necessary, since small quantities of Rh make Pt brittle when heated. Rh is separated from both Pt and Au by the $NaBrO_3$–NaBr method. Separation from Cu is effected by treating the solution with H_2SO_4 until the acidity is $0{\cdot}1N$, adding $MgCl_2,6H_2O$ until the concn. is $0{\cdot}1M$, and then passing H_2S into the hot solution. The sulphides are collected, washed with aq. H_2S, calcined to form the oxides, and reduced in a current of H_2. The Cu may then be removed with HNO_3 and determined electrolytically. The metallic Rh may be weighed after further washing and heating in H_2. To separate from Fe use is made of the fact that Rh may be pptd. quantitatively as sulphide in solutions of acidity up to $N/7$ HCl. The $Fe^{\cdot\cdot}$ in solution is oxidised and pptd. with aq. NH_3. To separate Rh from Pb the solution is heated with H_2SO_4 until SO_3 vapour is evolved. After cooling, diluting, and keeping for several hrs., it is filtered through a Gooch crucible, Pb pptd. by $2N$-H_2SO_4, collected, and weighed. The Rh solution is evaporated almost to dryness, and the Rh pptd. as sulphide and weighed as metal. M. S. Burr.

Sensitive flexible thermostat. J. R. Roebuck (Rev. Sci. Instr., 1932, [ii], 3, 93—100).—Full details are given for the construction and operation of a thermostat which remains const. to $<0{\cdot}01°$ between $-190°$ and 300°. C. W. Gibby.

Automatic temperature regulators. J. Fuchs (Chem. Fabr., 1932, 49—52).—A description of recent types of apparatus. E. S. Hedges.

Air thermoregulator. J. B. M. Coppock, J. Colvin, and J. Hume (Chem. and Ind., 1932, 140).—The pressure of air in a bulb placed in the furnace is balanced by a column of Hg in a vertical tube surrounded by more Hg in an annular column. The space above both the columns is evacuated and shut off from the atm. by a tap, and contact between the two is made by a Pt wire when the inner one rises. Changes in atm. temp. are compensated for by the annular column, and the action is independent of changes in the barometric pressure.
C. W. Gibby.

Oscillator for the crystal of an *X*-ray spectrograph. G. W. Fox (Rev. Sci. Instr., 1932, [ii], 3, 71—72).—The platform of the crystal holder is rotated by a worm gear, and itself reverses the direction of rotation of the worm by operating a fast-and-loose pulley mechanism. C. W. Gibby.

Formula for the evaluation of colorimetric measurements. M. Winkler (Chem.-Ztg., 1932, 56, 86—87).—Calculations made according to Beer's law give high results in dil., and low results in more conc., solutions. Correct results are obtained with the formula $(c_1+k)d_1=(c_2+k)d_2$, where k is the apparent colour of the solvent and is determined by colorimetric measurement of two solutions of known but different concn. A. R. Powell.

Interference optical lever for pressure gauges, galvanometers, etc. W. E. Roseveare (J. Amer. Chem. Soc., 1932, 54, 202—205).—A simple optical system is described by means of which it is possible to measure deflexions of a 3-metre optical lever with an average error of about 0·003 mm. The principle was used in the construction of an all-glass optical lever pressure gauge capable of measuring small pressure changes with errors of as little as 0·0002 mm.
H. F. Johnstone (*c*).

Radiation thermopiles. J. Strong (Rev. Sci. Instr., 1932, [ii], 3, 65—70).—A design of thermopile giving max. sensitivity with two junctions is described. They may be welded in position by a condenser discharge, eliminating delicate manipulation. Soldering of Bi–Sn and Bi–Sn alloy wires is facilitated if they are protected from tarnishing by storage in C_6H_6. In welding receivers to thermocouple wires by a condenser discharge the receiver must not be so thick that the thermocouple wires are heated sufficiently to destroy their temper. By vac. distillation of Ag on to Cu, films which can easily be removed are formed.
C. W. Gibby.

Vacuum thermocouples. J. Jaffray (Compt. rend., 1932, 194, 451—452; cf. this vol., 36).—The figures for K and n for the old and new models are respectively for 15° and 22°. If the temp. of the galvanometer is const. while that of the thermocouple rises, *e.g.*, from 0 to 40°, Δ decreases linearly. When the two instruments are at different temp. only K varies, n being almost independent of temp.
C. A. Silberrad.

Tellurium–bismuth vacuum radiation thermocouple. C. H. Cartwright (Rev. Sci. Instr., 1932, [ii], 3, 73—79).—The technique required for the prep. of thermocouples with Te wires welded to Au leaf receivers is described. They are three times as sensitive as those made with Bi alloy wires.
C. W. Gibby.

Simple automatic cryostat. F. Fehér (Z. Elektrochem., 1932, 38, 53—54).—A more satisfactory arrangement for regulating pressure has been substituted in a cryostat previously described (A., 1927, 335; 1928, 1348). The method of application for the difficult temp. range 10—30° is given.
M. S. Burr.

Micro-extraction apparatus. H. Hetterich (Mikrochem., 1932, 10, 379—383).—The apparatus described is especially suitable for the extraction of, *e.g.*, paint films. It consists essentially of a filter-plate, which carries the material to be extracted, supported on a perforated plate resting on a ridge formed in the extraction vessel. The lower end of the vessel is of smaller diam. than the upper part and fits into a stand which is placed on the water-bath. Extraction with $CHCl_3$ of samples of paints obtained from an Egyptian wall painting (3000 B.C.) showed the binder to be beeswax, and the pigments basic Cu carbonate, Ca Cu silicate, and Fe_2O_3.
H. F. Gillbe.

Continuous extraction of precipitates. M. A. Simmonds (Chem. Eng. Min. Rev., 1932, 24, 132).—An apparatus for the repeated washing of ppts. with the same small quantity of washing liquid is described.
N. H. Hartshorne.

Apparatus for taking water samples from different levels. J. A. Reyniers (Science, 1932, 75, 83—84). L. S. Theobald.

Simple apparatus for mercury distillation. M. Kleiber (Science, 1932, 75, 196). L. S. Theobald.

Air dryer for analytical balances. E. Löwenstein (Chem.-Ztg., 1932, 56, 127).—SiO_2 gel, of 2—6 mm. particle size, is more satisfactory than $CaCl_2$ or H_2SO_4. It will absorb up to 23% of its own wt. of H_2O, without change of form, and may be regenerated by heating at 130—150°. H. F. Gillbe.

High-vacuum distillation with the help of liquid air. L. Anschütz (J. pr. Chem., 1932, [ii], 133, 81—83; cf. A., 1926, 1118).—Lewin's apparatus (A., 1930, 884) is criticised. H. Burton.

Application of organic substances in high-vacuum practice, especially in the working of high-vacuum pumps. M. von Brandenstein and H. Klumb (Physikal. Z., 1932, 33, 88—93).—Using org. substances, such as Bu^{α}_2 phthalate, in simple air-cooled diffusion pumps, it is possible, with liquid air, to attain vac. of the order 10^{-3} dyne per sq. cm. A. J. Mee.

Vacuum technique for the chemist. K. Hickman (J. Franklin Inst., 1932, 213, 119—154).—Degrees of vac., apparatus for vac. distillation, and low-pressure gauges are described and discussed. N. M. Bligh.

New types of micro-balance. L. Fuchs (Mikrochem., 1932, 10, 456—459).—A criticism of various types; that of Welharticky and Pachmann is preferred to the Kuhlmann balance, as the latter tends to "stick" somewhat frequently and needs constant cleaning. H. F. Gillbe.

Preparative microchemistry. J. Winckelmann (Mikrochem., 1932, 10, 437—439).—Compounds prepared on a cover slip coated with hardened gelatin may be washed etc. without difficulty. Drop reactions also may be carried out on coated cover slips, and the specimen may be allowed to dry and be preserved by mounting in Canada balsam. Methods of preserving preps. under collodion, and of applying the formation of Liesegang rings to the prep. of permanent specimens, are described. H. F. Gillbe.

Apparatus for exact gas analysis using samples of about 5 c.c. E. Ott and A. Schmidt.—See B., 1932, 211.

Portable apparatus for gas analysis especially in mines. A. Schmidt.—See B., 1932, 211.

Safety device for pipettes. Von Hütter (Gas- u. Wasserfach, 1932, 75, 91—92).—A small glass cylinder is interposed between the operator's mouth and the pipette, being attached to the latter by a rubber connexion. Within the cylinder is a pear-shaped glass float which rests on projections on the cylinder walls. If the liquid enters the cylinder it rises and closes the upper orifice. C. Irwin.

Regulation of vacuum filtration. Anon. (Food Tech., 1932, 1, 233).—A non-return valve, of the Bunsen type or of glass, prevents sucking back in vac. filtration; a release tap is also useful. E. B. Hughes.

Magnesia apparatus for qualitative chemical analysis. E. Wedekind (Chem.-Ztg., 1932, 56, 107).—MgO rods made by the Steatit-Magnesia A.-G. are suitable for flame tests, borax bead tests, and the fusion tests for Cr and Mn, and may be used in place of Pt for these purposes. A. R. Powell.

Sensitive flames. G. B. Brown (Phil. Mag., 1932, [vii], 13, 161—195).—The conditions for producing flames sensitive to sound waves and the causes of the phenomenon have been investigated. H. J. Emeléus.

Action of a transverse electrostatic fiefd on a propane flame. J. K. McNeely, A. O. Brown, and C. D. Crosno (Iowa State Coll. J. Sci., 1931, 5, 269—283).—Flames are repelled from the positive plate. The colour changes as the voltage is increased from 4600 to 28,000 volts. Two types of ions are formed; one may be positive and the other positive or negative. Chemical Abstracts.

Improving the visibility of lecture experiments. H. von Wartenberg (Angew. Chem., 1932, 45, 209—210).—Burettes, nitrometers, etc. are illuminated from the rear by lamps placed behind a paper screen. H. F. Gillbe.

Geochemistry.

Distribution of ozone in the earth's atmosphere. D. Chalonge (J. Phys. Radium, 1932, [vii], 3, 21—42).—The inadequacy of available data and methods is discussed. A study of the radiation of the clear sky indicates that O_3 exists in diffuse layers in the atm., and a new theory is developed showing that it must exist from a height of 20—80 km. in quantities increasing with altitude. N. M. Bligh.

Variation of tension of fulminating matter as a function of temperature and mol. wt. E. Mathias (Compt. rend., 1932, 194, 413—416). C. A. Silberrad.

Mineralisation of the spring waters of the southern and eastern slopes of Mt. Alaghez. V. K. Voskressenski (Bull. Inst. rec. biol. Perm, 1931, 4, 407—425).—The carbonate hardness of spring water increased in the summer of 1928 with distance from the summit of the mountain. This increase was, however, not continuous, pointing to the possibility of intermittently acting demineralising factors. R. Truszkowski.

Lead and helium in oceanic alkali halides. O. Hahn (Naturwiss., 1932, 20, 86—87).—NaCl and KCl of oceanic origin may contain some $PbCl_2$, the

Pb probably arising as end-product in the disintegration of dissolved radioactive salts. The possibility of finding He is also discussed.

W. R. Angus.

Determination of dissolved oxygen content of the mud at the bottom of a pond. A. E. Cole (Ecology, 1932, **13**, 51—53).—Sampling apparatus is described in which the H_2O sample filters through an alundum cap into a glass tube in which contact with air is excluded by means of a paraffin layer.

A. G. Pollard.

Radioactivity and its significance in problems of geochemistry. O. Hahn (Sitzungsber. preuss. Akad. Wiss., Phys.-Math. Kl., 1932, II, 15 pp.).—A discussion of published work, mainly on the inclusion of Pb in the mixed-crystal form in rock-salt and sylvine, and the production of He in these salts and in carnallite. U and Th do not enter the space lattices of the minerals with which they are associated.

E. S. Hedges.

Siderolite from Bencubbin, Western Australia. E. S. Simpson and D. G. Murray (Min. Mag., 1932, **23**, 33—37).—The mass (54 kg.) found in 1930 consists of a skeleton of Ni-Fe (68·8%) with enclosed crystals up to 1 cm. across of greyish-white enstatite (13·5%) and dark olivine (12·5%). Detailed analyses are given of the metallic portion (Fe : Ni=15·1 : 1) and of the stony portion (MgO : FeO=8·5 : 1). The meteorite is classed as a mesosiderite with an unusually high percentage of Ni-Fe. L. J. Spencer.

Pallasite from Alice Springs, Central Australia. L. J. Spencer [with M. H. Hey] (Min. Mag., 1932, **23**, 38—42).—A fragment (1084 g.) found in 1924 in the desert near Alice Springs on the north side of the MacDonnell Ranges is a typical pallasite consisting of 40% olivine (with FeO : MgO=4·6 : 1) and 60% nickel–iron (with Fe : Ni=12·7 : 1). Small angular fragments of olivine are embedded in the kamacite, suggesting that the olivine had been broken up before kamacite crystallised out. The granular texture of the metal also suggests that the kamacite had been broken up with the development of Neumann lines before the separation of the taenite and plessite, and that the fragments had been partly redissolved in the residual melt, giving the reaction-rim of taenite. Finally, the plessite eutectic separated out in the interspaces. L. J. Spencer.

Hoba (South-West Africa), the largest known meteorite. L. J. Spencer [with M. H. Hey] (Min. Mag., 1932, **23**, 1—18).—A mass of metal measuring 10×9 ft. on the surface and estimated to weigh 60 metric tons was found in 1920 embedded in surface limestone on Hoba West farm near Grootfontein. It is surrounded by a zone 1 ft. thick of laminated "iron-shale" formed by the oxidation of the metal. Analysis gave Fe 83·44, Ni 16·24, Co 0·76, Cu 0·03, S, P traces, C 0·02=100·49%; *d* 7·96. This meteorite is a Ni-rich ataxite showing under a high magnification a very minute duplex structure similar to that of plessite. The magnetic "iron-shale" contains Fe_2O_3 58·14, FeO 13·25, NiO 16·13, CoO 0·39, H_2O 11·83=99·74%, corresponding with 51·84% of trevorite ($NiFe_2O_4$). A list is given of ten other known large meteoric irons ranging in weight from 33·1 to 3·4 metric tons. The largest known meteoric stone of 820 lb. was seen to fall on Feb. 17, 1930, at Paragould, Arkansas. L. J. Spencer.

Meteoric stone from Suwahib, Arabia. W. C. Smith [with M. H. Hey] (Min. Mag., 1932, **23**, 43—50).—A fragment (241 g.) found in 1931 in the Rub' al Khali desert, S.E. Arabia, has a glazed surface of limonite; *d* 3·52. Micro-sections show chondrules of enstatite and olivine with some glass and felspar and specks of nickel-iron and troilite. The meteorite is classed as a black spherical chondrite of the Cronstadt type. Insufficient material being available for a magnetic separation, a new method of analysis is described by M. H. Hey, in which the powder is heated at 250—300° in a current of dry Cl_2; the metallic portion is thereby attacked, but not the silicates. The analysis gave Fe 17·54, Ni 0·96, Co 0·12, S 1·98, SiO_2 38·48, TiO_2 0·20, Al_2O_3 4·42, FeO 10·16, MnO 0·28, CaO 1·90, MgO 21·25, Na_2O 1·33, K_2O 0·25=98·97%. L. S. Spencer.

Diatomaceous earth. II. Nature and amount of extraneous matter in diatomites. W. Hugill (Trans. Ceram. Soc., 1932, **31**, 75—78; cf. B., 1931, 657).—The origin, amount, and determination of the various kinds of impurities are discussed.

J. A. Sugden.

Structure of precious opal. E. Baier (Z. Krist., 1932, **81**, 183—218).—Precious opal consists of separate grains embedded somewhat as quartz in sandstone, and having a lamellar structure with microscopic twinning. The distances between lamellæ are of the order 200—500 mμ. It seems probable that the structure is due to the presence of calcite in the original SiO_2 gel, which has since disappeared.

C. A. Silberrad.

Structural characteristics of apatite-like substances and composition of phosphate rock and bone as determined from microscopical and *X*-ray diffraction examinations. S. B. Hendricks, W. L. Hill, K. D. Jacob, and M. E. Jefferson (Ind. Eng. Chem., 1931, **23**, 1413—1418).—*X*-Ray diffraction photographs of fluorapatite ($9CaO,3P_2O_5,CaF_2$), chlorapatite, hydroxyapatite [$Ca_{10}(OH)_2(PO_4)_6$], oxyapatite, and $Ca_3(PO_4)_2$ were made, using pure crystals or synthetically prepared compounds. Similar photographs of natural phosphates showed that animal bone is a carbonate apatite [$Ca_{10}CO_3(PO_4)_6,H_2O$] (taking chemical analysis into consideration). On fossilisation the CO_3 and H_2O are replaced by F. American phosphate rocks are chiefly fluorapatite often containing some excess F. Gypsum, quartz, etc. are present as impurities. Na in small amount apparently replaces Ca. Al_2O_3 is perhaps due to the presence of clay minerals. Nauru, Christmas and Ocean Island phosphates have the composition $Ca_{10}(OH,F)_2(PO_4)_6$, about half the OH being replaced by F. Curaçao phosphate was much lower in F content, and, unlike other samples, on ignition at 900° yielded $Ca_3(PO_4)_2$. C. Irwin.

Granites of Finland. E. L. Bruce (Trans. Roy. Soc. Canada, 1931, [iii], **25**, IV, 269—284).—A general geological study. N. H. Hartshorne.

Granite contact action in Eastern Ontario. H. C. Horwood (Trans. Roy. Soc. Canada, 1931,

[iii], 25, IV, 227—242).—A description and discussion of the variations in composition occurring at granite–gneiss and granite–limestone contacts. The variations are similar at both contacts, except for a CaO–K_2O exchange at the latter, and the granite loses most of its basic oxides. N. H. HARTSHORNE.

Upper cretaceous volcanic ash beds in Alberta. J. O. G. SANDERSON (Trans. Roy. Soc. Canada, 1931, [iii], 25, IV, 61—70).—Mainly geological. Analyses of Edmonton tuffs are recorded. N. H. HARTSHORNE.

Oölites [of Lorraine]. J. P. AREND (Compt. rend., 1932, **194**, 736—738).—By the putrefaction of a mass of animal matter mixed with ferruginous sediments and buried in schists and calcareous deposits, a colloidal solid suspension is formed consisting of carbonates and H carbonates of Fe^{II} and Ca, colloidal Al_2O_3 and SiO_2, and phosphates, and holding in suspension quartz grains, clay, and numerous remains of zoölites. This magma is stable until reached by O, when $Fe(OH)_3$ is formed: $2FeH_2(CO_3)_2+CaH_2(CO_3)_2+O=2Fe(OH)_3+CaCO_3+5CO_2$. The phosphate acts as coagulant, as is shown by shaking in air a solution of $(NH_4)_2Fe(SO_4)_2$ with varying amounts of $Ca_3(PO_4)_2$ and/or $NaHCO_3$. Flocculation of $Fe(OH)_3$ will begin where phosphate is most conc., but once begun the $Fe(OH)_3$ will deposit on any particle, usually microscopic. Each such particle forms the nucleus of an oölite grain, which then grows by accretion of $Fe(OH)_3$ gel carrying with it the Fe and Ca compounds of the intermicellary liquid. This alternates with deposition of Fe phosphates and adsorption of colloidal Al_2O_3 and SiO_2; the SiO_2 then reacts with the phosphates, liberating the acid which re-forms $Ca_3(PO_4)_2$. C. A. SILBERRAD.

Formation of coal. P. KRASSA (Angew. Chem., 1932, 45, 21—22).—A sample of "Palo podrido" (a product of the fungal decomp. of wood) from the virgin forests of S. Chile was found to contain 20·8% of anhyd. matter in which were present cellulose (84%), pentosans (3·3%), ash (0·26%), and 2% of reducing substances sol. in H_2O (this value was not altered by hydrolysis of the aq. extract with HCl). Photomicrographs indicate that this material possesses the structure of the cellulose of the original wood, and is formed by destruction of the lignin in preference to the cellulose. It is suggested that it might be an intermediate in the formation of the coal found in the same district. H. A. PIGGOTT.

Bacteria of coal. R. LIESKE (Ges. Abhandl. Kennt. Kohle, 1930, 9, 27—29; Chem. Zentr., 1931, ii, 1657).—Non-pathogenic bacteria which produce H_2 were found, but not those, described by Galle, which produce CH_4. A. A. ELDRIDGE.

Occurrence of bacteria in bituminous coal. R. LIESKE (Ges. Abhandl. Kennt. Kohle, 1930, 9, 30—34; Chem. Zentr., 1931, ii, 1657).

Bacterial content of the earth at great depths. R. LIESKE and E. HOFMANN (Ges. Abhandl. Kennt. Kohle, 1930, 9, 21—27; Chem. Zentr., 1931, ii, 1657). —Experiments were made down to 1089 m. Gram-positive spore-forming bacteria, rods of the *B. subtilis* group, and cocci were found.

A. A. ELDRIDGE.

Classification of peat soils. A. P. DACHNOWSKI-STOKES (J. Wash. Acad. Sci., 1932, 22, 50—59).—A discussion. C. W. GIBBY.

Organic Chemistry.

Configurative relationship of hydrocarbons. IV. Optical rotations of hydrocarbons of the *iso*amyl series. Configurative relationship of substituted carboxylic acids containing an *iso*butyl and an *iso*amyl group to those of the corresponding normal carboxylic acids. P. A. LEVENE and R. E. MARKER (J. Biol. Chem., 1932, **95**, 1—24).—d-γ-*Methylhexoic acid*, b. p. 115°/16 mm., $[\alpha]_D^{22}$ +3·09° (+13·59°), prepared from α-chloro-γ-methylpentane, gives the *Et* ester (I), b. p. 80°/20 mm., d_4^{22} 0·888, $[\alpha]_D^{22}$ +2·38°, which may be reduced by Na in PhMe to d-δ-*methylhexanol*, b. p. 77°/20 mm., d_4^{28} 0·818, $[\alpha]_D^{28}$ +2·19° (+11·9°) (the figures in parentheses are the corresponding calc. max. for [*M*] assuming no racemisation to have occurred). The carbinol and PBr_3 yield α-*bromo*-δ-*methylhexane*, b. p. 78°/44 mm., $[\alpha]_D^{28}$ +2·61° (+21·9°), which is converted through the Grignard compound into d-γ-*methylhexane*, b. p. 92°/760 mm., d_4^{28} 0·681, $[\alpha]_D^{28}$ +1·64° (+9·67°). The action of MgMeI on (I) affords the carbinol which, when dehydrated with $H_2C_2O_4$ (cf. A., 1931, 709), gives the unsaturated hydrocarbon, reduced by H_2 in presence of Pt to β-methyl-ε-ethylhexane, $[\alpha]_D^{22}$ +2·75°, also obtained by the action of Pd and NaOH on the Br-compound prepared from the carbinol.

The following are similarly prepared: d-γ-*methylheptoic acid*, b. p. 132°/22 mm., d_4^{24} 0·882, $[\alpha]_D^{24}$ +2·11° (*Et* ester, b. p. 104°/32 mm., d_4^{24} 0·859, $[\alpha]_D^{24}$ +1·41°); d-β-*methyl*-ε-n-*propylhexane*, b. p. 156°/760 mm., d_4^{25} 0·725, $[\alpha]_D^{25}$ +1·09°; l-γ-*methyloctoic acid*, b. p. 149°/22 mm., d_4^{25} 0·871, $[\alpha]_D^{25}$ −1·34° (*Et* ester, b. p. 112°/23 mm., d_4^{25} 0·861, $[\alpha]_D^{25}$ −0·64°), l-β-*methyl*-ε-n-*butylhexane*, b. p. 109°/100 mm., d_4^{25} 0·738, $[\alpha]_D^{25}$ −0·49°; l-γ-*methylnonoic acid*, b. p. 156°/22 mm., d_4^{25} 0·871, $[\alpha]_D^{25}$ −0·60° (*Et* ester, b. p. 120°/22 mm., d_4^{25} 0·862, $[\alpha]_D^{25}$ −0·12°), l-β-*methyl*-n-*amylhexane*, b. p. 122°/100 mm., d_4^{25} 0·739, $[\alpha]_D^{25}$ −0·05°; *l*-β-methylheptoic, $[\alpha]_D^{27}$ −4·21°, and *l*-β-methyloctoic acid, $[\alpha]_D^{27}$ −5·14° (resolved through the quinine salts in $COMe_2$ at −15°); l-δ-*methylnonane*, b. p. 76°/30 mm., d_4^{27} 0·726, $[\alpha]_D^{27}$ −1·56° (−2·47°); d-βδ-*dimethylhexoic acid*, b. p. 124°/20 mm., d_4^{30} 0·899, $[\alpha]_D^{30}$ +1·65° (*Et* ester, b. p. 85°/20 mm., d_4^{30} 0·856, $[\alpha]_D^{30}$ +1·13°); d-γε-*dimethylhexanol*, b. p. 105°/45 mm., d_4^{30} 0·815, $[\alpha]_D^{30}$ +1·46°; l-α-*bromo*-γε-*dimethylhexane*, b. p. 91°/45 mm., d_4^{30} 1·099, $[\alpha]_D^{30}$ −0·50°; d-γε-*dimethylhexane*, b. p. 111—112°/760 mm., d_4^{30} 0·696, $[\alpha]_D^{30}$ +2·99°; d-βε-*dimethylheptoic acid*, b. p. 140°/25 mm., d_4^{26} 0·901, $[\alpha]_D^{26}$ +2·44° (*Et* ester, b. p. 112°/30 mm., d_4^{25} 0·862, $[\alpha]_D^{25}$ +1·39°); d-βε-*dimethylheptanol*, b. p. 102°/18 mm., d_4^{27} 0·823, $[\alpha]_D^{27}$ +2·21°; l-α-*bromo*-γη-

dimethylheptane, b. p. 108°/25 mm., d_4^{27} 1·090, $[\alpha]_D^{27}$ $-2{\cdot}20°$; d-βε-*dimethylheptane*, b. p. 134°/760 mm., $[\alpha]_D^{27}$ $+4{\cdot}19°$; d-δθ-*dimethyloctanol*, b. p. 115°/15 mm., d_4^{27} 0·824, $[\alpha]_D^{27}$ $+0{\cdot}81°$; d-βε-*dimethyloctane*, b. p. 156°/760 mm., $[\alpha]_D^{28}$ $+1{\cdot}02°$.

The conclusions reached from considerations of the rotations are that the Pr^{β} group introduces a special rotatory contribution only when located directly on the asymmetric C atom or at a distance of only 1 C atom from it. The Bu^{β} has a higher negative val. than Bu^{α}, whereas *iso*amyl has only a slightly higher val. than the corresponding normal group. *d*-βδ-Dimethylhexoic acid is configuratively related to *l*-β-methylhexoic and will lead to a hydrocarbon of opposite sign to that obtained from *d*-β-methylheptoic acid. F. R. Shaw.

Highly-polymerised compounds. LX. Relationships between the length of chains of thread molecules and the specific viscosity of their solutions. H. Staudinger (Ber., 1932, **65**, [*B*], 267—279).—Comparison of the viscosities of compounds belonging to different polymeric homologous series shows that hydrocarbons with thread mols. of the same mol. wt. have the same sp. viscosity in chain-equiv. solution in the same solvent (C_6H_6 or tetrahydronaphthalene), independently of the presence of the C atoms in the main or side-chain, provided that the solutions are dil. Equally viscous solutions of hydrocarbons of the same concn. contain thread mols. of approx. equal chain length. Different hydrocarbons which show the same sp. viscosity in equally conc. solution have mol. wts. proportional to the chain-equiv. wts. The consts. for solutions of polyoxymethylenes and polyethylene oxides are approx. the same as those of the hydrocarbons. It appears that in these chains the no. of mols. and their length are the decisive factors and that the nature of the members of the chain is not vitally important. Higher consts. are observed for the polytriacetylcelloglucan diacetates in *m*-cresol and for cellulose in Schweitzer's reagent. The bearing of the length and diameter of the mols. on the viscosity and the nature of colloidal solution is discussed. H. Wren.

Polymerides and polymerisation. IV. Polymerisation of isoprene and βγ-dimethyl-$\Delta^{\alpha\gamma}$-butadiene. G. S. Whitby and R. N. Crozier (Canad. J. Res., 1932, **6**, 203—225; cf. A., 1931, 1031).—Polymerisation of isoprene, b. p. 33·4—33·9°/744 mm., or βγ-dimethyl-$\Delta^{\alpha\gamma}$-butadiene (prep. described) between 10° and 145° does not afford any open-chain diene, polymerisable to caoutchouc, such as the β-myrcene of Ostromisslenski. The products isolated are oily cyclic dimerides which are not intermediate steps in the conversion of the dienes into caoutchoucs. Dipentene is shown (from its tetrabromide) to be present in considerable amount in these oils, together with one or more other oily cyclic dimerides. During polymerisation the mol. wt. of the rubber increases as the percentage of polymerisation increases, and the higher is the temp., the lower is the mol. wt. of the rubber; as polymerisation progresses, the viscosity of sols of the product rises. Measurements of η and mol. wt. are made on samples of rubber dried in vac., after pptn. from C_6H_6–EtOH and subsequent treatment by a standardised method. Polymerisation of βγ-dimethylbutadiene at 85° is followed by observing the changing refractive index of the liquid. Fractional pptn. by EtOH of a solution of dimethylbutadiene caoutchouc in C_6H_6 gives fractions yielding sols of different η, showing that the rubber consists of a mixture of polymerides of different degrees of polymerisation. Caoutchouc sols show a marked decrease in η on keeping, probably due to oxidation of the synthetic rubber. $NPhMe_2$ prevents this decrease. Certain inorg. salts ($SbCl_5$, $SnCl_4$, etc.) polymerise these dimerides rapidly in the cold, yielding polymerides which may be isomerides of rubber. J. L. D'Silva.

Addition of sulphite to βγ-dimethylbutadiene. H. J. Backer and J. A. Bottema (Rec. trav. chim., 1932, **51**, 294—298).—βγ-Dimethylbutadiene (I) and saturated aq. NH_4HSO_3 (2 mols.) at 120° give 3 : 4-*dimethyl*-2 : 5-*dihydrothiophen* 1 : 1-*dioxide* (II), m. p. 135° (crystallographic data given), also formed from (I) and SO_2 in Et_2O at 100° or H_2SO_3 at room temp. (II) and Br in C_6H_6 afford the *dibromide*, m. p. about 215° (decomp.), hydrolysed by boiling H_2O to 3 : 4-*dihydroxy*-3 : 4-*dimethyltetrahydrothiophen* 1 : 1-*dioxide*, m. p. 175° (Ac_2 derivative, m. p. 138°). H. Burton.

Nuclear synthesis in the olefine series. III. Hexenes. C. G. Schmitt and C. E. Boord (J. Amer. Chem. Soc., 1932, **54**, 751—761).—The following are prepared by the methods previously described (A., 1930, 1269; 1931, 709): *Et* α-*chloro*iso*butyl ether*, b. p. 43°/24 mm.; *Et* αβ-*dibromo*iso*butyl ether*, b. p. 88—89°/22 mm.; α-*bromo*-β-*ethoxy*-γ-*methylpentane*, b. p. 74—75°/13 mm.; β-*bromo*-γ-*ethoxyhexane*, b. p. 73°/12 mm.; β-*bromo*-γ-*ethoxy*-γ-*methylpentane*, b. p. 79·5°/25 mm.; δ-*bromo*-γ-*methoxyhexane*, b. p. 65—66°/12 mm.; α-*bromo*-β-*ethoxy*-β-*methylpentane*, b. p. 81—82°/19 mm.; α-*bromo*-β-*ethoxy*-βγ-*dimethylbutane*, b. p. 78—79°/15 mm.; α-*bromo*-β-*ethoxy*-β-*ethylbutane*, b. p. 79—81°/17 mm.; impure β-*bromo*-γ-*ethoxy*-β-*methylpentane*, b. p. 65—67°/20 mm. The action of Zn in PrOH on the above β-Br-ethers gives the corresponding hexenes; the following are prepared: Δ^{α}-hexene, b. p. 63·4—63·7° (all b. p. are at 760 mm. unless stated otherwise) (dibromide, b. p. 89—90°/18 mm.); γ-*methyl*-Δ^{α}-*pentene*, b. p. 53·6—54·0° (*dibromide*, b. p. 99°/30 mm.); δ-*methyl*-Δ^{α}-*pentene*, b. p. 53·6—53·9° (dibromide, b. p. 87°/21 mm.); Δ^{β}-hexene, b. p. 67·9—68·1° (dibromide, b. p. 90°/16 mm.); δ-methyl-Δ^{β}-pentene, b. p. 57·7—58·5° (*dibromide*, b. p. 78°/22 mm.) and 54·2—55·2° (*dibromide*, b. p. 72—73°/18 mm.); Δ^{γ}-hexene, b. p. 66·6—67·0° (dibromide, b. p. 80—81°/13 mm.); β-methyl-Δ^{α}-pentene, b. p. 61·5—62·0° (*dibromide*, b. p. 87—88°/20 mm.); βγ-*dimethyl*-Δ^{α}-*butene*, b. p. 56·0—56·5° (*dibromide*, b. p. 80°/17 mm.); α-ethyl-Δ^{α}-butene, b. p. 66·2—66·7° (dibromide, b. p. 87°/21 mm.); β-methyl-Δ^{β}-pentene, b. p. 67·2—67·5° (dibromide, b. p. 71—72°/18 mm.). Other data (lit.) for the hexenes and their dibromides are recorded. The b. p. of the olefines are raised by accumulation of Me groups on the unsaturated C atoms and by movement of the double linking towards the centre of the chain. Branching of an alkyl group attached to an unsaturated C atom causes a lowering of the b. p. C. J. West (*b*).

Spectrochemistry of acetylenic derivatives. F. Straus and R. Kühnel (Ber., 1932, **65**, [*B*], 154—158; cf. this vol., 374).—The vals. of the increment for the acetylenic linking are calc. from the optical data for Δ^{α}-heptinene, prepared by purifying the technical material through the Na derivative. The Cu compound is less suitable, since it is not decomposed by oxy-acids and the concn. of the halogen acid employed cannot be so reduced that danger of subsequent halogenation is excluded. H. Wren.

Preparation of γ-chloroallyl bromide and iodide. L. Bert and E. Andor (Compt. rend., 1932, **194**, 722—724).—The bromide, b. p. 130°, and iodide, b. p. 58°/19 mm., are prepared (70% yield) by fission of Ph γ-chloroallyl ether (A., 1931, 952) with the theoretical quantity of HBr or HI in AcOH without cooling. J. W. Baker.

Iodination in liquid ammonia. T. H. Vaughn and J. A. Nieuwland (J. Amer. Chem. Soc., 1932, **54**, 787—791).—When C_2H_2 is passed into I+liquid NH_3, C_2I_2, decomp. 125±4° (detonated by a sharp blow), is obtained in 54—63% yield. C_2I_2 is also obtained from C_2HNa and I in liquid NH_3; the reaction is instantaneous. $COMe_2$ similarly gives 8—12% of CHI_3, also formed in smaller yield from COMeEt. NH_2Bu, $NHBu_2$, $CH_2(CO_2Et)_2$, and $CH_2Ac\cdot CO_2Et$ also react with I in liquid NH_3, but definite products could not be isolated; C_6H_6, C_2H_4, $CMe_2{:}CHMe$, C_3H_6, $CHPh_3$, and pentane do not react. C. J. West (*b*).

Detection of chloropicrin. E. V. Alexeevski (J. Chem. Ind. Russ., 1931, **8**, No. 20, 50—51).—Air containing chloropicrin (I) is passed through H_2O, and the solution is treated with Ca; HNO_2 formed by reduction of (I) is detected by Griess' reagent (β-$C_{10}H_7\cdot NH_2$ and sulphanilic acid). This method serves for the detection of 0·002 mg. in 1 c.c. of H_2O. It cannot be applied to the colorimetric determination of (I), owing to partial further reduction of HNO_2 to NH_3. R. Truszkowski.

Action of phenylhydrazine and of thiocarbamide on aliphatic nitro-compounds. A. K. Macbeth and W. B. Orr (J.C.S., 1932, 534—543).—Action of alkaline solutions of $NHPh\cdot NH_2$ on $C(NO_2)_4$ (and other aliphatic polynitro-compounds) indicates the successive removal of NO_2-groups forming $MeNO_2$. Determination of evolved H_2 directly and of $-NO_2$ in the reduced solution is described. Thiocarbamide (neutral or slightly acid) is reduced similarly; the gases evolved by its action on the HNO_2 produced in reduced solution are determined. A new method of prep. of K nitroform is described. D. E. Kahn.

New general reagent for enols. Mercurous nitrate. E. V. Zappi (Bull. Soc. chim., 1932, [iv], **51**, 54—59).—Esters, aldehydes, ketones, and phenols which possess an enolic structure, $\cdot C(OH){:}CH$, and substances possessing the ψ-imino-alcohol, $\cdot C(OH){:}NH$, thioimino-, $\cdot C(SH){:}NH$, carbylamine, carbimido-, thiocarbimido-, or oximino-structures in EtOH have a reducing action on $Hg_2(NO_3)_2$, giving a deposit of finely-divided Hg the intensity of which is proportional to the concn. of the enol present. The reaction is more general than the $FeCl_3$ reaction, and can be used to detect the presence of the enols in MeCHO (1 part in 15,000 parts), Et malonate (1 in 10,000), or Et acetoacetate (at least 1 in 15,000). The fact that camphor does not give the reaction confirms Bredt-Savelsberg's observation that enolisation of camphor occurs only in presence of NaOEt or Grignard reagent. Theobromine gives a positive result, confirming the enolic structure. Certain substances with active unsaturated groupings such as $CH_2R\cdot CH{:}CH_2$, $CH_2R\cdot CH{:}CHR$, and $CHR{:}CHR$, have a similar reducing action. R. Brightman.

Reduction of *l*-*n*-butylvinylcarbinol to ethyl-*n*-butylcarbinol. R. I. Johnson and J. Kenyon (J.C.S., 1932, 722; cf. A., 1925, i, 771).—The ethyl-*n*-butylcarbinol produced is dextrorotatory. D. E. Kahn.

Preparation of true acetylenic primary alcohols. R. Lespieau (Compt. rend., 1932, **194**, 287—288).—n-Δ^{δ}-*Pentinenyl alcohol* (from δ-bromo-*n*-Δ^{δ}-pentenyl alcohol), b. p. 154—155°/766 mm. (*Ag* salt, m. p. 115°, explodes at 200° on Maquenne block; *phenylurethane*, m. p. 42·5—43·5°), gives $\delta\epsilon\epsilon$-*tri-iodo*-n-Δ^{δ}-*pentenyl alcohol*, m. p. 112·5—113·5°. Me γ-iodo-*n*-propyl ether and Na acetylide in liquid NH_3 give the *Me ether* (II) of (I), b. p. 109—109·5° (*Ag* salt), which with Br gives, amongst other products, *Me* $\delta\epsilon$-*dibromo*-n-Δ^{δ}-*pentenyl ether*, b. p. 76—76·5°/6 mm., whence by HBr $\alpha\beta\epsilon$-*tribromo*-n-Δ^{α}-*pentene*, b. p. 120—121°/14 mm., was obtained. $\delta\epsilon$-*Dibromo*-n-Δ^{δ}-*pentenyl alcohol* has b. p. 127—128°/16 mm. (I) was also obtained in poor yield from γ-iodo-*n*-propyl alcohol and Na acetylide, and from (II). R. S. Cahn.

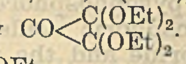
Action of hydriodic acid on glycerol. L. Sattler (J. Amer. Chem. Soc., 1932, **54**, 830—831).—*cyclo*Propanol is postulated as an intermediate in the formation of allyl iodide from glycerol and HI. C. J. West (*b*).

Complex ferric compounds of polyhydric alcohols. W. Traube and F. Kuhbier (Ber., 1932, **65**, [*B*], 187—190).—Addition of $FeCl_3$ in H_2O to a hot aq. solution of NaOH, $BaCl_2$, and mannitol yields the *compound* $C_6H_9O_6BaFe,2H_2O$ (also *heptahydrate*), converted by $NaHSO_4$ into the *substance* $C_6H_{10}O_6NaFe,3H_2O$. The *compound* $C_6H_9O_6CaFe,2H_2O$ dissolves more freely in cold than in hot H_2O. Sorbitol affords the *substances* $C_6H_9O_6BaFe,6H_2O$ and $C_6H_{10}O_6NaFe,4H_2O$, whereas the *compound* $[(C_3H_5O_3)_2FeOH]Ba_2,2H_2O$ is derived from glycerol. H. Wren.

Autoxidation of the ferric compounds of polyhydric alcohols. W. Traube and F. Kuhbier (Ber., 1932, 65, [*B*], 190—195; cf. preceding abstract).—Mannitol in 6% KOH is indifferent to O_2, whereas after addition of $FeCl_3$ marked autoxidation occurs. The products are CO_2, HCO_2H, and probably a hydroxymonocarboxylic acid, whereas H_2O_2 or $H_2C_2O_4$ could not be detected. Diminution in the concn. of KOH does not greatly affect the rate of reaction; change occurs more slowly in presence of K_2CO_3. It is not necessary that the polyhydroxycompound should be present entirely as the Fe^{III} complex. Sorbitol and erythritol resemble mannitol in their behaviour, whereas glycerol is not autoxidised. H. WREN.

Syntheses of glycol ethers. M. GODCHOT and M. IMBERT (Compt. rend., 1932, **194**, 378—380; cf. A., 1927, 444).—The action of 5 mols. of MgMeI on Et methyldiglycollate affords ββ-*dihydroxy*-αββ-*trimethyldipropyl ether* (I), b. p. 112°/10 mm., $d^{16\cdot5}$ 0·960, whilst with 4 mols. the product is α-*acetylethyl* β-*hydroxy*-β-*methylpropyl ether*, b. p. 108—109°/10 mm., d^{15} 0·983, converted by excess of MgMeI into (I). Similarly, MgPhBr affords ββ-*dihydroxy*-βββ′β′-*tetraphenyl*-α-*methyldiethyl ether*, m. p. 94°, converted on warming in AcOH into β-*methyl*-ααα′α′-*tetraphenyldiethylene dioxide*, m. p. 126—127°. The action of MgMeI on Et dilactylate affords a mixture of optical isomerides of *di*(*di*-β-*hydroxy*-αβ-*dimethyl*)*propyl ether*. The (*r*-) form, which predominates, has m. p. 76°; *meso*-form, m. p. 56°. Similarly, MgPhBr affords two inactive forms, m. p. 122° and 149°. MgMeI with Et phenyldiglycollate yields β-*hydroxy*-α-*phenyl*-β-*methylpropyl* β-*hydroxy*-β-*phenylpropyl ether*, m. p. 84—85°. J. L. D'SILVA.

Affinity capacity and migratory power. XIX. Affinity capacity of the amyl and *iso*amyl radicals compared with that of hydrogen. (MLLE.) J. LEVY and R. PERNOT (Bull. Soc. chim., 1931, [iv], **49**, 1838—1840).—Δ^{α}-Heptene oxide, b. p. 143—145°, and *iso*heptene oxide, b. p. 140—145°, obtained by perbenzoic acid oxidation of the hydrocarbons in Et_2O, do not isomerise on distillation. In presence of $ZnCl_2$ they resinify, but when passed over kieselguhr at 275—280° the former yields heptaldehyde and the latter *iso*heptaldehyde (*semicarbazone*, m. p. 114°), the oxide ring being ruptured on the side of the amyl and *iso*amyl radicals. Similarly, the dehalogenation with $AgNO_3$ of the iodohydrin from *iso*heptene affords Me *iso*amyl ketone and the amyl and *iso*amyl radicals have thus affinity capacities superior to that of H. R. BRIGHTMAN.

Compounds of bivalent carbon. V. Rearrangement products of carbon monoxide diethylacetal formed by the action of alkoxides on ethyl diethoxyacetate. H. SCHEIBLER, W. BEISER, and W. KRABBE (J. pr. Chem., 1932, [ii], **133**, 131—153; cf. this vol., 143).—Interaction of dry NaOEt and $CH(OEt)_2\cdot CO_2Et$ (I) at 100° in vac. gives CO, a distillate containing EtOH and a little $C(OEt)_2$, and a dark-coloured residue which is decomposed by H_2O or by dry H_2SO_4 or HCO_2H in Et_2O into EtOH, a little $C(OEt)_2$, unchanged (I), tetraethoxyethylene, and fractions of high b. p. The $[\text{:}C(OEt)_2]_2$ accompanies (I) in a fraction b. p. 70—90°/18 mm., and is identified by its reducing action on alkaline $KMnO_4$ and the formation of *Et diethoxyorthoacetate* (II), b. p. 75°/12 mm., 170°/1 atm., by the action of cold aq. NaOH, owing to hydrolysis of (I) and addition of the EtOH formed to $[\text{:}C(OEt)_2]_2$; (II) and $CH(OEt)_2\cdot CO\cdot NH_2$ are also formed from this fraction by the action of $NaNH_2$ in Et_2O or of NH_3 in EtOH. The reducing power of this fraction is not diminished by distillation at atm. pressure, and it is therefore concluded that $C(OEt)_2$ is not formed by decomp. of its dimeride, as previously suggested. The mechanism $CH(OEt)_2\cdot CO_2Et+NaOEt\longrightarrow C(OEt)_2\text{:}C(OEt)\cdot ONa+EtOH$; $C(OEt)_2\text{:}C(OEt)\cdot ONa\longrightarrow C(OEt)_2+C(OEt)\cdot ONa$ is suggested. The higher-boiling fractions contain a *substance*, $CO,2C(OEt)_2$, b. p. 140—142°/18 mm., possibly  $CO{<}\begin{matrix}C(OEt)_2\\C(OEt)_2\end{matrix}$. KOEt gives the same results as NaOEt.

$Mg(OEt)_2$ and $Al(OEt)_3$ react similarly to NaOEt at 170—200°, but very little CO or other gas is evolved, and the saline residue gives resins on decomp. with acids. Mg(OEt)Cl and Mg(OEt)Br behave similarly, giving EtCl or EtBr and the $EtOH–C(OEt)_2$ fraction at 145—150°. Separation of EtOH from the fraction b. p. 78°/1 atm. did not give $C(OEt)_2$ in a state of purity, and there was evidence of the presence of compounds of the type $C(OEt)_2,C_2H_4$ or $C(OEt)_2,2C_2H_4$, and also of a little Bu_2O or BuOEt. H. A. PIGGOTT.

Organic peroxides. I. Propyl and *iso*propyl hydrogen peroxide. S. S. MEDVEDEV and E. N. ALEXEEVA (Ber., 1932, **65**, [*B*], 133—137).—*Pr^{β} H peroxide*, b. p. 107—109°, prepared in about 50% yield by the action of 30% H_2O_2 and KOH on $Pr^{\beta}{}_2SO_4$, is relatively stable in quartz vessels or in acidic or neutral aq. solutions. In alkaline solution, it decomposes rapidly, giving $COMe_2$. Acid $KMnO_4$ acts only in presence of Mn^{II} salts. Quinol is unaffected by it in anhyd. Et_2O, but transformed into quinhydrone in H_2O or moist Et_2O. It liberates I quantitatively from HI. When treated with $Ba(OH)_2$, Pr^{β} H peroxide affords the *salt* $Pr^{\beta}O\cdot O\cdot Ba\cdot OCO_2H,3H_2O$, converted by terephthalyl chloride into *$Pr^{\beta}{}_2$ perterephthalate*, $C_6H_4(CO\cdot O\cdot OPr^{\beta})_2$, m. p. 59°, which slowly decolorises indigotin, does not liberate I from KI solutions, and slowly passes into $COMe_2$ and terephthalic acid in faintly acidic solution. Pr^{α} H peroxide could not be obtained pure and is isolated as the *salt* $Pr^{\alpha}O_2Ba\cdot CO_3H,3H_2O$. It decomposes in aq. solution, yielding EtCHO. $Pr^{\beta}{}_2$ perterephthalate decomposes so rapidly into EtCHO that it could not be analysed. H. WREN.

Pentaerythrityl thioethers. H. J. BACKER and N. D. DIJKSTRA (Rec. trav. chim., 1932, **51**, 289—293). —Pentaerythrityl thioethers, $C(CH_2\cdot SR)_4$, are obtained in good yield from $C(CH_2Br)_4$ (1 mol.) and NaSR (5 mols.) in EtOH; the alkyl mercaptans used are prepared by hydrolysis of alkyl*iso*thiocarbamides with KOH. The following are described: *tetra-methyl*, b. p. 209—211°/15 mm.; -ethyl, b. p. 218—220°/15 mm.; -*propyl*, b. p. 222—225°/3 mm.; -iso*propyl*, b. p. 192—193°/2 mm.; -*allyl*, b. p. 214—217° (slight decomp.)/2 mm.; -*butyl*, b. p. 226—230°/2 mm.; -iso*butyl*, b. p. 206—208°/2 mm.; -tert.-*butyl*, m. p. 123·5°; -*benzyl*, m. p. 73°, and -*phenyl*, m. p. 86°, *pentaerythrityl thioethers*. H. BURTON.

***iso*Propyl sulphate and benzyl *p*-toluenesulphonate.** S. S. MEDVEDEV and E. N. ALEXEEVA (Ber., 1932, **65**, [*B*], 131—133).—$Pr^{\beta}{}_2SO_4$, b. p. 94°/7 mm., is obtained in 25% yield by the action of a deficiency of SO_2Cl_2 in Et_2O on $NaOPr^{\beta}$ in Et_2O at −15° to −10°. The reported instability of the compound is not observed in the absence of traces of mineral acid. $Pr^{\alpha}{}_2SO_4$ is obtained similarly in 50%

yield. CH_2Ph *p*-toluenesulphonate, m. p. 58°, can be preserved for more than a week in a desiccator over $CaCl_2$, but decomposes within 15—20 min. over H_2SO_4. H. WREN.

Esters of pyrophosphorous, hypophosphoric, and pyrophosphoric acids. III. Diethylphosphoroyl chloride and the preparation of tetraethyl pyrophosphite therefrom. A. E. ARBUSOV and B. A. ARBUSOV (Ber., 1932, **65**, [*B*], 195—199; cf. A., 1931, 1268).—*Diethylphosphoroyl chloride*, $(OEt)_2PCl$, b. p. 63—65°/30 mm., 153—155°/760 mm., d_0^{20} 1·0747, is prepared in 4—4·5% yield by the action of Cl_2 on $NaEt_2PO_3$ in presence of ligroin, the main product being *Et_4 pyrophosphite*, $O[P(OEt)_2]_2$, b. p. 146—147°/3·5 mm., d_0^0 1·2045. The chloride reacts almost explosively with H_2O, is very readily oxidised, and dissolves Cu_2Cl_2 without yielding cryst. products. With NaOEt it affords Et_3PO_3; it yields Et_4 pyrophosphite with $NaEt_2PO_3$ in Et_2O. It can also be obtained by the interaction of 2 mols. of NaOEt on PCl_3, but its subsequent separation from Et_3PO_3 is difficult. H. WREN.

Enzymic hydrolysis of phosphoric esters and spontaneous hydrolysis of phosphosalicylic acid. C. MANAKA (J. Biochem. Japan, 1931, **14**, 191—213).—Resorcinol-diphosphoric acid and the following mono-*o*-phosphoric esters were prepared: chloroethyl; αβ-*dichloropropyl*; αα′-*dichloro*iso*propyl*; *pyrocatechol*; *resorcinol*; *quinol*; *o*-, *m*-, and *p*-carboxyphenyl. The enzymic hydrolysis of these esters was investigated and their relation to the structure of the substrates discussed. Phosphosalicylic acid has a min. stability at p_H 5·5. The dissociation curve, determined by electrometric titration, indicates that at p_H 5·5 the dissociation of one OH and of the CO_2H group is complete, whilst the remaining OH remains undissociated. F. O. HOWITT.

Glycidol. III. Reactions with acid chlorides. T. H. RIDER (J. Amer. Chem. Soc., 1932, **54**, 773—776; cf. A., 1930, 737).—Glycidol (I) heated with AcCl, gives 69% of *monochlorohydrin diacetate*, b. p. 96·5—97°/0·4—0·6 mm., converted by MeOH–HCl into AcOMe and monochlorohydrin (II), which contains both α- and β-isomerides. (I) and p-$NO_2\cdot C_6H_4\cdot COCl$ (1 : 1) give a mixture, b. p. 205—207°/0·8 mm., of the mononitrobenzoates of monochlorohydrin, whilst (II) affords a product, b. p. 207°/1·5 mm. (I) and p-$NO_2\cdot C_6H_4\cdot COCl$ (1 : 2) give 85% of a mixture, m. p. 97—98°, of the di-*p*-nitrobenzoates of α- and β-monochlorohydrins; (II) similarly affords a *di*-p-*nitrobenzoate*, m. p. 108—109°. β-Monochlorohydrin di-*p*-nitrobenzoate has m. p. 121—122°.

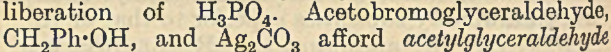
C. J. WEST (*b*).

Synthetic glycerides. III. Mixed triglycerides of the distearin series. H. E. ROBINSON, J. N. ROCHE, and C. G. KING (J. Amer. Chem. Soc., 1932, **54**, 705—710).—The following are new: α-, m. p. 42·7°, and β-, m. p. 47·2°, -*hexodistearins*; α-, m. p. 47·6°, and β-, m. p. 51·8°, -*octodistearins*; α-, m. p. 48·2°, and β-, m. p. 56·2°, -*decodistearins*. The solubilities and n_D^{70} of these and α-, m. p. 50·6°, and β-, m. p. 59·8°, -laurodistearins, α-, m. p. 58·5°, and β-, m. p. 63·5°, -myristodistearins, and α-, m. p. 62·6°, and β-, m. p. 68°, -palmitodistearins are recorded. The m. p. of the glycerides increase with rise in the C content, and the *sym.*-compounds have higher m. p., higher *n*, and lower solubilities than their *as*-isomerides. $SOCl_2$ is preferred for the prep. of acyl chlorides. *Glyceryl* α-*hexoate* (iso*propylidene* derivative, b. p. 124°/3 mm.) has b. p. 162°/4 mm.

C. J. WEST (*b*).

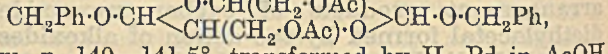
Preparation of esters of glycerol and amino-acids and of mixed esters of amino-acids and fatty acids. I. WEIZMANN and L. HASKELBERG (Bull. Soc. chim., 1932, [iv], **51**, 59—72).—The following glycerides have been obtained by the action of the corresponding Na salt of the amino-acid on α-chloro- or -bromo-hydrin at 100°: dl-*alanylglyceride* [β′γ′-*dihydroxypropyl* α-*aminopropionate*], m. p. 219°; α-*glycylglyceride*, decomp. 200—250°. The following mixed glycerides were obtained from α-iodohydrin, by conversion into the α-iododiglyceride with acyl chloride in presence of pyridine or quinoline and heating the α-iododiglyceride with the Na salt of the NH_2-acid at 150—160°: α-*glycyldipalmitin*, m. p. 215°; α-*glycyldistearin*, m. p. 170° after softening at 122°; α-dl-*alanyldipalmitin*, m. p. 216°; α-dl-*alanyldistearin*, m. p. 223°; α-dl-*leucyldipalmitin*, m. p. 218°; and α-dl-*leucyldistearin*, m. p. 150°; *dipalmitin* α-*iodohydrin* has m. p. 43·6°. The NH_2-group exerts a dominant influence on the properties of the mixed glycerides. With triketohydrindene the aminoglycerides yield the blue coloration characteristic of aminocarboxylic acids, the mixed aminoglycerides reacting less readily than the aminoglycerides. R. BRIGHTMAN.

Glyceraldehyde-γ-phosphoric acid. H. O. L. FISCHER and E. BAER (Ber., 1932, **65**, [*B*], 337—345).—Glyceraldehyde methyl*cyclo*acetal is converted by $POCl_3$ in quinoline followed by H_2SO_4 and Ag_2CO_3 and finally by $Ba(OH)_2$ into the *Ba* salt,



$$\mathrm{PO_3Ba\cdot O\cdot CH_2\cdot CH}<\begin{matrix}\mathrm{CH(OMe)\cdot O}\\ \mathrm{O\cdot CH(OMe)}\end{matrix}>\mathrm{CH\cdot CH_2\cdot O\cdot PO_3Ba},$$

which could not be hydrolysed without extensive liberation of H_3PO_4. Acetobromoglyceraldehyde, $CH_2Ph\cdot OH$, and Ag_2CO_3 afford *acetylglyceraldehyde benzyl*cyclo*acetal*,



$$\mathrm{CH_2Ph\cdot O\cdot CH}<\begin{matrix}\mathrm{O\cdot CH(CH_2\cdot OAc)}\\ \mathrm{CH(CH_2\cdot OAc)\cdot O}\end{matrix}>\mathrm{CH\cdot O\cdot CH_2Ph},$$

m. p. 140—141·5°, transformed by H_2–Pd in AcOH into acetylglyceraldehyde, m. p. 118·5°, and by $Ba(OH)_2$ in aq. EtOH into *glyceraldehyde benzyl*cyclo*acetal*, m. p. 109—110°. The last-named is converted by $POCl_3$ in quinoline into *glyceraldehyde benzyl*cyclo*acetalphosphoric acid* ($+2H_2O$ or $+0{\cdot}5H_2O$, decomp. 185—188°), which yields a *dibrucine* and *Ba* salt, but titrates electrometrically as a monobasic acid. Its reductive fission leads to *glyceraldehyde-γ-phosphoric acid*, $CHO\cdot CH(OH)\cdot CH_2\cdot O\cdot PO_3H_2$ (2 : 4-*dinitrophenylhydrazone*). H. WREN.

Complexes of zinc and cadmium iodides with alkylsulphonium iodides. (SIR) P. C. RÂY, N. ADHIKARI, and S. K. BANERJEE (J. Indian Chem. Soc., 1931, **8**, 739—751).—CdI_2 (1 mol.), Et_2S (or Et_2S_2) (2 mols.), and EtI (2 mols.) in cold $COMe_2$ give the compound (I), $(Et_3S)_2CdI_4$, m. p. 156—157° (lit. 145°), the conductivity of which (in H_2O) is of the same order as that of K_2CdI_4. The following *complexes* are prepared similarly, using R_2S, R′I, and CdI_2:

$(Et_2MeS)CdI_3$, m. p. 75°; $(Et_2PrS)_2CdI_4$, m. p. 150°; $(Et_2BuS)CdI_3$, m. p. 116°; $(Me_3S)_2CdI_4$, m. p. 204°; $(Me_2EtS)_2CdI_4$, m. p. 185°; $(Me_2PrS)_2CdI_4$, m. p. 120°; $(Me_2BuS)CdI_3$, m. p. 130°; $(Pr_3S)_2CdI_4$, m. p. 151—152°; $(Pr_2EtS)CdI_3$, m. p. 77—78°; $(Bu_3S)_2CdI_4$, m. p. 110°. The *compound*, $(Et_3S)_2CdBr_2I_2$ (conductivity data given) is prepared from Et_2S, EtBr, and CdI_2 or from Et_2S, EtI, and $CdBr_2$. (I) and NH_3 in $COMe_2$ give Et_3SI and $CdI_2,2NH_3$.

ZnI_2, Me_2S (or Me_2S_2), and MeI (in the mol. ratio 1 : 2 : 2) in $COMe_2$ give the *complex*, Me_3S_4,ZnI_6, m. p. 208°; with EtI, the *compound*, $(Me_2EtS)_2ZnI_4$, m. p. 184—185°, results. The *complexes*, $(Et_3S)_2ZnI_4$ (II) (conductivity data given), m. p. 149°; $(Et_2MeS)_2ZnI_4$, m. p. 173—174°, and $(Et_2PrS)_2ZnI_4$, m. p. 145°, are also described. (II) and NH_3 in $COMe_2$ afford Et_3SI and $ZnI_2,4NH_3$. H. BURTON.

Aliphatic sulphonyl fluorides. W. DAVIES and and J. H. DICK (J.C.S., 1932, 483—486).—Aliphatic sulphonyl fluorides can be prepared from the corresponding chlorides (cf. A., 1931, 1405) and are more stable than these. The following are described: *methane-* (I), *ethane-*, *α-chloroethane-*, cyclo*hexane-*, *ω-toluene-sulphonyl fluorides* (b. p. 124·2°/754 mm.), 134—135°, 138—139°, 218°, m. p. 90—91°). (I) forms a *piperidide*, m. p. 48°, b. p. 167—168°/4 mm.

D. E. KAHN.

Esterification with mixed anhydrides and mixtures of anhydrides. II. A. ROLLETT and F. SCHOLZ (Monatsh., 1932, 59, 1—6; cf. A., 1931, 934).—When BzCl, NaOAc, and EtOH are heated together in the mol. proportions 1 : 1 : 2 the max. yield of BzOEt is reached at 100°. This decreases rapidly with fall of temp., so that at 70° the same total yield of ester contains only about half as much BzOEt. At 50° the total yield is diminished, but the proportions of the two esters remain practically the same as at 70°. Decomp. of the anhydride is practically complete in 2 hr. at 50°, but even at this temp. there is considerable esterification by EtOH of the acid set free.

M. S. BURR.

Relation between Kolbe's reaction and hydrogen-ion concentration. Mechanism of Kolbe's reaction. H. R. MATSUDA.—See this vol., 348.

Parallelism between colour and reactivity of a chromophoric group. (MME.) RAMART-LUCAS (Compt. rend., 1932, 194, 726—728).—Theoretical. The chromophores CO_2H in $Me\cdot[CH_2]_n\cdot CO_2H$ and NH_2 in $Me\cdot[CH_2]_n\cdot NH_2$, respectively, give rise to the same absorption spectra in all cases where $n>2$, and such compounds also exhibit the same velocity of chemical reaction (*e.g.*, esterification and reaction with allyl bromide, respectively). J. W. BAKER.

[Ring-chain tautomerism of partly acetylated polyhydric alcohols.] H. HIBBERT (Ber., 1932, 65, [*B*], 199—200).—Cases similar to that examined by Meerwein and Sönke (A., 1931, 1395) have been investigated by the author, who has also considered the possibility of equilibrium mixtures.

H. WREN.

Properties of conjugated compounds. XV. Catalytic hydrogenation of butadiene-α-carboxylic acids. E. H. FARMER and R. A. E. GALLEY (J.C.S., 1932, 430—439; cf. A., 1928, 613, 1111).—Separative and degradative (oxidation with $KMnO_4$) analyses are used to determine the proportions of αβ-, αδ-, γδ-, and αβγδ-additive products obtained from β-vinylacrylic, sorbic, α-methyl- and βδ-dimethylsorbic acids by action of $Pd–H_2$ (1 mol.). The proportions are found to be different for each acid.

D. E. KAHN.

Walden inversion. XVII. Optical rotations in homologous series of carboxylic acids. P. A. LEVENE and R. E. MARKER (J. Biol. Chem., 1932, 95, 153—164).—The optical rotations are given of a series of acids, $CHRR'\cdot[CH_2]_n\cdot CO_2H$, where R is const., R′ is a normal alkyl radical progressively increased, and *n* varies from 0 to 3; the significance of these figures is discussed. (The figures in parentheses are the calc. max. for [*M*].) l-δ-*Methyloctoic*, b. p. 127°/5 mm., d_4^{25} 0·901, $[\alpha]_D^{25}$ −0·37° (−3·67°), l-δ-*methylnonoic*, b. p. 130°/3 mm., d_4^{25} 0·897, $[\alpha]_D^{25}$ −0·50° (−1·6°), l-δ-*methyldecoic*, b. p. 135°/3 mm., d_4^{25} 0·893, $[\alpha]_D^{25}$ −0·18° (−0·6°), and d-ε-*methyloctoic acid*, b. p. 139°/20 mm., d_4^{25} 0·899, $[\alpha]_D^{25}$ +2·49° (+12·22°), have been prepared from Et malonate and the corresponding bromomethylparaffin, whilst CO_2 and the Grignard compound of the paraffin have given d-γ-*methylhexoic*, b. p. 115°/16 mm., d_4^{22} 0·923, $[\alpha]_D^{22}$ +3·09° (+13·6°), d-γ-*methylheptoic*, b. p. 132°/22 mm., d_4^{24} 0·882, $[\alpha]_D^{24}$ +2·11° (+6·9), l-γ-*methyloctoic*, b. p. 149°/22 mm., d_4^{25} 0·871, $[\alpha]_D^{25}$ −1·33° (−4·1°), l-γ-*methylnonoic*, b. p. 156°/22 mm., d_4^{25} 0·871, $[\alpha]_D^{25}$ −0·59° (−1·9°), and d-δ-*methylheptoic acid*, b. p. 128°/20 mm., d_4^{26} 0·893, $[\alpha]_D^{26}$ +2·47° (+11·07°). l-β-*Methylhexylamine*, b. p. 62°/22 mm., d_4^{27} 0·773, $[\alpha]_D^{27}$ −11·75°, has been prepared from β-methylheptoic acid. F. R. SHAW.

Conjugated double linkings. XXII. Extended Thiele's rule. R. KUHN and M. HOFFER (Ber., 1932, 65, [*B*], 170—175; cf. A., 1928, 291).—Reduction of a number of unsaturated fatty acids by Na–Hg causes addition of 2 H atoms preferably at the ends of the conjugated system. $\Delta^{\alpha\gamma\epsilon}$-Octatrienoic acid is transformed in 65% yield into $\Delta^{\beta\delta}$-*octadienoic acid*, b. p. 134—135°/11 mm., m. p. about 2°, $d_4^{17.5}$ 0·9703 [*amide*, m. p. 124° (corr.)]. Cautious oxidation by $KMnO_4$ (O=8) converts it into $EtCO_2H$ in 70% yield. Prolonged boiling with 15% NaOH causes partial isomerisation of the $\Delta^{\beta\delta}$-acid to $\Delta^{\alpha\gamma}$-*octadienoic acid*, m. p. 74° (corr.), oxidised to $PrCO_2H$. $\Delta^{\alpha\gamma\epsilon\eta}$-Decatetraenoic acid gives $\Delta^{\beta\delta\zeta}$-*decatrienoic acid*, m. p. 96° (corr.) after softening at 94°, oxidised to $EtCO_2H$. The dihydro-acids are isolated in 50—65% yield, the remainder being polymerised, mainly dimerised. From sorbic acid "dihydrodisorbic acid" ($2C_6H_8O_2+2H$) is obtained as a non-homogeneous, viscous oil of aliphatic structure, since catalytic hydrogenation establishes the presence of two double linkings in the acid and its ester. Its formation is probably due to a pinacol condensation of 2 mols. of acid each of which has absorbed 1 H atom.

H. WREN.

History of the development of the chemistry of fats. E. ANDRÉ (Bull. Soc. chim., 1932, [iv], 51, 1—29, 145—170).—A lecture.

Action of potassium hydroxide on halogen derivatives of palmitic acid. M. ROBINET (Bull.

Soc. chim. Belg., 1931, 40, 710—725).—α-Iodopalmitic acid and KOH in hot EtOH give a difficultly separable mixture of α-hydroxypalmitic (*α-ethoxypalmitic acid*, m. p. 45°) and *Δ^α-hexadecenoic acid* (I), m. p. 49°; (I) with HI in AcOH gives *β-iodopalmitic acid*, m. p. 48—49°, converted by KOH–EtOH into (I) (the structure of which is proved by ozonolysis in $CHCl_3$) and *β-hydroxypalmitic acid*, m. p. 83—83·5° (*Ac* derivative, m. p. 58°). HBr leads similarly to *β-bromopalmitic acid*, m. p. 44°. R. S. Cahn.

d-Ricinoleates of l-α-phenylethylamine and l-ephedrine. E. André and C. Vernier (Compt. rend., 1932, 194, 469—471).—The d-*ricinoleates* of *l*-α-phenylethylamine, m. p. 39·5—40°, and *l*-ephedrine, m. p. 54·2°, are prepared from acids of slightly different $[\alpha]_D$. Both give on regeneration d-*ricinoleic acid*, $[\alpha]_D^{23}$ +7·9°. From the mother-liquors of the ephedrine salt a salt of indefinite m. p. was obtained, and gave on regeneration an acid of lower $[\alpha]_D$. It is concluded that natural ricinoleic acid is a mixture of isomerides. H. A. Piggott.

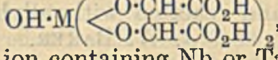
Structure of couepic acid. E. Rossmann (Rec. trav. chim., 1932, 51, 248—252).—The density and optical exaltation of couepic acid indicate that it is not a geometrical isomeride of α- and β-elæostearic acids as suggested by van Loon and Steger (A., 1931, 1034). Couepic acid may contain a *cyclo*butane ring. H. Burton.

Oxidation of metabolites. I. Mechanism of the oxidation of α-hydroxy-fatty acids with potassium permanganate. II. Shift in the point of rupture in a given α-hydroxy-fatty acid in the presence or absence of free alkali. E. J. Witzemann (J. Biol. Chem., 1932, 95, 219—245, 246—262).—I. Oxidation of a series of α-hydroxy-*n*-fatty acids with known amounts of $KMnO_4$ in neutral or slightly alkaline solution takes place thus: $CH_2R{\cdot}CH(OH){\cdot}CO_2H$, (A) $+2O \longrightarrow CH_2R{\cdot}CO_2H + H_2O + CO_2$, and (B) $+5O \longrightarrow RCO_2H + 2H_2O + 2CO_2$. The percentage of (B) formed is: lactic 16, α-hydroxy-butyric 52, -valeric 84, -hexoic 88, and -heptoic, -octoic, -decoic, -lauric, -palmitic, and -stearic acid 100.

II. Oxidation of lactic, α-hydroxy-butyric, -valeric, and -hexoic acids with $KMnO_4$ in presence of varying amounts of alkali shows a shift of the point of rupture of the chain from loss of 1 to 2 C atoms as soon as there is 1 mol. of alkali in excess, more alkali tending to complete oxidation. When 2 C atoms are lost, $H_2C_2O_4$ may be isolated, showing that these are severed together. Loss of 1 C atom is due to oxidation of the α-keto-acid, whilst loss of 2 C atoms follows the oxidation of its enolic isomeride. F. R. Shaw.

Polymerisation and ring formation. X. Reversible polymerisation of six-membered cyclic esters. W. H. Carothers, G. L. Dorough, and F. J. Van Natta (J. Amer. Chem. Soc., 1932, 54, 761—772).—Examples (lit. and new) of the reversible polymerisation of six-membered cyclic esters are discussed. The following conclusions are reached: reversible polymerisation is generally characteristic of six-membered cyclic esters; ester-rings containing five or more than six atoms are not polymerised by heat. The tendency of the six-membered cyclic esters to polymerise is closely related to their susceptibility towards hydrolysis; both tendencies are diminished by the presence of substituent groups. The polymerides formed are linear poly-esters and, in certain cases, the chains are open and terminated by OH and CO_2H groups. Both polymerisation and depolymerisation consist essentially of a process of ester interchange. The peculiar position occupied by the six-membered cyclic esters is readily explained by stereochemical considerations based on the Sachs–Mohr theory. *Et propylphenoxypropylmalonate*, b. p. 195—200°/4 mm., *δ-bromo-α-propylvaleric acid*, b. p. 148—150°/5 mm., and *α-propyl-δ-valerolactone*, b. p. 118—120°/10 mm., are described. Details are given for the prep. of lactide, and polymerides of δ-valerolactone and of the lactone of hydroxyethyl-glycollic acid are described. C. J. West (*b*).

Ethyl acetoacetate–choleic acid. H. Sobotka and J. Kahn (Ber., 1932, 65, [*B*], 227—232).—Deoxycholic acid and Et acetoacetate give an additive *product* (3 : 1), m. p. 154° (corr.); analogous *compounds* of choleic acid with acetyl- and benzoyl-acetone have been prepared. In the solid compound the Et acetoacetate is present exclusively or nearly exclusively in the enolic form. In EtOH or amyl alcohol this preponderance of enol is not maintained, but the acetoacetate equilibrium is displaced appreciably towards the enolic side in comparison with the normal equilibrium. A similar effect is recorded with cholic or dehydrocholic acid. The action of the bile acids is not due to an unsp. H-ion effect, but these compounds, with cholesterol and digitonin, appear to belong to a group which modifies the enolising action of the solvent. In EtOH at 0°, the maximal enol vals. are not observed until a very short time after dissolution is complete. With tri-choleic acid–benzoyl- or –acetyl-acetone, the max. val. of 99% enol is attained after 1 min. The behaviour of choleic acid–Et acetoacetate in the solid, molten, and dissolved state towards Br suggests that it must undergo a change in mol. or co-ordinative structure before it can add Br at the double linking. Probably mol. dissociation of the co-ordination compound takes place at a rate which exceeds the velocity of tautomerisation. H. Wren.

Behaviour of oxalate and tartrate solutions of niobium and tantalum oxides. F. H. Edmister and G. G. Albritton (J. Amer. Chem. Soc., 1932, 54, 438—442).—Freshly-pptd. hydrated oxides of Nb and Ta dissolve slowly in hot aq. tartaric acid to form niobo- and tantalo-tartaric acids,  $OH{\cdot}M\left(<\begin{matrix}O{\cdot}CH{\cdot}CO_2H\\O{\cdot}CH{\cdot}CO_2H\end{matrix}\right)_2$, where M=Nb or Ta. The ion containing Nb or Ta migrates towards the anode. A similar migration of the metal-containing ion of the complex formed similarly, using $H_2C_2O_4$, indicates the structure $H_5M(C_2O_4)_5$. The complex salts are not affected by acids. F. D. Snell (*b*).

Thermal stability of some alkylated malonic acids. F. C. B. Marshall (Rec. trav. chim., 1932, 51, 233—238).—The dialkylmalonic acids are more stable towards heat than the unsubstituted acid, and the latter than the monoalkyl derivatives. The order is that of the m. p. No simple relation between the results and polar and steric influences can be deduced. M. S. Burr.

Mechanism of racemisation. A. N. Campbell and A. J. R. Campbell.—See this vol., 346.

Pectin. II. Typical reaction of *d*-galacturonic acid and pectin. F. Ehrlich (Ber., 1932, 65, [*B*], 353—358; cf. A., 1929, 1273).—Aq. solutions of α- or β-*d*-galacturonic acid give a white, flocculent ppt. with basic Pb acetate, sol. in excess of the reagent. The clear solution when heated in boiling H_2O becomes pink and turbid and rapidly deposits a dark blood- to bile-red ppt. Complete redissolution of the ppt. is unnecessary provided that the solution is distinctly alkaline to litmus. 1 mg. of the acid can be thus detected. Reaction is independent of light and atm. O_2 and occurs slowly at room temp. Glycuronic acid behaves somewhat similarly to galacturonic acid, but the coloration is yellow to rust-brown. Gluconic, galactonic, and arabonic acid remain clear and colourless when heated with basic Pb acetate, saccharic and mucic acids afford dense white ppts. unchanged when heated, pyruvic and hydroxypyruvic acids yield white ppts. becoming pale yellow, or grey when heated, whilst saccharic and dihydroxymaleic acids do not give red colours. Pb pectate and tetragalacturonate become yellowish to orange-yellow when heated. The application of the reaction to the detection of pectin and galacturonic acid in plant material is described. The presence of galacturonic acid or pectin residues in wood is established. It appears that the OH′ of the basic Pb acetate attacks the CHO group of galacturonic acid with formation of the corresponding ketogalactonic acid, which is further degraded to a C_4 or C_5 compound. Under certain conditions the basic Pb salt of a carbonylcarboxylic acid is produced the peculiar colour of which is attributed to certain by-products of the change. H. Wren.

Synthesis of hexuronic acids. I. Synthesis of *dl*-galacturonic acid from mucic acid. C. Niemann and K. P. Link (J. Biol. Chem., 1932, 95, 203—211).—Mucic acid monolactone is reduced by Na–Hg in acid solution to cryst. *dl*-galacturonic acid, isolated as the Ba salt (cf. Fischer, A., 1891, 1193; 1892, 824). F. R. Shaw.

Preparation of *d*-mannuronolactone. E. Schoeffel and K. P. Link (J. Biol. Chem., 1932, 95, 213—218).—Alginic acid obtained from *Macrocystis pyrifera* is hydrolysed by 2·5% H_2SO_4 to mannuronic acid (Ba salt), which when crystallised from AcOH gives *d*-mannuronolactone. F. R. Shaw.

Mechanism of production of thiol acids (RSH) and sulphonic acids (RSO_3H) from dithio-acids (RS_2R). II. Action of mercuric salts. P. W. Preisler and D. B. Preisler (J. Biol. Chem., 1932, 95, 181—188).—The reaction between dithiodi-β-propionic acid and $HgBr_2$ proceeds to at least 75% formation of β-sulphopropionic acid (Ba salt, $+5H_2O$) and $CO_2H{\cdot}CH_2{\cdot}CH_2{\cdot}S{\cdot}HgBr$, the latter also being obtained from $HgBr_2$ and β-thiolpropionic acid. The reaction $3RS{\cdot}SR+3H_2O=5RSH+RSO_3H$ is accelerated by the removal of RSH as the slightly ionised derivative of $BrHg^+$. F. R. Shaw.

Polymerisation reactions under high pressure. II. Mechanism of the reaction. J. B. Conant and W. R. Peterson (J. Amer. Chem. Soc., 1932, 54, 628—635; cf. A., 1930, 735).—Peroxides are essential for the polymerisation of aliphatic aldehydes and isoprene under high pressures. A chain mechanism is suggested which seems to account for all the observed facts. Attempts to stabilise the polymeric aldehydes were not successful. *cyclo*Hexene oxide is polymerised with great difficulty. The rate of decomp. of the polymeride from PrCHO in dioxan is studied; the polymeride shows no positive test for an OH group, since treatment with various reagents either has no effect or causes decomp.

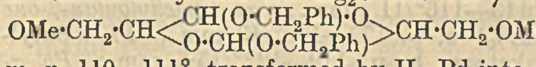
C. J. West (*b*).

Photo-reduction of carbonic acid to formaldehyde. N. R. Dhar and A. Ram.—See this vol., 349.

Action of diazomethane on formaldehyde and formic acid. L. Irrera (Gazzetta, 1932, 62, 30—33; cf. A., 1907, i, 185, 478; 1909, i, 553).—No definite products can be isolated from the reaction between CH_2O and diazomethane. HCO_2H with diazomethane gives MeOAc. E. E. J. Marler.

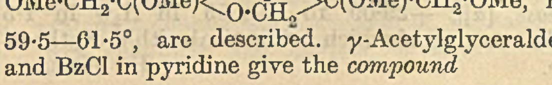
Derivatives of tribromoethyl alcohol [Avertin]. S. Chechik (J. Amer. Pharm. Assoc., 1932, 21, 20—24).—Choral and bromal with tribromoethyl alcohol give the *compounds* $CCl_3{\cdot}CH(OH){\cdot}O{\cdot}CH_2{\cdot}CBr_3$, m. p. 69—70°, and $CBr_3{\cdot}CH(OH){\cdot}O{\cdot}CH_2{\cdot}CBr_3$, m. p. 60—62°. With aq. H_2SO_4 or HNO_3 the alcohol affords *di(tribromoethyl) ether*, m. p. 63°, and with H_2SO_4–EtOH it gives *Et* ββ*β-tribromoethyl ether*, m. p. 60—62°. ββ*β-Tribromoethyl* N-*phenylcarbamate*, m. p. 66—67°, and ββ*β-tribromo-β′-hydroxydiethyl ether*, m. p. 70—71°, are described. E. H. Sharples.

Derivatives of trioses and their transformations. H. O. L. Fischer and E. Baer (Ber., 1932, 65, [*B*], 345—352).—Glyceraldehyde benzyl*cyclo*acetal is converted by MeI and Ag_2O into the *γ-Me ether*,



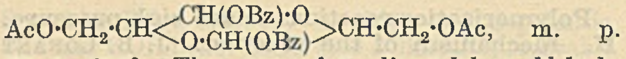
$$OMe{\cdot}CH_2{\cdot}CH{<}\begin{matrix}CH(O{\cdot}CH_2Ph){\cdot}O\\O{\cdot}CH(O{\cdot}CH_2Ph)\end{matrix}{>}CH{\cdot}CH_2{\cdot}OMe,$$

m. p. 110—111°, transformed by H_2–Pd into dimeric *glyceraldehyde γ-Me ether*, m. p. 120—121° (2 : 4-*dinitrophenylhydrazone*, m. p. 123—124°), which passes when treated with anhyd. pyridine at 125—130° into *α-hydroxy-γ-methoxyacetone* (2 : 4-dinitrophenylhydrazone, m. p. 175°). α-Hydroxy-γ-acetoxyacetone is transformed by $CH(OEt)_3$ and NH_4Cl in EtOH into the *diethylacetal*, b. p. 89—91°/0·3 mm., hydrolysed by aq. $Ba(OH)_2$ in H_2O to *dihydroxyacetone diethylacetal*, m. p. 90°. Glyceraldehyde is converted by MeCHO in presence of 84% H_3PO_4 into dimeric *ethylideneglyceraldehyde*, m. p. 309—310° (corr. in sealed capillary), obtained also by use of saturated MeOH–HCl. *Dihydroxyethylideneacetone*, m. p. 161—162°, is obtained from $CO(CH_2{\cdot}OH)_2$, MeCHO, and H_3PO_4. Glyceraldehyde, PhCHO, and P_2O_5 afford benzylideneglyceraldehyde. *Glyceraldehyde methyl*cyclo*acetal γ-Me ether*, m. p. 99—100°, and *dihydroxyacetone methyl*cyclo*acetal γ-Me ether*,



$$OMe{\cdot}CH_2{\cdot}C(OMe){<}\begin{matrix}CH_2{\cdot}O\\O{\cdot}CH_2\end{matrix}{>}C(OMe){\cdot}CH_2{\cdot}OMe,$$

m. p. 59·5—61·5°, are described. γ-Acetylglyceraldehyde and BzCl in pyridine give the *compound*



$AcO\cdot CH_2\cdot CH<\begin{matrix}CH(OBz)\cdot O\\ O\cdot CH(OBz)\end{matrix}>CH\cdot CH_2\cdot OAc$, m. p. 203·5—204°. The prep. of βγ-*diacetylglyceraldehyde*, b. p. 90—96°/0·8 mm., is described. H. Wren.

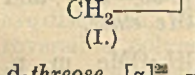
Conversion of ketones into liquid hydrocarbons. A. Maihle and Renaudie (Compt. rend., 1932, **194**, 462—464).—Passage of $COMe_2$, $COEt_2$, and $COPr^{\alpha}_2$ over SiO_2 gel at 700—750° yields mainly gases, comprising CO, CH_4, olefines (mainly C_2H_4 with $COEt_2$ and C_3H_6 with $COPr_2$), and a little H_2, and a small amount of liquid product consisting mainly of C_6H_6 and in addition PhMe, *m*-xylene, $C_{10}H_8$, anthracene, and higher hydrocarbons. H. A. Piggott.

Formation of semicarbazones with bromo- and chloro-acetone. A. P. J. Hoogeveen and M. P. J. M. Jansen (Rec. trav. chim., 1932, **51**, 260—264).—Chloroacetonesemicarbazone, m. p. about 150° (decomp.) (lit. 163—165°), and *bromoacetonesemicarbazone*, m. p. 135° (decomp.), heated with H_2O or EtOH give hydrazinedicarbondiamide and the semicarbazone of $COMe\cdot CH_2\cdot OH$. *Diacetonyl sulphide*, m. p. 85°, is obtained in poor yield from $COMe\cdot CH_2Br$ and aq. Na_2S. H. Burton.

Ethyl ethers of α-glycols. III. Dialkyl ketones derived from ethyl ethers. D. Bardan (Bull. Soc. chim., 1931, [iv], **49**, 1875—1880).—The following ketones have been obtained by dehydration of the Et ethers of α-glycols with $H_2C_2O_4$ or 20% H_2SO_4: $COMePr^{\beta}$ (yield 58%), b. p. 92—95° (semicarbazone, m. p. 112°); γ-ethylpentan-β-one, b. p. 38—42°/19 mm., 138—140°/760 mm. (semicarbazone, m. p. 99°); ξ-*methyl*-γ-iso*amylheptan*-β-*one*, b. p. 119—124°/29 mm.; γ-propylhexan-β-one (50%), b. p. 80—88°/29—30 mm., 174—176°/760 mm. (*semicarbazone*, m. p. 67—68°); Me benzhydryl ketone (yield 90%), m. p. 61—62° (semicarbazone, m. p. 168°); δ-*ethylhexan*-γ-*one*, b. p. 54—57°/14 mm. (*semicarbazone*, m. p. 50—51°); δ-*propylheptan*-γ-*one*, b. p. 73—75°/15·5 mm.; δ-*butyloctan*-γ-*one* (yield 96%), b. p. 113—116°/11 mm.; αα-*diphenylbutan*-β-*one* (yield 48%) b. p. 177—180°/13 mm.; *Ph* α-ethylpropyl ketone, b. p. 119—122°/15·5 mm.; *Ph* α-*propylbutyl ketone* (yield 50%), b. p. 127—133°/16—17 mm.; *Ph* α-*butylamyl ketone*, b. p. 148—151°/13 mm.; Ph benzhydryl ketone, m. p. 134·5°. R. Brightman.

Preparation of pinacolone. D. E. Badertscher and F. C. Whitmore (J. Amer. Chem. Soc., 1932, **54**, 825—826).—Addition of a dil. solution of Mg *tert.*-BuCl in Et_2O to an excess of AcCl in Et_2O gives 40% of Me *tert.*-Bu ketone. Somewhat lower yields are obtained with other combinations of *tert.*-Grignard reagents and acyl halides. C. J. West (*b*).

***d*-Threose.** W. Freudenberg (Ber., 1932, **65**, [*B*], 168—170).—*d*-Diacetylxylal (cf. A., 1929, 1277) in AcOH is transformed by O_3 and subsequent treatment with Zn dust and Et_2O into d-*threose* 2 : 3-*diacetate* (I), m. p. 140—142°, $[\alpha]^{25}_{D}$ +83·52° to +34·31° in $CHCl_3$ in 5 hr. Hydrolysis with aq. $Ba(OH)_2$ affords d-*threose*, $[\alpha]^{25}_{D}$ +29·09° to +19·59° in H_2O in 1·5 hr., the osazone of which is identical with *d*-erythrosazone. H. Wren.



(I.)

Colorimetric micro-determination of pentoses. K. Suminokura (J. Biochem. Japan, 1931, **14**, 343—359).—The substance (1—20 mg.) is distilled in a current of steam and CO_2 at 150° with 12·5*N*-H_2SO_4 in presence of K_2SO_4 and $ZnSO_4$. Furfuraldehyde is then colorimetrically determined in the distillate by xylidine and AcOH. F. O. Howitt.

Volumetric determinations of pentoses and pentosans. G. M. Kline and S. F. Acree (Bur. Stand. J. Res., 1932, **8**, 25—35).—The yield of furfuraldehyde from pentoses or pentosans is not improved by steam-distillation (B., 1923, 1238A). The loss arises from incomplete conversion of the xylose into furfuraldehyde, since recovery of the latter by either distillation method is quant. Nitrates, which reduce the yield, are best removed by nitron before addition of HCl, and loss of the aldehyde occurs by exposure of the distillate to air, whilst not all the aldehyde is collected in the 360 c.c. of distillate given in the official method. Comparison of (1) gravimetric thiobarbituric acid method (A., 1917, ii, 53), (2) electrometric KBr–$KBrO_3$ titration method (*loc. cit.*, 1923), and (3) Powell and Whittaker's excess Br-titration method (J.S.C.I., 1924, **43**, 35T) for determination of furfuraldehyde shows that (3) is much more rapid and accurate than (1) or (2) especially for amounts $<$0·01 g. for which the pptn. method gives very low results. J. W. Baker.

Pentose reactions. II. Derivatives of xylose. C. D. Hurd and L. L. Isenhour (J. Amer. Chem. Soc., 1932, **54**, 693—698; cf. this vol., 279).—Xylosan (I), $[\alpha]_D$ +68·3° in H_2O, formed when xylose is heated at the b. p. of xylene/2 mm., is readily oxidisable, shows a normal mol. wt. in cold AcOH, but is termol. in H_2O. When a solution in AcOH is heated to 100°, polymerisation occurs and the colourless solution turns brown. The unimol. form of (I) changes at 95—97° and atm. pressure to a dark brown solid, which is converted at 205—210° (without melting) into another form, and when heated under 0·3 mm. darkens slightly and shrinks at 119—120°, and is apparently converted into a new product at 163—165°. Acetylation of (I) in the cold gives a Ac_2 derivative, $[\alpha]_D$ +38° in $CHCl_3$, which darkens at 88—89°, and becomes much darker at 95—100° (with apparent polymerisation), and is termol. in C_6H_6. Diacetyllyxosan or a mixture with diacetylxylosan is formed from BzO_2H and diacetylxylal. Glucosan has properties closely resembling those of (I). C. J. West (*b*).

Precipitation of sugars and polyhydric alcohols by heavy metal hydroxides in alkaline medium. P. Fleury and J. Courtois (Compt. rend., 1932, **194**, 728—731).—The amount of glucose or mannitol absorbed by the metal hydroxide when alkali [NaOH, or better, $Ba(OH)_2$ or aq NH_3] is added at 0° to a solution of the sugar and a heavy metal nitrate increases in the order Zn, Hg, Bi, Co, Ni, Pb, Cr, Cu, Cd, Al, Fe. Since comparable results are obtained with various sugars and polyhydric alcohols, the absorption is of general character. Greater absorption occurs with acetates than with mineral acid anions. J. W. Baker.

Rates of formation of the active reductants of several sugars. M. H. Roepke and J. M. Ort.—See this vol., 345.

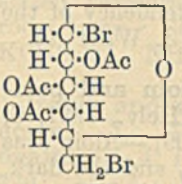
The methylglucoses of Pacsu. II. R. Schinle (Ber., 1932, 65, 315—320; cf. A., 1931, 1399; Pacsu, this vol., 254).—Re-examination of Pacsu's "4 : 5 : 6-trimethylglucose dibenzylmercaptal," m. p. 98°, $[\alpha]_D^{18}$ −63·9° in pyridine, shows the compound to contain only 1 OMe and hence to be 4-*methylglucose dibenzylmercaptal*. This view is confirmed by the prep. of the Ac_4 derivative, m. p. 69—70°. Removal of the mercaptal residues followed by treatment with $NHPh\cdot NH_2$ affords, therefore, 4-*methylglucosazone*, m. p. 159°, $[\alpha]_D^{21}$ −13° in EtOH (final val.). Since methylation of *iso*propylideneglucose dibenzylmercaptal, m. p. 94°, followed by hydrolysis with 0·1*N*-HCl affords 2-methylglucose dibenzylmercaptal, m. p. 191°, it follows that the $\colon CMe_2$ group is attached in the 5 : 6 position. The di*iso*propylidene compound which yields a 4-methylglucose has the groups in the positions 2 : 3 and 5 : 6. H. Wren.

Catalytic fission of triphenylmethyl ethers by hydrogen and oxygen. F. Micheel (Ber., 1932, 65, [*B*], 262—265).—Mannitol in pyridine is converted by the successive action of CPh_3Cl and Ac_2O into 1 : 6-*ditriphenylmethylmannitol* 2 : 3 : 4 : 5-*tetra-acetate*, m. p. 180—181°, $[\alpha]_D^{20}$ +46·4° in $CHCl_3$, transformed by HCl–$CHCl_3$ into mannitol 2 : 3 : 4 : 5-tetra-acetate, m. p. 123—125°, $[\alpha]_D^{20}$ +3° in $CHCl_3$. In AcOH in presence of spongy Pt it is converted by H_2 into the tetra-acetate and $CHPh_3$, whereas with a mixture of H_2 and O_2 it affords the tetra-acetate, ditriphenylmethyl peroxide, and $CHPh_3$. 6-Triphenylmethyl-α-methylglucose 2 : 3 : 4-triacetate with H_2 yields a mixture of methylglucoside 2 : 3 : 4- and 2 : 3 : 6-triacetate (acetylated to α-methylglucoside 2 : 3 : 4 : 6-tetra-acetate, m. p. 101°) and $CHPh_3$. These products are also obtained when a mixture of H_2 and O_2 is used; the peroxide does not appear to be formed. H. Wren.

Reactions of trimethylamine compounds of sugars. F. Micheel and H. Micheel (Ber., 1932, 65, [*B*], 258—261).—Glucosidotrimethylammonium bromide and CPh_3Cl in $CHCl_3$ afford 6-*triphenylmethylglucosidotrimethylammonium bromide* (I), m. p. 183—185°, $[\alpha]_D^{18}$ +14·8° in EtOH, and 6-*triphenylmethylglucosidopyridinium chloride*, m. p. 177°, $[\alpha]_D^{18}$ +42·4° in EtOH. *Glucosidopyridinium chloride* has m. p. 176°. 6-Triphenylmethyl-β-methylglucoside, m. p. 103—105°, $[\alpha]_D^{20}$ −45·5° in $CHCl_3$, is obtained from (I) and NaOH–MeOH. Triacetyl-β-xylosido- and triacetyl-β-*iso*rhamnosido-trimethylammonium bromide are very slowly decomposed by alkali. There appears little tendency towards the formation of a 1 : 3 ring. H. Wren.

Products of oxidation of *d*-galactose by atmospheric oxygen and ammoniacal copper oxide at room temperature. (Mlle.) Y. Garreau and J. Parrod (Compt. rend., 1932, 194, 657—659).—By passing air through an aq. solution of *d*-galactose containing $Cu(OH)_2$ and NH_3 (A., 1931, 852) are obtained $H_2C_2O_4$, glyoxaline, 4-d-*lyxotetrahydroxybutylglyoxaline*, m. p. 132° (*picrate*, m. p. 164°), and its 2-$OH\cdot CH_2$ derivative, m. p. 201°. J. W. Baker.

1 : 6-Acetodibromogalactopyranose. H. H. Schlubach and E. Wagenitz (Ber., 1932, 65, [*B*], 304—308).—The action of HBr on β-penta-acetylgalactose for 6 hr. at room temp yields 1 : 6-*acetodibromogalactopyranose* (I), m. p. 100°, $[\alpha]_D^{20}$ +203° (±0·5°) in $CHCl_3$, converted by Ag_2CO_3 and MeOH into *triacetyl-β-methylgalactoside* 6-*bromohydrin*, m. p. 92°, $[\alpha]_D^{21}$ −4·9° (±0·9°) in $CHCl_3$. The bromohydrin in MeOH is converted by H_2–Pd into *triacetyl*-β-*methyl*-d-*fucoside*, m. p. 98·5°, $[\alpha]_D^{20}$ −5·9° (±0·5°) in $CHCl_3$, hydrolysed by NaOMe in MeOH to β-*methyl*-d-*fucoside*, m. p. 120°, $[\alpha]_D^{20}$ −24·4 (±0·5°) in $CHCl_3$, and thence by *N*-H_2SO_4 to *d*-fucose. H. Wren.



(I.)

Preparation of crystalline methyl-*d*-gulosides by means of co-ordination compounds with calcium chloride. H. S. Isbell (Bur. Stand. J. Res., 1932, 8, 1—8).—By refluxing α-*d*-gulose, $CaCl_2,H_2O$, and anhyd. HCl in MeOH, neutralisation with $CaCO_3$, and evaporation are obtained the *compounds* α-S,$CaCl_2,2H_2O$, m. p. 185—190°, $[\alpha]_D^{20}$ +66·8° in H_2O, converted by crystallisation from EtOH into $(\alpha\text{-}S)_2,CaCl_2,3H_2O$, $[\alpha]_D^{20}$ +82·8° in H_2O, m. p., after becoming anhyd., 215° (decomp.); β-S,$CaCl_2,2H_2O$, m. p. 155°, $[\alpha]_D^{20}$ −45·7° in H_2O, converted by crystallisation from EtOH into $(\beta\text{-}S)_2,CaCl_2$, m. p. 238° (decomp.), $[\alpha]_D^{20}$ −64·9° in H_2O (S=methyl-*d*-guloside). From these, either by treatment with $Ag_2C_2O_4$ (α) or by crystallisation from hot H_2O (β), are obtained α-, +H_2O, m. p. 77°, $[\alpha]_D^{20}$ +109·4° in H_2O (converted by Ac_2O and pyridine into its Ac_4 derivative, m. p. 98°, $[\alpha]_D^{20}$ +97·3° in $CHCl_3$), and β-, m. p. 176°, $[\alpha]_D^{20}$ −83·3° in H_2O (Ac_4 derivative, m. p. 66—67°, $[\alpha]_D^{20}$ −32·1° in $CHCl_3$), -*methyl*-d-*guloside*. J. W. Baker.

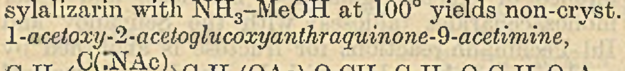
Modification of the Selivanov and Ihl–Pechmann reactions for fructose. C. I. Kruisheer (Rec. trav. chim., 1932, 51, 273—278).—The interference of glucose, galactose, mannose, and other monosaccharides (aldoses) with the Selivanov and Ihl–Pechmann reactions for fructose is abolished by oxidation of the aldose with I+NaOH and removal of excess I (as Cu_2I_2 by treatment with $CuSO_4$ and Na_2SO_3), prior to carrying out the reactions. The interference of di- and poly-saccharides is only partly abolished by this treatment, owing to the production of aldose during the heating with HCl and *m*-$C_6H_4(OH)_2$ or $NHPh_2$. The new technique can be applied to the determination of 0·05% of fructose in urine. H. Burton.

Mechanism of carbohydrate oxidation. XV. Behaviour of 3-glucosidoarabinose hepta-acetate towards aqueous solutions of potassium hydroxide. W. L. Evans and C. C. Clark (J. Amer. Chem. Soc., 1932, 54, 698—705; cf. this vol., 148).—The amounts of lactic acid and pyruvaldehyde obtained by the alkaline degradation of 3-glucosidoarabinose hepta-acetate are approx. the same as those from cellobiose and maltose under the same conditions, in accordance with the view that 3-glucosidoarabinose is an intermediate in the alkaline degradation of the disaccharides. The yields of HCO_2H from maltose and approx. 3·2*N*-KOH, and cellobiose and 2*N*-KOH, tend towards lower vals. than those for the hepta-acetate; since small amounts of HCO_2H in much AcOH are determined only with difficulty, the vals. reported only indicate the tendency of the reaction. C. J. WEST (*b*).

Anthraglucosides, especially aloin and peristaltin. F. HAUSER (Pharm. Acta Helv., 1931, 6, 79—85; Chem. Zentr., 1931, ii, 1709).—Aloin was boiled for 30 min. with aq. $Na_2B_4O_7$ and the dark, fluorescent (green) solution treated with HCl; the ppt. when recryst. (C_6H_6, AcOH) had m. p. 194—195°. Its yellow solution in dil. NaOH in absence of air exhibited a green fluorescence, and in air became red from the surface downwards, finally not fluorescing. Aëration of the alkaline solution followed by acidification affords aloe-emodin, m. p. 224°. Aloin is aloe-emodinanthranol-*d*-arabinoside (the 9- or 10-$CHO\cdot[CH\cdot OH]_3\cdot CH_2\cdot O$ derivative of 1 : 8-dihydroxy-3-hydroxymethylanthracene, preferably the 9-compound, the 10-derivative representing barbaloin). Peristaltin from Cortex Rhamni purshianæ behaves similarly; the glucosides are therefore rhamnosides of the anthranols of crysophanic acid, of frangulaemodin Me ether, and of cascarol. A. A. ELDRIDGE.

Composition of salinigrin. H. A. D. JOWETT (J.C.S., 1932, 721—722).—Salinigrin is identical with piceoside; its aglucone is *p*-hydroxyacetophenone. D. E. KAHN.

Coupling of hydroxyanthraquinones with salicin. A. MÜLLER (Ber., 1932, 65, [*B*], 329—337; cf. A., 1931, 826, 940).—Alizarin is converted by acetobromosalicin and Ag_2O in quinoline into 2-*acetosalicosylalizarin* [1 : 2-*dihydroxyanthraquinonyl* 2-o-β-*acetoglucoxybenzyl ether*], m. p. 188°, $[\alpha]_D^{20}$ —26·19° in $CHCl_3$, transformed by Ac_2O in pyridine into 2-*acetosalicosyl*-1-*acetylalizarin*, m. p. 198°, and by NaOH–EtOH into 2-*salicosylalizarin* (+0·5H_2O), m. p. 267—269° (*Na* salt). Treatment of acetosalicosylalizarin with NH_3–MeOH at 100° yields non-cryst. 1-*acetoxy*-2-*acetoglucoxyanthraquinone*-9-*acetimine*,



$$C_6H_4{<}\genfrac{}{}{0pt}{}{C(:NAc)}{CO\text{———}}{>}C_6H_2(OAc)\cdot O\cdot CH_2\cdot C_6H_4\cdot O\cdot C_6H_7O_5Ac_4,$$

m. p. 205° (decomp.) after darkening at 185°, transformed by boiling HCO_2H into 2-acetosalicosyl-1-acetylalizarin, m. p. 198°. With MeI and Ag_2O, acetosalicosylalizarin gives the *Me ether*, $C_{36}H_{34}O_{14},H_2O$, m. p. (indef.) 126—128° after softening at 85°, $[\alpha]_D^{20}$ —42·05° in $CHCl_3$. Chrysazin, acetobromosalicin, and Ag_2O in quinoline afford 1 : 8-*dihydroxyanthraquinonyl* 8-o-β-*acetoglucoxybenzyl ether* (8-*acetosalicosylchrysazin*), m. p. 159°, $[\alpha]_D^{20}$ —60·83° in $CHCl_3$, whence by Ac_2O in pyridine, 1-*acetyl*-8-*acetosalicosylchrysazin*, m. p. 206—207°. With NH_3–MeOH at 60—80°, acetosalicosylchrysazin gives the *imine dihydrate*, $C_{29}H_{25}O_9N,2H_2O$, m. p. 215°, whereas at 100° the *imine*, m. p. 245°, is produced. Treatment of the imine with Ac_2O in pyridine yields 9-*imino*-1 : 8-*dihydroxyanthraquinonyl* 8-o-β-*acetoglucoxybenzyl ether*, m. p. 140—142°, with some acetylacetosalicosylchrysazin. It is hydrolysed by dil. HCl (which does not attack acetylacetosalicosylchrysazin) to acetosalicosylchrysazin. With NaOAc and Ac_2O the imine yields an (?) anthrapyridine derivative. H. WREN.

[Hydrolysis of polysaccharides.] F. KLAGES (Ber., 1932, 65, [*B*], 302—304).—In reply to Freudenberg and others (A., 1930, 1025), it is shown mathematically that the differentiation between main valency chain mols. and small mols. cannot be effected by measurements of the rates of hydrolysis of polysaccharides. H. WREN.

Heavy metal catalysts. I. Fission of starch by artificial peroxidase. T. OMORI.—See this vol., 346.

Starch. A. ECKERT and A. MARZIN (J. pr. Chem., 1932, [ii], 133, 110—113).—Amylopectin is readily obtained from starch by treatment with boiling 0·1*N*-MeOH–HCl, whereby the amylose is dissolved. The yields of amylopectin from potato, arrowroot, maize, wheat, and rice starches are 83, 80, 75, 63, and 80%, respectively. H. BURTON.

Cellulose. J. DUCLAUX (Bull. Soc. chim. Belg., 1932, 41, 1—29).—A lecture.

Molecular structure of cellulose and of amylose. W. N. HAWORTH (Nature, 1932, 129, 365).—Evidence has been obtained that cellulose is a limited straight chain containing not more than 100 cellobiose or 200 glucose units, representing a mol. wt. of approx. 30,000. Similarly, the amylose portion of starch has 10 maltose or 20 α-glucose units in a limited chain with a mol. wt. ≯ 4000. L. S. THEOBALD.

Synthesis of ethylcellulose. S. N. USCHAKOV and I. M. SCHNEER (Plast. Massi, 1931, 1, 17—26).—Bleached cotton linters containing 92% of α-cellulose was mercerised with 20 mols. of 50% NaOH during 48 hr., the excess of alkali removed by pressing the material until it contained 110—125% of moisture, and the alkali-cellulose heated with 4—35 mols. of EtCl; C_6H_6 was added to keep the vol. const. when less than 12 mols. of EtCl were employed. The best results were obtained by using 6 mols. of EtCl. Increased length of heating (from 8 to 18 hr.) increases both the yield and the OEt content (up to 99% and 39%, respectively) and raising the temp. to 130° has a similar effect, but above 130° the yield diminishes and the product is coloured; the optimum temp. is 120—130°. Mercerisation with 40% alkali leads to diminished yields and impaired quality; increased duration of mercerisation causes a slight improvement. Removal of the residual H_2O by means of C_6H_6 or PhMe (moisture content 90—40%) raises the OEt content of the product at the expense of its tensile qualities and viscosity. The viscosity also decreases from 20 to 5 when the amount of EtCl is raised from 6 to 35 mols.; treatment of the finished material with H_2O or EtOH–NH_3 under pressure does not cause an appreciable diminution of its viscosity. Ethylcellulose, especially with an OEt content >45%, is very resistant to dilute H_2SO_4, NH_3, and H_2O. G. A. R. KON.

***X*-Ray examination of cellulose xanthate.** I. SAKURADA and K. HUTINO (Sci. Papers Inst. Phys.

Chem. Res. Tokyo, 1932, **17**, 294—296).—Cellulose xanthate giving a characteristic *X*-ray diagram different from that of alkali-cellulose and having a fibre period of 10·3±0·2 Å. has been prepared. The composition corresponds with the formula $C_{12}H_{19}O_9{\cdot}CS_2Na$. R. CUTHILL.

Chemical reactivity of certain classes of amines. M. GRUNFELD (Compt. rend, 1932, **194**, 892—895).—In agreement with views previously expressed (this vol., 365) the velocity of formation of substituted malonamides by interaction of bases of the type $R{\cdot}[CH_2]_2{\cdot}NH_2$ with $CH_2(CO_2Et)_2$ in EtOH at 100° is the same for *n*-amyl-, *n*-octyl-, and *n*-dodecyl-amines (24% in 30 hr.), a similar agreement (9·5% in 30 hr.) being observed with δ-amino-*n*-heptane, *cyclo*hexyl- and 2-methyl*cyclo*hexyl-amine [all of type $NH_2{\cdot}CH({\cdot}[CH_2]_2R')$. The following are described: s-*di*-n-*dodecyl*-, m. p. 120—121°; *di*(cyclo*hexyl*)-, m. p. 273° (block); *di*-(2-*methyl*cyclo*hexyl*)-, m. p. 265° (block), -*oxamide*: s-*phenyl*-n-*dodecylcarbamide*, m. p. 84—85°; s-*di*-n-*octyl*-, m. p. 126°; *di*-n-*dodecyl*-, m. p. 127°; *di*-(α-n-*propyl*-n-*butyl*)-, m. p. 147°; *di*(cyclo*hexyl*)-, m. p. 167·5° (block); and *di*-(2-*methyl*-cyclo*hexyl*)-, m. p. 210·5° (block), -*malonamide*. J. W. BAKER.

Some complex peroxides of hexamethylenetetramine. A. PERRET and A. M. KRAWCZYNSKI (Compt. rend., 1932, **194**, 376—378).—Interaction of hexamethylenetetramine and Bz_2O_2 in EtOH or $CHCl_3$ affords the *products* $C_6H_{12}N_4,Bz_2O_2$, m. p. 135—136°, and $2C_6H_{12}N_4,Bz_2O_2$, decomp. 193° after partial melting at 136°. Reaction of the base with BzO_2Ac gives the *compounds* $C_6H_{12}N_4,BzO_2Ac$, m. p. 134—135°, and $3C_6H_{12}N_4,BzO_2Ac$, decomp. 205°. Other additive products cannot be obtained by varying the proportions of the reactants. J. L. D'SILVA.

Configurations of α- and β-forms in the sugar series. II. Configuration of glucosamine. F. MICHEEL and H. MICHEEL (Ber., 1932, **65**, [*B*]. 253—258; cf. A., 1930, 455).—α-Acetobromo-*d*-xylose in C_6H_6 is transformed by NMe_3 in EtOH–H_2O into 2 : 3 : 4-*triacetyl*-β-*xylosidotrimethylammonium bromide*, m. p. 181° (decomp.), $[\alpha]_D^{20}$ −20·8° in H_2O. Similarly, acetobromo*iso*rhamnose affords 2 : 3 : 4-*triacetyl*iso-*rhamnosidotrimethylammonium bromide*, m. p. 162—163°, $[\alpha]_D^{18}$ +8·3° in H_2O. Acetobromoglucosamine hydrobromide and NMe_3 in EtOH yield non-cryst. *triacetylglucosaminotrimethylammonium bromide hydrobromide*, transformed by boiling HCl–MeOH into β-*glucosaminotrimethylammonium chloride hydrochloride*, m. p. 140—143°, $[\alpha]_D^{18}$ +16·0° in H_2O. Probably glucosamine has the glucose configuration. H. WREN.

Hydrolysis of chitin by hydrochloric acid. II. L. ZECHMEISTER and G. TÓTH (Ber., 1932, **65**, [*B*], 161—162; cf. A., 1931, 1279).—The isolation of chitotriose as the *undeca-acetate*, $C_{18}H_{24}O_{13}N_3Ac_{11}$, m. p. 315° (corr., decomp.), $[\alpha]_D^{20}$ +33° in AcOH, from the products of the hydrolysis of chitin by HCl is described. Fresh solutions of chitin in HCl (*d* 1·21) are lævorotatory, but become inactive at room temp. in about 8 hr. If the strongly lævorotatory solution is so diluted with ice that a ppt. is not produced, the val. of $[\alpha]_D$ decreases immediately. Determination of mol. wt. in boiling AcOH is advocated for peracetylated sugars. H. WREN.

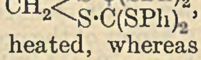
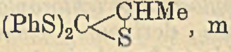
Preparation of diacetoneamine. T. SUZUKI and C. HORIE (Bull. Inst. Phys. Chem. Res. Tokyo, 1932, **11**, 383—388).—Addition of the following substances to $COMe_2$ saturated with NH_3 causes formation of the stated percentage of diacetoneamine in 24 hr. at room temp.: SO_2, 25; NH_4NO_2, 41; NH_4NO_3, 45· KCNS, 27; NH_4CNS, 31; NH_4OAc, 17%. R. S. CAHN.

Imide and amide chlorides of non-aromatic acids. I. Preparation of substituted glyoxalines. A. HEYMONS (Ber., 1932, **65**, [*B*], 320—329; cf. A., 1930, 613).—*Heptoethylamide*, b. p. 154°/15 mm., from heptoyl chloride and NH_2Et, is converted by gradual addition of PCl_5 to its solution in C_6H_6 at 0° into α-*chloro*-Δ^α^-*heptenylhepto*-NN′-*diethylamidine*, $C_5H_{11}{\cdot}CH_2{\cdot}C({:}NEt){\cdot}NEt{\cdot}CCl{:}CH{\cdot}C_5H_{11}$ (*chloroplatinate*, m. p. 119°), which passes slowly at room temp., very rapidly when heated, into 1-*ethyl*-4(5)-*amyl*-2-*hexylglyoxaline ethochloride*, m. p. 99° (*chloroplatinate*, m. p. 130°; corresponding *ethiodide*, m. p. 81°). When heated above its m. p. the ethochloride yields EtCl and 1-*ethyl*-4(5)-*amyl*-2-*hexylglyoxaline*, b. p. 193—199°/15 mm. (non-cryst. *picrate*, *hydrochloride*, and *oxalate*). NHEt·OAc and PCl_5 yield the chlorovinyl base, $C_8H_{15}N_2Cl$ (chloroplatinate, decomp. 188°), which is so sensitive towards alkali that when liberated from its hydrochloride it is mainly hydrolysed either to *acetylacet*-NN′-*diethylamidine*, b. p. 102—103°/12 mm. [*chloroplatinate*, m. p. 161° (decomp.); non-cryst. *picrate* and *hydrochloride*; *picrolonate*, m. p. 189°], or to NHEt·OAc. The chlorovinyl base is readily isomerised to the corresponding, very hygroscopic *ethochloride*, which loses EtCl when heated and forms 2-methyl-1-ethylglyoxaline (picrate, m. p. 171°). The instability of the chloroalkenyl bases diminishes with increasing size of the acid residue and increase in the number of C atoms of the group attached to N. *Hexoethylamide*, b. p. 152—154°/14 mm., yields α-*chloro*-Δ^α^-*hexenylhexo*-NN′-*diethylamidine* (*chloroplatinate*, m. p. 127°), from which are derived 1-*ethyl*-4-*butyl*-2-*amylglyoxaline ethochloride* (*chloroplatinate*, m. p. 135°), and 1-*ethyl*-4(5)-*butyl*-2-*amylglyoxaline*, b. p. 168—174°/14 mm. (non-cryst. *hydrochloride* and *oxalate*; *picrates*, m. p. 96° and 71°, respectively). $CH_2Ph{\cdot}CO{\cdot}NHEt$ yields the very unstable β-*chlorostyrylphenylacet*-NN′-*diethylamidine* [*chloroplatinate*, m. p. 171° (decomp.)] and 4(5)-*phenyl*-2-*benzyl*-1-*ethylglyoxaline*, b. p. 225—235°/14 mm. (non-cryst. *ethochloride*; *picrates*, m. p. 155—157° and 133—135°, respectively). Et·CO·NHEt yields the unstable α-*chloropropenylpropion*-NN′-*diethylamidine* (*chloroplatinate*, m. p. 195°) and 4(5)-*methyl*-1 : 2-*diethylglyoxaline*, b. p. 103—112°/14 mm. (*ethochloride*, m. p. 103°; *hydrochloride*; *picrate*). *Propionylpropion*-NN′-*diethylamidine*, b. p. 113—116°/13 mm. (non-cryst. *hydrochloride*; *picrate*, m. p. 76°), is described. 2-*Methyl*-1-*benzylglyoxaline benzyl chloride*, m. p. 208°, has been prepared. H. WREN.

Chemistry of three-carbon system. XXVIII. Nitriles of butenoic and hexenoic acids. Analysis of unsaturated nitriles by halogen addition. R. A. LETCH and R. P. LINSTEAD (J.C.S., 1932, 443—456; cf. A., 1929, 1294).—Nitriles of butenoic, *n*- and *iso*-hexenoic acids are prepared; bromometric and iodometric methods for analysing the mixtures of αβ)- and βγ-unsaturated nitriles are discussed. Corresponding nitriles are obtained from unsaturated amides. Δ^{α}-n-*Hexenoamide*, m. p. 122°, yields Δ^{α}-*hexenonitrile*, b. p. 50°/10 mm.; Δ^{β}-n-*hexenoamide*, m. p. 86°, yields Δ^{β}-*hexenonitrile*, b. p. 58/15 mm. Dehydration of *n*-valeraldehyde cyanohydrin yields α-*hydroxy*-n-*hexonitrile*, b. p. 116°/14 mm.; α-*cyano*-Δ^{α}-*hexenoic acid*, m. p. 102°, and *iso*valeraldehyde cyanohydrin yield mixtures of nitriles. Tautomeric changes undergone by nitriles with alkalis are followed quantitatively; heat has little effect. Δ^{β}-*n*-Hexenonitrile and NaOEt gave β-*ethoxy*-n-*hexenonitrile*, b. p. 82°/11 mm. D. E. Kahn.

Syntheses with diazomethane. VII. Reaction of aldehydes and ketones. F. Arndt, J. Amende, and W. Ender.—See this vol. 383.

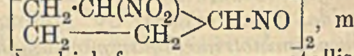
Supposed optical activity of ethyl diazosuccinate. II. A. Weissberger and H. Bach (Ber., 1932, 65, [*B*], 265—267; cf. this vol., 151).—Homogeneous *Et diazosuccinate*, m. p. about −24°, [α] ±0°, is prepared by diazotising Et *l*-aspartate in presence of H_2SO_4, washing the product in Et_2O with NH_3 and then with H_2O, distilling in a high vac., and crystallisation from a mixture of Et_2O and light petroleum. The " optically active ester " is treated with H_2 in presence of colloidal Pd and the product distilled in a high vac., thus giving Et *d*-malate, α_D +7·92° or +8·06° (*l*=1). H. Wren.

Aliphatic diazo-compounds. III. Action of aliphatic diazo-compounds on thion esters and a new type of ethane derivatives. A. Schönberg, S. Nickel, and D. Cernik (Ber., 1932, 65, [*B*], 289—293; cf. A., 1931, 218).—Addition of Ph_2CS_3 to diazomethane in Et_2O yields 4 : 4 : 5 : 5-*tetraphenylthioltrimethylene* 1 : 3-*disulphide*,  $CH_2{<}\genfrac{}{}{0pt}{}{S\cdot C(SPh)_2}{S\cdot C(SPh)_2}$, decomp. about 140° when rapidly heated, whereas with diazoethane the product is 1 : 1-*diphenylthiol*-2-*methylethylene sulphide*,  $(PhS)_2C{<}\genfrac{}{}{0pt}{}{CHMe}{S}$, m. p. 64—67° to a turbid liquid. 4 : 5-*Dimethylthiol*-4 : 5-*di*-α-*naphthyltrimethylene* 1 : 3-*disulphide*, m. p. (indef.) 140° (decomp.), is obtained from $C_{10}H_7\cdot CS_2Me$. Reversible changes in colour are observed when the following solutions are heated: $C_{10}H_7\cdot CS_2Me$ in BzOEt; Ph diphenyldithioacetate in $C_6H_4Me_2$; Ph_2CS_3 in BzOEt; Ph_2 diselenide in PhMe. H. Wren.

Thermal reactions of *cyclo*paraffins and *cyclo*olefines. G. Egloff, H. T. Bollman, and B. L. Levinson (J. Physical Chem., 1931, 35, 3489—3552).—The literature on the reactions of hydrogenated cyclic compounds (naphthenes) and unsaturated compounds of the type of tetrahydronaphthalene and *cyclo*hexene at various temp. and pressures and in the presence of different catalysts is reviewed. The reactions which occur are: C–C scission, hydrogenation or dehydrogenation, polymerisation or depolymerisation, and isomeric change. Any or all of these may take place when a hydrocarbon is treated with some activating agent, such as heat or a reagent. L. Kelley (*c*).

Slow combustion of 1 : 3-dimethyl*cyclo*pentane in heterogeneous system. G. Chavanne and O. Miller (Bull. Soc. chim. Belg., 1931, 40, 611—625; cf. A., 1927, 452).—Slow oxidation of the liquid at 80° yields a number of products, which have been investigated. AcOH, α-keto-β-methyl-*n*-hexoic acid, and Me *iso*amyl ketone preponderate. C. W. Davies.

Preparation of 1 : 1-dimethyl*cyclo*hexane and 1 : 1-dimethyl*cyclo*pentane. Stability of these hydrocarbons to oxygen. G. Chavanne, M. O. Miller, and (Mlle.) Cornet (Bull. Soc. chim. Belg., 1931, 40, 673—688).—Reduction of 1 : 1-dimethyl-5-chloro-Δ^4-*cyclo*hexen-3-one by H_2 in presence of Ni at 215° (or less well by Adams' method) gives mainly 1 : 1-dimethyl*cyclo*hexan-3-one (I), b. p. 178—178·5°/748 mm., 72—73°/25 mm. [semicarbazone, m. p. 219° (lit. 203°)], and 1 : 1-dimethyl*cyclo*hexan-3-ol (II) (p-*nitrobenzoyl* derivative, m. p. 83°), with a little 1 : 1-dimethyl*cyclo*hexane (III) and unsaturated hydrocarbons. (I) affords (II) on reduction in presence of Pt. Dehydration of (II) by *p*-toluenesulphonic acid gives a mixture of 1 : 1-dimethyl-Δ^2- or -Δ^3-*cyclo*hexane, readily reduced to (III). 1-Chloro-1-methyl*cyclo*pentane and MgMeI give 1-methyl-Δ^1-*cyclo*pentene and some (10%) 1 : 1-dimethyl*cyclo*pentane (IV). Catalytic reduction of 1 : 1-dimethyl*cyclo*pentan-2-one affords the alcohol (*allophonate*, m. p. 158—159°), which with *p*-toluenesulphonic acid at 145° gives 1 : 2-dimethyl- and some 1 : 1-dimethyl-*cyclo*pentene, both reduced catalytically to the saturated compounds. Cyclisation of ββ-dimethyladipic acid [prepared by oxidation of the mixture of (I) and (II) with HNO_3] by Al_2O_3 gives 1 : 1-dimethyl*cyclo*hexan-3-one, reduced in presence of Ni at 165° to the corresponding *alcohol*, b. p. 157—161°, which with Al_2O_3 at 350° yields 1 : 1-dimethyl-Δ^2-*cyclo*pentene, readily reduced in AcOH in presence of Pt-black to (IV), m. p. −77°. (III) and (IV) are stable to O_2 at 110° and 80°, respectively. It is considered that O_2 attacks hydrocarbons at the CH⋮ group. R. S. Cahn.

Reaction of unsaturated hydrocarbons with nitrous anhydride and nitrogen peroxide. Products of the action of nitrous anhydride on *cyclo*pentene. N. I. Demjanov and V. V. Williams (Bull. Acad. Sci. U.S.S.R., 1931, 1123—1140; cf. A., 1899, i, 845).—Previous work on this subject is discussed. The action of N_2O_3 on *cyclo*pentene in Et_2O yields: (1) the ψ-*nitrosite*,  $\left[\genfrac{}{}{0pt}{}{CH_2\cdot CH(NO_2)}{CH_2 - CH_2}{>}CH\cdot NO\right]_2$, m. p. 104—105° (decomp.), which forms an uncrystallisable nitrolamine when treated with NH_2Ph in EtOH, and is converted by the action of KOMe into a mixture of nitro*cyclo*pentene, b. p. 105—108°/30 mm., d_{20}^{20} 1·1305, with methoxynitro*cyclo*pentane (not obtained pure); with NaOMe, the latter gives the *Na* derivative, $OMe\cdot CH_2\cdot C_3H_6\cdot CNa\cdot NO_2$. (2) A liquid product which gives *cyclo*pentanone, 1 : 2-*diamino*cyclo*pentane* (*picrate*, m. p. 221°), and 1-*hydroxy*-2-*amino*cyclo-*pentane*, m. p. 63—64° (*picrate*, m. p. 155°), on reduction with Sn and HCl. T. H. Pope.

Slow combustion of 1 : 3-dimethyl*cyclo*hexane in heterogeneous system. G. Chavanne, (Mme.) Pahlavouni, and (Mlle.) Katzenstein (Bull. Soc.

chim. Belg., 1931, 40, 626—641; cf. A., 1930, 768).—Absorption of O_2 at room temp. is extremely slow in diffused light, more rapid in sunlight. On prolonged treatment with O_2 at 100° the liquid gives mainly 1 : 3-dimethyl*cyclo*hexanol, with AcOH, a methyl-ε-ketoheptoic acid, and other products.

C. W. Davies.

Synthesis and nitration of phenyl*cyclo*hexane. O. Neunhoeffer (J. pr. Chem., 1932, [ii], **133**, 95—109).—*cyclo*Hexyl chloride, C_6H_6, and $AlCl_3$ give a mixture of (mainly) phenyl*cyclo*hexane (I), some *p*-di*cyclo*hexylbenzene (II), m. p. 102° [oxidised by HNO_3 (*d* 1·04) to *p*-$C_6H_4(CO_2H)_2$], and a little 1-phenyl-2-methyl*cyclo*pentane [oxidised by O_3 (above 15% concn.) to 2-methyl*cyclo*pentane-1-carboxylic acid]. The yield of (I) increases and that of (II) diminishes when a large excess of C_6H_6 is used. Nitration of (I) with Ac nitrate in AcOH gives *p*- (III), b. p. 142°/0·5 mm., and *o*-, b. p. 113°/0·5 mm., m. p. 45°, -nitrophenyl*cyclo*hexanes in the ratio 78 : 22 (cf. Mayes and Turner, A., 1929, 550); (III) exists in trimorphous forms (m. p. 54°, 56°, and 57°). Electrolytic reduction of (III) gives *p-cyclo*hexylaniline, converted by the usual methods into (I), m. p. 6°, *p*-iodophenyl*cyclo*hexane, b. p. 117°/0·5 mm., m. p. 4°, and p-cyclo*hexylbenzonitrile*, b. p. 123°/0·5 mm., m. p. 41°. o-cyclo*Hexylaniline*, b. p. 106°/0·5 mm., m. p. 13° (*Ac*, m. p. 101°, and *Bz*, m. p. 154°, derivatives), is also prepared by electrolytic reduction of the NO_2-derivative.

H. Burton.

Benzylidene*cyclo*hexane. D. N. Kursanov (J. Gen. Chem. Russ., 1931, **1**, 926—932).—Mg *cyclo*hexyl bromide reacts with PhCHO giving 34% of phenyl*cyclo*hexylcarbinol and 18% of $CH_2Ph{\cdot}OH$; the carbinol was converted into the K xanthate, which gave 70% of the corresponding *Me* ester, m. p. 54—55°, by the action of MeI in C_6H_6. The ester when heated under reduced pressure gave *benzylidene*cyclo*hexane*, b. p. 117—118°/10 mm., d_4^{20} 0·9579, oxidised by $KMnO_4$ to *cyclo*hexanone and BzOH. The hydrocarbon differs from that previously obtained from *cyclo*hexene and $CH_2Ph{\cdot}OH$ (A., 1931, 349), which is considered to be identical with Auwers and Treppmann's benzyl*cyclo*hexene (A., 1915, i, 789).

G. A. R. Kon.

Synthesis of homologues of benzene by the Friedel–Crafts method. B. V. Tronov, (Mlle.) L. V. Ladigina, and I. M. Karpenko (J. Gen. Chem. Russ., 1931, **1**, 910—916).—Study of the formation of CH_2Ph_2 from C_6H_6 and CH_2PhCl in the presence of $AlCl_3$, $SiCl_4$, $SnCl_4$, PCl_3, $SbCl_3$, and $SbCl_5$ suggests that the activity of the halogen in the catalyst and the capacity of the central atom to assume a higher valency are of no importance (cf. A., 1931, 610). All the compounds capable of catalysing the reaction have a tendency to form mol. complexes and this is held to support the view that the formation of such a complex is the first stage in the reaction. This takes place owing to the attraction between the positive nucleus of the central atom of the catalyst and one of the (alternate) C atoms of the C_6H_6 ring which, according to Lowry's theory, have a complete octet of electrons. As the result, the H atom attached to the C in question is more readily removed (cf. Dougherty, A., 1929, 421). Compounds such as PCl_3 and $SbCl_3$ are also capable of complex formation, but the central atom is attracted only to the positively-charged C atoms of the C_6H_6 ring, and this will tend to increase the control of the latter over the attached H atoms; these compounds cannot therefore catalyse the reaction between C_6H_6 and CH_2PhCl. Complex formation between the catalyst and the C_6H_6 ring of CH_2PhCl, with a consequent increase in the reactivity of the halogen, may explain the much greater reactivity of CH_2PhCl as compared with EtBr; the activities of the halogen in the two compounds are approx. equal, but EtBr is incapable of complex formation.

G. A. R. Kon.

Solubility of water in benzene, toluene, and *cyclo*hexane. D. N. Tarassenkov and E. V. Poloshinzeva (Ber., 1932, **65**, [*B*], 184—186).—Known wts. of H_2O and hydrocarbon are heated until complete dissolution is attained and the temp. of appearance and disappearance of turbidity are determined. The solubilities of H_2O in C_6H_6, PhMe, and *cyclo*hexane are recorded for the temp. intervals, +5° to 73°, −9° to +93°, and +14° to +53°, respectively.

H. Wren.

Steric hindrance in the hydrolysis of benzylidene chloride. G. Lock and F. Asinger.—See this vol., 345.

Nitrobenzenesulphonhydrazides. A. A. M. Witte (Rec. trav. chim., 1932, **51**, 299—319).—Curtius and Lorenzen's interpretation (A., 1899, i, 148) of the reaction between benzenesulphonhydrazide and I is incorrect, since *s*-dibenzenesulphonhydrazide is unaffected by conc. HI in boiling EtOH. *m*-$NO_2{\cdot}C_6H_4{\cdot}SO_2Cl$ (in C_6H_6) added to cold N_2H_4,H_2O gives m-*nitrobenzenesulphonhydrazide* (I), m. p. 126—127° (decomp.) [*Ac*, m. p. 155° (decomp.); *Bz*, m. p. 177°; *benzylidene*, m. p. 153°; iso*propylidene*, m. p. 153° (decomp.); *anisylidene*, m. p. 134°; *cinnamylidene*, m. p. 188° (decomp.); *salicylidene*, m. p. 168°; *piperonylidene*, m. p. 171°; *benzenesulphonyl*, m. p. 180—185°, and m-*nitrobenzenesulphonyl*, decomp. 200—210° without melting, derivatives], converted by I in boiling EtOH into 3 : 3′-dinitrodiphenyl disulphoxide (II). *p*-$C_6H_4Cl{\cdot}NO_2$ and Na_2S_2 give $(p\text{-}NO_2{\cdot}C_6H_4{\cdot}S{\cdot})_2$, and $(p\text{-}NO_2{\cdot}C_6H_4)_2S$, which are oxidised by fuming HNO_3 to *p*-$NO_2{\cdot}C_6H_4{\cdot}SO_3H$ [NH_4; *Na* (+$3H_2O$); *Ca* (+$8H_2O$), and *Ba* (+$3H_2O$), salts] and 4 : 4′-*dinitrodiphenyl sulphoxide*, m. p. 173° [corresponding sulphone, m. p. 254° (lit. 282°)], respectively. p-*Nitrobenzenesulphonhydrazide* (III), m. p. 146—147° (decomp.) [*Ac*, m. p. 218°; *Bz*, m. p. 227°; *benzylidene*, m. p. 142°; iso*propylidene*, m. p. 172°; *anisylidene*, m. p. 160°; *salicylidene*, m. p. 178—179°; *piperonylidene*, m. p. 185°, and p-*nitrobenzenesulphonyl*, decomp. 235—236° (darkens slowly above 180°), derivatives], is similarly converted by I into 4 : 4′-*dinitrodiphenyl disulphoxide* (IV), m. p. 159°. (I) and (III) heated to about 145° or at about 110° in presence of a little I, give (II) and (IV), respectively. 2 : 2′-*Dinitrodiphenyl disulphoxide*, chars about 200°, is obtained in small amount from I and *o*-nitrobenzenesulphonhydrazide, m. p. 97° (lit. 101°) (Ac_2, m. p. 194°; *benzylidene*, m. p. 91°; iso*propylidene*, m. p. 144°, and *piperonylidene*, m. p. 177°, derivatives). p-*Nitrobenzenesulphon-phenylhydrazide*, m. p. 150°, and -*p*-nitrophenylhydrazide, m. p. 172—173° (lit. 160° and 171—172°), and 4-*chloro*-2-*nitrobenzenesulphonphenylhydrazide*, m. p. 151°, are described. Oxidation of the reaction product from 1 : 4-dichloro-2-nitrobenzene and Na_2S_2 with fuming HNO_3 gives 4-chloro-2-nitrobenzenesulphonic acid (the hydrazide could not be prepared) and a little 4 : 4′-dichloro-2 : 2′-dinitrodiphenyl sulphoxide. H. Burton.

Spectrochemistry of acetylenic derivatives. K. von Auwers (Ber., 1932, 65, [*B*], 146—153).—Re-examination of the data of Krestinski and Persianzeva (A., 1931, 1412), in such a manner as to eliminate the influence of variation in mol. wt. shows that their conclusion that each new conjugation CPh⋮C increases the exaltations in refractive and dispersive power is invalid and that the supposition that the high exaltations are due in part to the alcoholic nature of the compounds is without foundation. Comparison of the recorded spectroscopic data of a series of ethylenic and acetylenic substances indicates no marked difference in the exaltation of the refractive indices for compounds with a sample conjugation except in the instances of ethylenic and acetylenic ketones and propiolonitrile. Similar results are obtained with compounds with three unsaturated groups, exceptions being $\Delta^{\alpha\gamma}$-α-phenylpentadi-inene and phenylpropiolonitrile. Diphenyldiacetylene exhibits an unusually high exaltation, but comparison with diphenylbutadiene is complicated by the occurrence of the latter in three forms. The dispersive power of acetylenic compounds is usually less enhanced than that of ethylenic derivatives. The consts. of *cis-cis-* and *cis-trans-*diphenylbutadiene, Ph propargyl ether, and Et propiolate are recorded. H. Wren.

***p*-Bromophenylacetylene.** C. Dufraisse and A. Dequesnes (Bull. Soc. chim., 1931, [iv], 49, 1880—1882).—*p*-Bromoacetophenone and PCl_5 afford about 52% of αα-*dichloro*-α-p-*bromophenylethane*, b. p. 126—127°/18 mm., converted by 25% EtOH–KOH into p-*bromophenylacetylene*, m. p. 64—65°, b. p. 88—90°/16 mm., and α-chloro-*p*-bromostyrene, b. p. 118—122°/18 mm., yielding with Br a *dibromide*, m. p. 55—56°, and with KOAc in EtOH a white substance, m. p. 92°. R. Brightman.

Orientation effects in diphenyl series. XI. Quantitative mono- and di-nitration of 4 : 4′-difluorodiphenyl. (Miss) F. R. Shaw and E. E. Turner (J.C.S., 1932, 509—513).—Mononitration of 4 : 4′-difluorodiphenyl (I) gives not less than 97% of 2-NO_2-compound (II). Nitration of (II) yields 35—36% of 4 : 4′-*difluoro*-2 : 2′-*dinitrodiphenyl* (III), m. p. 165°, and 64—65% of 2 : 3′-$(NO_2)_2$-compound; the action of KOH on the nitration product produces 4-*fluoro*-2 : 3′-*dinitro*-4′-*ethoxydiphenyl*. The synthesis of (III) is described. Dinitration of (I) is more complicated than for Br and Cl analogues. D. E. Kahn.

2-Nitro-4′ : 4″-dimethyltriphenylmethane. I. Tanasescu and A. Silberg (Bull. Soc. chim., 1932, [iv], **51**, 97—99).—Condensation of *o*-nitrobenzylidene chloride with PhMe in presence of $AlCl_3$ affords 2-*nitro*-4′ 4″-*dimethyltriphenylmethane*, oxidised by CrO_3–H_2SO_4 to 2-nitrobenzophenone-4′-carboxylic acid, m. p. 234—235°. HNO_3 or $KMnO_4$ did not oxidise the nitrotriphenylmethane. R. Brightman.

Polycyclic aromatic hydrocarbons. IX. Synthesis of methyl and *iso*propyl homologues of 1 : 2-benzanthracene. J. W. Cook (J.C.S., 1932, 456—472; cf. A., 1930, 903; this vol., 153).—6- and 7-iso*Propyl*-1 : 2-*benzanthracenes*, m. p. 130° and 125°, respectively (*picrates*, m. p. 118°, 152°; *quinones*, m. p. 94°, 114°), are synthesised from 1-*cuminoyl*-2-*naphthoic* (I), m. p. 215°, and 2-*cuminoyl*-1-*naphthoic* (II) *acid*, m. p. 160°, respectively. (I) and (II) (*acetoxylactones*, m. p. 215° and 126°, respectively) are derived from cumene and naphthalene-1 : 2-dicarboxylic anhydride. 3-(III) and 10-iso*Propyl*-1 : 2-*benzanthracenes* (IV), m. p. 92° and 94°, respectively, are synthesised, the latter from 1 : 2-benz-10-anthrone by the Grignard method. 1-iso*Propylnaphthalene* (V), b. p. 132°/12 mm. (*picrate*, m. p. 83·5—86°), is formed from the *dimeride* of 1-*iso*propenylnaphthalene, m. p. 194°. (V) condensed with phthalic anhydride forms 4′-iso*propyl*-1′-*naphthoyl*-2-*benzoic acid*, m. p. 206—208°, from which the *quinone* of (III), m. p. 154°, is derived. Pyrolysis of Me derivatives of 1 : 2-benzanthracene is described and the accompanying intramol. migrations are discussed. The following are described: 1 : 2-*benzanthracene*, m. p. 158—159°; 6-, 7-, 2′-, and 3′-*methyl*-1 : 2-*benzanthracene*, m. p. 151°, 182°, 149°, 160° [*picrates*, m. p. 152°, —, 180°, 144°; *quinones*, m. p. 174° (not new), 167°, 189°, 168°]; 6 : 7-, 2′ : 6-, 2′ : 7-, 3′ : 6-, and 3′ : 7-*dimethyl*-1 : 2-*benzanthracenes*, m. p. 174°, 164°, 236°, 186°, 189° (*picrates*, m. p. 170°, 199°, —, —, —; *quinones*, m. p. 193°, 160°, 177°, 205°, 157°); 1-(3′ : 4′-*dimethylbenzoyl*)-2-*methylnaphthalene*, m. p. 109°; 1-*benzoyl*-2 : 6- and -2 : 7-, 1-m-*toluoyl*-2 : 6- and -2 : 7-, 1-p-*toluoyl*-2 : 6- and -2 : 7-*dimethylnaphthalenes*, m. p. 84°, 91°, 82°, 115°, 109°, 98°. D. E. Kahn.

Hydrogenation of rubrene. Two stereoisomeric dihydrorubrenes, $C_{42}H_{30}$. C. Dufraisse, B. Masumoto, and R. Buret (Bull. Soc. chim., 1932, [iv], 51, 74—80).—With gaseous HI in Et_2O rubrene affords about 70—95% of a mixture of two stereoisomeric *dihydrorubrenes*, needles, m. p. 241—242° (paraffin bath), 249—250° (block), and massive crystals, m. p. 224—225° (paraffin bath), 230—231° (block), together with some ψ-rubrene. The needles, m. p. 241—242°, are converted into the massive crystals by heating with Na amyloxide in amyl alcohol. Hydrogenation with Na and amyl alcohol similarly affords a mixture of the dihydrorubrenes together with three other substances, m. p. 214°, 241°, and 307°. The dihydrorubrenes were not further hydrogenated with HI at 150°; at 180° a small amount of substance, m. p. about 110°, was formed. Hydrogenation with Na in anhyd. media, *e.g.*, xylene, also affords a mixture of the dihydrorubrenes on decomp. with H_2O. It is suggested that addition takes place in 1 : 4-positions, yielding two racemic diastereoisomerides. R. Brightman.

Hydrocarbons, isomeric with rubrene obtained by reduction of 9 : 11-diphenyl-9 : 12 : 10 : 11-dibenzo-9 : 11-dihydronaphthac-

ene. M. Badoche (Compt. rend., 1932, 194, 891—892).—Decomp. of the Na additive compound (by Schlenk's method, A., 1914, i, 396) of the hydrocarbon $C_{42}H_{26}$ (I), obtained by dehydrogenation of rubrene, with H_2O, affords the *hydrocarbon* $C_{42}H_{28}, +2C_6H_6$, m. p. 155—156°, and solvent-free, m. p. 302—303°, and a (?) stereoisomeric *form*, $+C_6H_6$, m. p. 216—217°, and solvent-free, m. p. 337—338°, isomeric with rubrene, which are oxidised by PbO to (I) and hence result from the normal addition of Na to the double linking. On the basis of Dufraisse and Enderlin's structure for (I) (this vol., 261) these two hydrocarbons are probably stereoisomeric forms of 9 : 11-diphenyl - 9 : 12 : 10 : 11-dibenzo-9 : 10 : 11 : 12-tetrahydronaphthacene. J. W. Baker.

Modified Curtius reaction. VI. Reaction with chaulmoogric and hydnocarpic acids and their dihydro-derivatives. C. Naegeli and E. Vogt-Markus (Helv. Chim. Acta, 1932, 15, 60—75).—This reaction is readily applied to the acid chlorides derived from the above acids providing active NaN_3 (prep. described) is used. Chaulmoogryl chloride (best prepared from purified PCl_3 and the acid at 70—80°) (p-*chaulmoogrylamidoazobenzene*, m. p. 123°, sinters at 115°) thus affords μ-(Δ²-cyclo*pentenyl*)-*dodecylamine*, b. p. 190°/15 mm., m. p. 18° (45% yield) [*Ac* derivative, m. p. 60°, $[\alpha]_D^{19}$ +45·3° in EtOH (45% yield), together with a *substance*, m. p. 81—92°; *hydrochloride* (78% yield), m. p. 151°, $[\alpha]_D^{21}$ +55·0° in EtOH], converted by KNCO into the corresponding *carbamide*, m. p. 107°. Hydnocarpic acid (prep. from hydnocarpus oil described) is similarly converted into κ-(Δ²-cyclo*pentenyl*)*decylamine*, b. p. 169—170°/12 mm., m. p. 5—6° [*Ac* derivative, m. p. 53—57° (together with the above *substance*, m. p. 80—90°); *hydrochloride*, m. p. 146°, $[\alpha]_D^{20}$ +59·55°; *chloroplatinate*; *picrate*, m. p. 109°; *carbamide*, m. p. 112°]. Dihydrochaulmoogric acid (by reduction of chaulmoogric acid with PtO_2 and H_2 at 2—3 atm.) affords μ-cyclo*pentyldodecylamine*, b. p. 187°/12 mm., m. p. 13·5—15° [*Ac* derivative, m. p. 73° (and substance, m. p. 80—90°); *hydrochloride*, m. p. 195° (previous softening); *chloroplatinate*; *picrate*, m. p. 110°; *carbamide*, m. p. 109°], whilst dihydrohydnocarpic acid gives κ-cyclo*pentyldecylamine*, b. p. 187°/16 mm., m. p. 2—3·5° [*Ac* derivative (43% yield), m. p. 64° (and a *substance*, m. p. 83—87°); *hydrochloride*, m. p. 162° (and a *substance*, m. p. 85—88°); *chloroplatinate*; *picrate*, m. p. 124°; *carbamide*, m. p. 122·5°]. J. W. Baker.

p-Toluenesulphonates as derivatives for the identification of aromatic amines. C. R. Noller and P. Liang (J. Amer. Chem. Soc., 1932, 54, 670—673).—The *p*-toluenesulphonates of aromatic amines can, in general, be readily prepared in a pure state and are satisfactory derivatives for identification. The following *p*-toluenesulphonates are described, of which those of the italicised bases are new: NH_2Ph, m. p. 238·4° (all m. p. are corr.); *o*-, m. p. 189·7—190·5°; and *m*-toluidine, m. p. 174·6—176·1°; p-*toluidine*, m. p. 197·7—199·2°; m-4-*xylidine*, m. p. 180·4—181·3°; *o*-, m. p. 192·9—193·6°, and *p*-chloroaniline, m. p. 213—231°; m-*chloroaniline*, m. p. 209·8—210·3°; o-, m. p. 206·1—206·6°, m-, m. p. 204·1—205·0°, and p-*bromoaniline*, m. p. 214·2—234·2°; o-, an oil, m-, m. p. 213·5—215·5°, and p-*nitroaniline*, m. p. 232·2—234·7°; o-, m. p. 224·7—226·2°, and m-*aminophenol*, an oil; *p*-aminophenol, m. p. 252·1—253·6°; o-, m-, and p-*aminobenzoic acids*, m. p. 224·1—224·6°, 255·9—256·5°, and 236·5—241·5°, respectively; p-*aminoacetophenone*, m. p. 177·8—179·3°; α-, m. p. 248·4—249·9°, and β-$C_{10}H_7 \cdot NH_2$, m. p. 217·3—219·1°; o-, m. p. 194·1—195·6°, and p-*aminodiphenyl*, m. p. 253·8—254·9°; $NH_2 \cdot CH_2Ph$, m. p. 184·5—185·5°; *dibenzylamine*, m. p. 158·3—159·3°; *tribenzylamine*, m. p. 205—207·7°; *benzylaniline*, m. p. 148·3—148·8°; *dibenzylaniline*, oil; o-, m-, and p-*phenylenediamine*, m. p. 267·3—268·8°, 296·8—297·8°, and above 340°, respectively; 2 : 4-*diaminotoluene*, m. p. 270·8—271·3°. C. J. West (*b*).

Ternary compounds of sulphur dioxide with ketones and amines. F. Feigl and E. Feigl (Z. anorg. Chem., 1931, 203, 57—63).—The following *compounds* are described: $C_{10}H_7 \cdot NH_2,SO_2,COMe_2$ (decomp. 110—120°); $(C_6H_4)_2(NH_2)_2,SO_2,COMe_2$ (decomp. 108—110°); $(C_6H_4)_2(NH_2)_2,SeO_2,COMe_2$; $C_6H_4(NO_2) \cdot NH_2,SO_2,COMe_2$ (m. p. 108°); $C_6H_4Me \cdot NH_2,SO_2,COMe_2$ (m. p. 77—78°); $C_5H_5N,SO_2,COMe_2$ (m. p. 80—82°); $C_9H_7N,SO_2,COMe_2$ (m. p. 85—86°); $C_5H_{10}N,SO_2,COMe_2$; $NH_2Me,SO_2,COMe_2$; $CH_2Ph \cdot NH_2,SO_2,COMe_2$; $Ph \cdot [CH_2]_2 \cdot NH_2,SO_2,COMe_2$; $N(CH_2Ph)_3,SO_2,COMe_2$ (m. p. 118—119°); $NPh{:}CHPh,SO_2,COMe_2$ (m. p. 112—113°); $C_{10}H_7 \cdot NH_2,SO_2,COMeEt$ (m. p. 83—84°); NH_2Ph,SO_2,C_6H_9OMe (decomp. 110°) (from aniline and 2-methyl*cyclo*hexanone), $NH_2Ph,SO_2,COPhMe$, and $C_6H_4Me \cdot NH_2,SO_2,COPhMe$ (m. p. 108—110°). E. S. Hedges.

Addition of cyclic amines to butenonitriles [allyl cyanide]. A. Mevis (Bull. Soc. chim. Belg., 1931, 40, 726—736).—Allyl cyanide and NH_2Ph at 150—180° in presence of catalysts, best CuCl or CuO, afford β-*anilinobutyronitrile*, m. p. 57—58°, b. p. 169—172°/13—14 mm. (*NO*-derivative), in 40% yield; hot, conc. HCl partly decomposes and partly hydrolyses this to the *hydrochloride* of β-*anilinobutyric acid* [*Et* ester, b. p. 160·8°/13·5 mm. (*hydrochloride*, m. p. 172—173°); *anilide*, m. p. 212—213°]. *p*- and (more slowly) *o*-toluidine give similarly β-p- and -o-*toluidinobutyronitrile*, m. p. 67—68° and 78—79·5°, b. p. 176—178°/11·5 mm. and 173—176°/11·6 mm., respectively. $NHPh_2$ isomerises the cyanide to crotononitrile. R. S. Cahn.

Analogy between the benzidine change and the dissociation of oxides of nitrogen. New reagent for the recovery of secondary bases from nitrosoamines and for purifying amines. E. C. S. Jones and J. Kenner (J.C.S., 1932, 711—715).—Objections to regarding the decomp. of hydrazobenzene into NH_2Ph and azobenzene and the benzidine change as due to dissociation into radicals are refuted. The reduction of nitrosoamines in strongly acid (HA) solution is regarded as preceded by dissociation into the radicals NHPhRA and NO; this view is supported by the smooth decomp. of the NO-derivatives of NHPhMe, NHPhEt (I), $NHPh_2$, piperidine (II), and triacetoneamine by CuCl in conc. HCl at room temp. into NO and the free base. The NO-derivatives of

(I) and (II) have b. p. 93°/0·5 mm. and 85°/0·5 mm., respectively. CuCl in EtOH–HCl forms colourless, complex *salts* (1 mol. of CuCl and 1 mol. of hydrochloride) with the following bases: NHPhMe, m. p. 210—220° (decomp.); (I), m. p. 120—130° (decomp.); NH_2Ph, m. p. 150—160° (decomp.); *m*-toluidine, m. p. 131—140° (decomp.) *vic.-m*-xylidine, m. p. 180—190° (decomp.). CuCl in conc. aq. HCl can be used to purify commercial samples of the last four bases. R. S. CAHN.

Molecular compounds of centralite [*s*-diphenyldiethylcarbamide]. L. MÉDARD (Mém. Poudres, 1930—1931, 24, 174—210).—Anhyd. $SnCl_4$ (Cl-free) reacts with $CO(NPhEt)_2$ (*C*) to give a greyish-green *complex*, probably $SnCl_4,2C$, converted into a violet *compound* by Cl, but too unstable to isolate, since it is decomposed by all solvents. A similar additive *compound* is obtained with anhyd. HCl. Thermal analysis indicates the existence of additive *compounds* (all of type *AC*) of *C* with the following substances (*A*): PhOH, m. p. 41·8°; pyrogallol, pyrocatechol, m. p. 64·3°; resorcinol, m. p. 42°; β-naphthol, m. p. 49—50°; $NHPh_2$, dissociates at 37—38°; doubtful evidence of combination is obtained with *p*-cresol, and ββ-dinaphthol, whilst no compounds are formed with $C_{10}H_8$, anthracene, *m*-$C_6H_4(NO_2)_2$, borneol, *cyclo*hexanol, $Pr^{\alpha}OH$, $Pr^{\beta}OH$, α- and β-$C_{10}H_7\cdot NH_2$, NH_2Ph, $NPhEt_2$, glycerol di- or tri-nitrate, or trinitrotoluene. $CO(NMePh)_2$ similarly forms *compounds* with pyrogallol, m. p. 118—119°, and pyrocatechol, but not with $NHPh_2$. $Hg(NO_3)_2$ acts on carbonyl compounds to give the nitrate of the stronger oxonium base: $Hg(NO_3)_2,H_2O+2COR_2\longrightarrow 2COR_2,HNO_3+HgO$ and thus the oxonium nitrates of camphor, CHPh:CH·CHO, cineole, phenanthraquinone, and $COMe_2$ (cf. A., 1915, i, 257) are obtained. The nitrates of *C* and $CO(NMePh)_2$ are similarly obtained, but could not be separated from HgO, but with $CO(NEtPh)(NEt\cdot C_6H_4Me$-*p*) centrifuging separates the liquid *nitrate* which is only slowly decomposed by H_2O. The action is sp. to salts of the weak base $Hg(OH)_2$ [salts of $Cu(OH)_2$ and $Pb(OH)_2$ do not so react], but evidence of perchlorate formation with the aid of $Hg(ClO_4)_2$ was obtained.

J. W. BAKER.

Nitro- and amino-triphenylguanidines. E. DYER and T. B. JOHNSON (J. Amer. Chem. Soc., 1932, 54, 777—787).—*p*-$NO_2\cdot C_6H_4\cdot NCS$ and NH_2Ph in C_6H_6 give 97% of p-*nitrodiphenylthiocarbamide* (I), m. p. 160°; with *p*-$NO_2\cdot C_6H_4\cdot NH_2$ in C_6H_6 and a little pyridine, 94% of pp′-*dinitrophenylthiocarbamide*, m. p. 195—196°, results. BzNCS with *m*- and *p*-$NO_2\cdot C_6H_4\cdot NH_2$ in C_6H_6 give *benzoyl*-m- and -p-*nitrophenylthiocarbamide*, m. p. 164—165° and 182°, respectively. (I) and MeI in MeOH afford 72% of the S-*Me* derivative (III), m. p. 121—122°, of *p*-nitrodiphenyl-ψ-thiocarbamide, converted by NH_2Ph into βγ-*diphenyl*- α-p-*nitrophenylguanidine* (IV), m. p. 172—173°, also formed from (I), NH_2Ph, and I in pyridine. β-*Phenyl-αγ-di*-p-*nitrophenylguanidine* (V) (+EtOH), m. p. 168—169°, is obtained together with γ-*phenyl*-αβ-*di*-p-*nitrophenylguanidine* (VI) (+EtOH), m. p. 191—193°, from (II), NH_2Ph, and I in pyridine. (VI) is converted into (V) by conc. HCl at 100°, whilst (V) passes into (VI) at 170—175°/30 min. (V) is also prepared in 40% yield from *p*-$NO_2\cdot C_6H_4\cdot NH_2$ and $NPh:CCl_2$, whilst (VI) results in 26% yield from (III) and *p*-$NO_2\cdot C_6H_4NH_2$. Tri-*p*-nitrophenylguanidine and (VI) are formed in equal amounts from (I) and *p*-$NO_2\cdot C_6H_4\cdot NH_2$. β-*Phenyl-αγ-di*-m-*nitrophenylguanidine*, m. p. 175—176°, is prepared in 65% yield from $NPh:CCl_2$ and *m*-$NO_2\cdot C_6H_4\cdot NH_2$. αβγ-*Tri*-p-*nitrophenylguanidine*, m. p. 244—245°, results from (II), *p*-$NO_2\cdot C_6H_4\cdot NH_2$, and I in pyridine. Catalytic reduction (PtO_2) of (IV) in AcOEt gives βγ-*diphenyl*-α-p-*aminophenylguanidine*, m. p. 152—153°. β-*Phenyl-αγ-di*-p-*aminophenylguanidine*, m. p. 167—168°, is prepared similarly from (V) or (VI). β-*Phenyl-αγ-di*-m-*aminophenylguanidine*, m. p. 138—139°, and αβγ-*tri*-p-*aminophenylguanidine*, m. p. 215°, are described. These NH_2-derivatives are inactive towards tubercle bacilli. C. J. WEST (*b*).

Aromatic thionylamines. L. ANSCHÜTZ and Z. M. DELIJSKI (Annalen, 1932, 493, 241—250).—3 : 5-Dichloro-*o*-toluidine and $SOCl_2$ in C_6H_6 at 80° give 3 : 5-*dichloro-2-thionylaminotoluene*, b. p. 139—140°/11 mm., m. p. 52°, which can be steam-distilled without appreciable decomp., and is more stable than 3 : 5-*dibromo-2-thionylaminotoluene*, b. p. 166—167·5°/10 mm., m. p. 64°. A Cl atom *ortho* to the ·N:S:O group has a stronger retarding effect on the reactivity than an *o*-Br atom; conversely, the Br-amine reacts more readily with $SOCl_2$ than the Cl-amine. 3 : 5-Dichloro-2-aminobenzoic acid and $SOCl_2$ in Et_2O give 3 : 5-*dichloro-2-thionylaminobenzoyl chloride*, b. p. 116—118°/0·02 mm., m. p. 87—89°. *o*-Thionylaminobenzoyl chloride (A., 1929, 696) and dry HCl in Et_2O afford o-*aminobenzoyl chloride hydrochloride* (I), sublimes partly at 35°/0·02 mm., and eliminates HCl at 40—100°, forming (probably) dianthranilide. *o*-Aminobenzoyl chloride could not be obtained from (I) by sublimation/high vac. in presence of MgO, $Mg(OH)_2$, $MgCO_3$, or HgO, or by treatment with NMe_3 or $NPhMe_2$ in Et_2O. (I) and MeOH (EtOH) give the hydrochloride of Me (Et) anthranilate, whilst with Mg acetylenyl bromide, *di*-o-*aminobenzoylacetylene*, $(o\text{-}NH_2\cdot C_6H_4\cdot CO\cdot C:)_2$, m. p. 161—162° (decomp.) after previous sintering, results. H. BURTON.

Dinaphthyl bases. I. Syntheses and properties. W. M. CUMMING and G. HOWIE (J.C.S., 1932, 528—534).—Reduction of 4 : 4′-, 3 : 3′-, and 2 : 2′-dinitro-1 : 1′-dinaphthyl is investigated. The 4 : 4′- and 2 : 2′-dinitro-compounds afford in EtOH with $(NH_4)HS$ and Na_2S, 4′-*nitro-4-amino*-1 : 1′-*dinaphthyl*, m. p. 195—196° (*Ac* derivative, m. p. 243—244°), and 2′-*nitro-2-amino*-1 : 1′-*dinaphthyl*, m. p. 251°, respectively. Reduction of each of the $(NO_2)_2$-isomerides with Zn dust and AcOH affords 4 : 4′-diamino-, m. p. 202° (lit. 198°) (Ac_2 derivative, m. p. 363—364°; Bz_2 derivative, m. p. 319—320°; *picrate*, m. p. 146—147°), 3 : 3′-*diamino*-, m. p. 270°, and 2 : 2′-diamino-, m. p. 191° [Ac_2 derivative, m. p. 235—236°; Bz_2 derivative, m. p. 235°; *picrate*, m. p. 185° (decomp.)], -1 : 1′-dinaphthyl, respectively. The 2 : 2′-diamino-compound suffers ring closure to give 2 : 2′-imino-1 : 1′-dinaphthyl (*picrate*, m. p. 218—219°). Reduction of 1 : 1′- and 3 : 3′-dinitro-2 : 2′-dinaphthyl is investigated. With NH_4HS and Na_2S, the 1 : 1′-dinitro-compound affords 1′-*nitro*-1-*amino*-2 : 2′-*di*-

naphthyl, m. p. 264°. 1 : 1′-Diamino-2 : 2′-dinaphthyl, m. p. 281° (lit. 253—259°) (Ac_2 derivative, m. p. 229—230°; Bz_2 derivative, m. p. 277—278°), gives, contrary to A., 1886, 245, on elimination of the NH_2 groups, 2 : 2′-dinaphthyl. By ring closure, the 1 : 1′-diamine affords 1 : 1′-imino-2 : 2′-dinaphthyl (*picrate*, m. p. 242—243°). 3 : 3′-Dinitro-2 : 2′-dinaphthyl on reduction with Zn and AcOH affords an unidentified *compound*, $C_{40}H_{26}O_3N_2$, m. p. about 350°, whereas 1-nitro-2 : 2′-dinaphthyl affords 1-amino-2 : 2′-dinaphthyl (*Ac* derivative, m. p. 225—226°). The NH_2-bases described couple with azo-components to give colours unaffected by acids. The absorption spectra of many of these substances have been measured. J. L. D'Silva.

Perylene and its derivatives. XXXIII. Constitution of diaminoperylenes. K. Funke (Monatsh., 1932, 59, 184—193).—Naphthidine (improved prep. given; cf. J.C.S., 1923, **123**, 2464) or, better, its hydrochloride is converted by $AlCl_3$ (3 pts.) at 130° into a *diaminoperylene* (*hydrochloride*; NN′-Bz_2 and -Ac_2 derivatives, both not melted at 340°; *diurethane*, not melted at 340°), purified through its *dibenzylidene* derivative, m. p. 267—268° (corr.) (decomp.), and differing from the known (3 : 9 and 3 : 10) diamino-derivatives. The Friedel–Crafts reaction with perylene-3 : 10-dicarboxyl chloride and C_6H_6 gives an insol. product (formed by self-condensation of the chloride). No violanthrone was obtained. H. Burton.

Action of cyanogen on β-arylhydroxylamines. D. Vorländer, F. Hoelkeskamp, and P. Günther (Ber., 1932, 65, [*B*], 359—364).—NHPh·OH in Et_2O at 0° is converted by C_2N_2 into *dicyanophenylhydroxylamine*, OH·NPh·C(:NH)·CN or O:NPh:C(NH_2)·CN, m. p. about 136° (decomp.) after darkening at 100—110° (*hydrochloride*; *sulphate*; *Cu*$^{\cdot\cdot}$, *Ni*, *Fe*$^{\cdot\cdot}$, *Hg*$^{\cdot\cdot}$ salts), converted by HCl in anhyd. Et_2O into (?) the *amide hydrochloride*, $C_8H_9O_2N_3$,HCl, decomp. 180—190°. With H_2S the dicyano-compound in EtOH affords dithio-oxamide, whilst it is transformed by alkali into $PhNO_2$ and thence into azoxybenzene and alkali oxalate. Reduction with Zn dust and AcOH gives NH_2Ph. NHPh·OH and dicyanophenylhydroxylamine give a grey product, decomp. above 330°, probably formed to some extent as by-product of the prep. of the dicyano-compound. *Acetyldicyanophenylhydroxylamine*, m. p. about 149° (decomp.) after darkening at 138°, is prepared by means of Ac_2O. With $COMe_2$ or COPhMe in presence of alkali, the dicyano-derivative gives *products*, $C_{11}H_{13}O_2N_3$, m. p. 139° and 134°, respectively. With dil. HCl, dicyanophenylhydroxylamine gives a blue *dye* not identical with indigotin; the $COMe_2$ compound behaves similarly. *Dicyano-o-tolylhydroxylamine*, m. p. about 169° (decomp.), its *Ac* derivative, m. p. about 178° (decomp.), and its *compounds* with $COMe_2$ and COPhMe, m. p. 177° and 96°, respectively, are described. *Dicyano-p-tolylhydroxylamine*, m. p. about 140° (decomp.), and its *Ac* derivative, m. p. about 151° (decomp.), have been prepared. H. Wren.

Dehydrogenation of amines and hydrazines by unsaturated compounds. L. A. Pinck and G. E. Hilbert (J. Amer. Chem. Soc., 1932, 54, 710—716).—9-Aminofluorene is dehydrogenated to fluorenoneimine by di(diphenylene)ethylene (I), benzylidenefluorene, azobenzene, indigotin, and methylene-blue in liquid NH_3. Hydrazobenzene is similarly converted by (I) into azobenzene. Various non-reacting systems are given. These results favour Wieland's theory of dehydrogenation as a mechanism of biological oxidation. C. J. West (*b*).

Properties and reactions of phenylhydrazine. E. G. R. Ardagh, B. Kellam, F. C. Rutherford, and H. T. Walstaff (J. Amer. Chem. Soc., 1932, 54, 721—727).—Details are given for the iodometric determination (cf. A., 1926, 189) of $NHPh{\cdot}NH_2$ in presence of EtOH. Pure $NHPh{\cdot}NH_2$,HCl is obtained by adding a solution of the distilled base in EtOH with continual stirring to an excess of HCl in EtOH; the reverse procedure often gives a product containing NH_2Ph,HCl and NH_4Cl. Optimum conditions for the prep. of the phenylhydrazones of COPhMe and $COPh_2$ are studied. C. J. West (*b*).

Action of halogens on arylazoacetoacetates and related compounds. I. F. D. Chattaway and R. J. Lye (Proc. Roy. Soc., 1932, **A**, 135, 282—299).—*Et* 2 : 4 : 6-*tribromobenzeneazoacetoacetate* (*Et* αβ-*diketo*-n-*butyrate*-α-2 : 4 : 6-*tribromophenylhydrazone*) (I), m. p. 123° (*Ac* derivative, m. p. 129—130°) (from diazotised tribromoaniline and Et acetoacetate), with Br (1 mol.) in AcOH containing a little H_2O or NaOAc gives *Et* α-*bromoglyoxylate*-2 : 4 : 6-*tribromophenylhydrazone* (II), m. p. 102°, but with Br (1 mol.) in AcOH alone at 100° gives *Et* 2 : 4 : 6-*tribromobenzeneazo-γ-bromoacetoacetate* (III), m. p. 160° (decomp.), and with Br (2 mols.) in AcOH alone at 100° affords *Et* 2 : 4 : 6-*tribromobenzeneazo*-γγ-*dibromoacetoacetate* (IV), m. p. 110°, whilst with excess of Br under similar conditions ββω-*tribromo-α-ketopropaldehyde*-2 : 4 : 6-*tribromophenylhydrazone*, dimorphic, m. p. 135—136°, is obtained. The last compound was also prepared from Br and α-*ketopropaldehyde*-2 : 4 : 6-*tribromophenylhydrazone*, m. p. 146° [obtained from diazotised tribromoaniline and Et acetoacetate or by hydrolysis of (I) by aq.-alcoholic KOH], in hot AcOH. (II) with NH_3 in EtOH gives *Et* α-*aminoglyoxylate*-2 : 4 : 6-*tribromophenylhydrazone*, m. p. 137°. (III), also obtained from diazotised tribromoaniline and Et γ-bromoacetoacetate, best with KOAc in hot EtOH, affords 4-*hydroxy*-3-*carbethoxy*-1-(2′ : 4′ : 6′-*tribromophenyl*)*pyrazole*, m. p. 160° (*Bz* derivative, m. p. 155°), whilst (IV) gives similarly 5-*bromo*-4-*hydroxy*-3-*carbethoxy*-1-(2′ : 4′ : 6′-*tribromophenyl*)*pyrazole*, m. p. 208°. *Et* 2 : 4 : 6-*trichlorobenzeneazoacetoacetate*, m. p. 96° (*Ac* derivative, m. p. 122°), with Cl_2 in AcOH at room temp. gives *Et* α-*chloroglyoxylate*-2 : 4 : 6-*trichlorophenylhydrazone* (V), m. p. 74° (giving with NH_3 in EtOH the corresponding α-*amino*-compound, m. p. 136°), prepared also from diazotised trichloroaniline and Et γ-chloroacetoacetate, whilst with Cl_2 in dry $CHCl_3$ a mixture of (V) and *Et* 2 : 4 : 6-*trichlorobenzene-γ-chloroacetoacetate*, m. p. 106—107°, is obtained. The last compound with KOAc in EtOH affords 4-*hydroxy*-3-*carbethoxy*-1-(2′ : 4′ : 6′-*trichlorophenyl*)*pyrazole*, m. p. 158—159° [*Bz* derivative, m. p. 150—151°; 5-*Cl*-derivative (VI), m. p. 178°]. The

following compounds were prepared by analogous methods: *Et* α-*chloroglyoxylate*-2 : 4 : 6-*tribromophenylhydrazone*, m. p. 108—109°; *Et* α-*bromoglyoxalate*-2 : 4 : 6-*trichlorophenylhydrazone*, m. p. 75·5°; *Et* 2 : 4 : 6-*tribromobenzeneazo-γ-chloroacetoacetate* [from diazotised tribromoaniline and Et γ-chloroacetoacetate or (I) and Cl_2], m. p. 170—171° (decomp.) [yielding (VI) with KOAc]; *Et* 2 : 4 : 6-*trichlorobenzeneazo-γ-bromoacetoacetate*, m. p. 112—113° (by both methods); *Et* 2 : 4 : 6-*trichlorobenzeneazo-γγ-dibromoacetoacetate*, m. p. 84—85°; 5-*bromo*-4-*hydroxy*-3-*carbethoxy*-1-(2′ : 4′ : 6′-*trichlorophenyl*)*pyrazole*, m. p. 190—191° (*Bz* derivative, m. p. 147°); α-*ketopropaldehyde*-2 : 4 : 6-*trichlorophenylhydrazone*, m. p. 164—165°; ββω-*tribromo*-α-*ketopropaldehyde*-2 : 4 : 6-*trichlorophenylhydrazone*, m. p. 100—101°; 5-*chloro*-4-*hydroxy*-3-*carbethoxy*-1-(2′ : 4′ : 6′-*trichlorophenyl*)*pyrazole*, m. p. 195—197°.
R. S. Cahn.

Hydrogenation of cyclic compounds. II. G. Roberti (Annali Chim. Appl., 1932, **22**, 3—10).—PhOH, *cyclo*hexanol, and NH_2Ph were subjected to hydrogenation by methods described previously (B., 1931, 833). *cyclo*Hexanol was not obtained from PhOH nor *cyclo*hexylamine from NH_2Ph; these compounds may occur as intermediate products. From PhOH and NH_2Ph hydrocarbons resulting from the condensation of two rings are obtained. In all reactions *cyclo*hexane and *cyclo*hexene are formed, the latter in considerable amount in the fraction of light hydrocarbons obtained from NH_2Ph.
O. F. Lubatti.

Replacement of bromine in bromophenols by the nitro-group. III. 2 : 3 : 4 : 6-Tetrabromophenol and 2 : 4 : 6-tribromo-3-iodophenol. Halogen effect in position 3. H. H. Hodgson and E. W. Smith (J.C.S., 1932, 503—505).—The influence of halogen in position 3 on the reactivity of the Br atoms towards HNO_3 in the 3-halogeno-2 : 4 : 6-tribromophenols is explained on current electronic theory. Nitration of 2 : 3 : 4 : 6-tetrabromophenol at room temp. gives a mixture of 2 : 3 : 4-tribromo-6-nitrophenol, m. p. 123° (lit., 121°), and 3 : 4 : 6-tribromo-2-nitrophenol. 3-Bromo-4-nitrophenol affords with Br 2 : 3 : 6-*tribromo*-4-*nitrophenol*, m. p. 151° (decomp.). Bromination of 3-iodophenol affords 2 : 4 : 6-*tribromo*-3-*iodophenol*, m. p. 91°, which when treated with HNO_3 at room temp. gives 2 : 6-*dibromo*-3-*iodo*-4-*nitrophenol*, m. p. 145°, identical with the Br_2-derivative of 3-iodo-4-nitrophenol. 3-Iodo-6-nitrophenol gives with Br 2 : 4-*dibromo*-3-*iodo*-6-*nitrophenol*, m. p. 173°.
J. L. D'Silva.

Nitration of *p-tert.*-butylphenol. O. H. Schaaf (J. pr. Chem., 1932, [ii], **133**, 173—176).—The action of cold HNO_3–H_2SO_4 on *p-tert.*-butylphenol gives the (?) 2 : 6-$(NO_2)_2$-derivative, m. p. 96° (cf. A., 1881, 898); further nitration at —5° causes oxidation and *tetranitro*-p-*isopropylphenol*, m. p. 122°, and CO_2 are formed.
H. A. Piggott.

Bromo-derivatives of *o*-anisidine. F. Madesani (Gazzetta, 1932, **62**, 51—62).—Aceto-*o*-anisidide reacts with 1 mol. of Br to give the *Ac* derivative, m. p. 159—160°, of 4-bromo-*o*-anisidine (*Bz* derivative, m. p. 108°; 5-*bromo*-2-*methoxydiphenylthiocarbamide*, m. p. 170°; 5-*bromo*-2-*methoxy*-2′ : 4′-*dinitrodiphenylamine*, m. p. 166—168°), which is also obtained by reduction of 4-bromo-*o*-nitroanisole, and with 2 mols. of Br to give the Ac derivative, m. p. 146°, of 3 : 4-dibromo-*o*-anisidine (I), m. p. 102—103° (hydrochloride, m. p. 210°; 5 : 6-*dibromo*-2-*methoxydiphenylthiocarbamide*, m. p. 156°; 5 : 6-*dibromo*-2-*methoxy*-2′ : 4′-*dinitrodiphenylamine*, m. p. 154—155°). *o*-Anisidine reacts with 1 mol. of Br to give 3-*bromo*-o-*anisidine* (II), m. p. 65° [hydrochloride, m. p. 225° (decomp.); *Ac* derivative, m. p. 165°; *Bz* derivative, m. p. 90°; 6-*bromo*-2-*methoxydiphenylthiocarbamide*, m. p. 145°; 6-*bromo*-2-*methoxy*-2′ : 4′-*dinitrodiphenylamine*, m. p. 180°] [bromination of the Ac derivative of (II) gives (I)], and with 2 mols. of Br to give 3 : 5-dibromo-*o*-anisidine, m. p. 20—25° (hydrochloride, m. p. 200°; Ac derivative, m. p. 185°; *Bz* derivative, m. p. 158°). 4 : 6-Dibromo-*o*-anisidine (A., 1883, 662) (oxalate, m. p. 148—150°; *Ac* derivative, m. p. 137°; *Bz* derivative, m. p. 118°; 3 : 5-*dibromo*-2-*methoxydiphenylthiocarbamide*, m. p. 155°) is obtained from *o*-nitrophenol. The results of this work support the views of Bargellini (A., 1930, 1282) as to the relative directing influences on halogen substitution of alkoxy-, NH_2, and NHAc groups.
E. E. J. Marler.

Sulphonation of *o*-anisidine and aceto-*o*-anisidide. R. Child (J.C.S., 1932, 715—720).—Sulphonation of *o*-anisidine with 20% oleum in H_2SO_4 gives 2-anisidine-4-sulphonic acid (I), decomp. about 300°, also obtained by reduction of 2-nitroanisole-4-sulphonic acid (modified prep.) with Sn and HCl. The NH_2-acid yields (Sandmeyer) 2-chloroanisole-4-sulphonic acid [Na salt; *amide*, m. p. 130—131°; *acid chloride* (II), m. p. 81—82°]. *o*-Chloroanisole and $ClSO_3H$ at 0° give (II) and 3 : 3′-*dichloro*-4 : 4′-*dimethoxydiphenylsulphone*, m. p. 165—166°, also obtained by chlorination of *pp*′-dimethoxydiphenylsulphone, m. p. 129°, in boiling AcOH. Aceto-*o*-anisidide and $ClSO_3H$ at 50° give 2-*acetamidoanisole*-4-*sulphonyl chloride* (III), m. p. 152—153° (75% yield) (corresponding *amide*, m. p. 226°) [also prepared from the Na salt of (I)], which with Na_2SO_3 yields 2-*acetamidoanisole*-4-*sulphinic acid* (IV), $+H_2O$, m. p. 117—119° (decomp.)]. The Ag salt of (IV) with MeI affords 2-*acetamidoanisyl*-4-*methylsulphone*, m. p. 186°. Reduction of (IV) with SO_2 and HI gave 2-*acetamidoanisyl* 4-*disulphoxide*, m. p. 226°, and with Zn dust and alcoholic HCl, 2-acetamidoanisyl 4-mercaptan, m. p. 121—122° (4-*Me sulphide*, m. p. 109—110°), oxidised by $FeCl_3$ to 2 : 2′-*diacetamidodianisyl* 4 : 4′-*disulphide*, m. p. 153°, which with boiling conc. HCl gives the 2 : 2′-$(NH_2)_2$-compound, m. p. 105° [*dihydrochloride*, m. p. 268° (decomp.)] (could not be demethylated). Reduction of (III) by Zn dust and HCl gives impure disulphide, which is best purified by hydrolysis, crystallisation, and re-acetylation.
R. S. Cahn.

Reduction of Schiff bases. I. Reduction of methylene-*p*-aminophenol and its probable structure. E. C. Wagner (J. Amer. Chem. Soc., 1932, 54, 660—669).—Reduction of $p\text{-}OH\cdot C_6H_4\cdot N\colon CH_2$, *M* 124—179 (in PhOH), 408 (in $CMe_3\cdot OH$), with Zn and dil. H_2SO_4 gives a mixture (accounting for about 90% of the original substance) of $p\text{-}NH_2\cdot C_6H_4\cdot OH$, $p\text{-}NHMe\cdot C_6H_4\cdot OH$, and $p\text{-}NMe_2\cdot C_6H_4\cdot OH$; some of the *p*-$NH_2\cdot C_6H_4\cdot OH$ is regenerated by hydrolysis. It is concluded that polymerised *p*-$OH\cdot C_6H_4\cdot N{:}CH_2$ is a cyclic compound containing the 1 : 3-dimethinediazidine or a similar larger ring. C. J. West (*b*).

2 : 3 : 5 : 6-Tetrachloro-*p*-anisidine and its derivatives. E. Bureš and J. Hutter (Časopis Českoslov. Lék., 1931, **11**, 29—33, 57—62; Chem. Zentr., 1931, ii, 225).—The following were prepared: *p*-methoxyacetanilide, m. p. 128°; 2 : 3 : 5 : 6-tetrachloro-*p*-methoxyacetanilide, m. p. 230°; -*p*-anisidine- [sulphate; hydrochloride (decomp.)]; -*p*-methoxydiacetanilide, m. p. 101°; -*p*-methoxybenzanilide, m. p. 194°; -*p*-anisylmethylamine, m. p. 93°; -*p*-bromoanisole, m. p. 98°; -*p*-iodoanisole, m. p. 62—63°; -*p*-hydroxyanisole, m. p. 103—104°; -anisole, m. p. 54°. A. A. Eldridge.

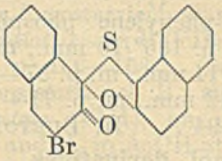
Organic peroxides. II. Reaction between perbenzoic acid or benzoyl peroxide and triphenylmethyl. S. S. Medvedev and E. N. Alexeeva (Ber., 1932, **65**, [*B*], 137—142).—Interaction of BzO_2H and C_2Ph_6 yields small amounts of BzOH and CPh_3 peroxide, a *substance*, $C_{38}H_{30}O$, m. p. (indef.) 232—234°, which gives a colourless solution in molten $C_{10}H_8$ and the isomeric *phenoxypentaphenylethane*, m. p. 236—238° (decomp.), which absorbs O_2 when exposed in solid or dissolved condition to the atm. and dissolves in $C_{10}H_8$, yielding a solution of which the colour darkens with rise in temp. and fades as the temp. is reduced. When heated somewhat below its m. p. it gives CPh_4 and $COPh_2$. Phenoxypentaphenylethane and the substance $C_{38}H_{30}O$ (above) are stable towards Br and are transformed by Ac_2O into the *ether* $(CPh_3\cdot CPh_2\cdot C_6H_4)_2O$, m. p. 255—260°. The substance $C_{38}H_{30}O$ yields CPh_4 when heated. When Bz_2O_2 and C_2Ph_6 (1 : 1) interact, a part of the former remains unchanged and CPh_3 peroxide is not produced. The sole products are $COPh_2$, CPh_4 (products of the thermal decomp. of phenoxypentaphenylethane), and BzOH; since the last-named substance is isolated mainly after treatment of the mixture with KOH–EtOH, it is probably present initially as Bz_2O.

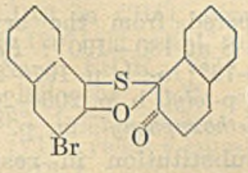
H. Wren.

Derivatives of β-naphthol. A. Wahl and R. Lantz (Compt. rend., 1932, **194**, 464—467).—The following are prepared by heating the appropriate diamine or its derivative with 1-chloro- or 1-bromo-β-naphthol, using xylene or an excess of the base as solvent, at 100—140°; 1-m-*aminophenylamino*-, m. p. 161°; 1-4′-*amino*-2′-*tolylamino*- (?), m. p. 188° (*hydrochloride*) (from *m*-toluylenediamine); 1-m-*dimethylaminoanilino*-, m. p. 154°; and 1-p-*amino-anilino*-β-*naphthol*, m. p. 185—186° [p-N-*Ac* derivative, m. p. 215—216° (from *p*-aminoacetanilide)].

H. A. Piggott.

Isomeric 3-bromo-derivatives of dehydro-β-naphthol 1-sulphide. J. A. C. McClelland and S. Smiles (J.C.S., 1932, 637—641).—The isomerides (I) and (II) are capable of independent existence, and attempts at interconversion failed. Dehydro-β-naphthol 1-sulphide with Br in $CHCl_3$ gives 3-*bromodehydro*-β-*naphthol* 1-*sulphide* (I), m. p. 155°, converted by AcI into αββ′α′-*dinaphthathioxin*, m. p. 210°. The structure of (I) is proved (*a*) by its reduction by Zn and H_2O to the *iso*sulphide, cryst., whence 3-*bromo*-β-*naphthol* 1-*sulphide*, m. p. 192°,

(I.)


(II.)


also prep. from 3-bromo-β-naphthol and β-naphthol-1-bromothiol in CCl_4, was obtained; (*b*) by the rules of substitution of β-naphthaquinones; (*c*) because it does not yield a phenylhydrazone, and (*d*) by bromination in $CHCl_3$ to 3 : 4-*dibromodehydro*-β-*naphthol* 1-*sulphide*, m. p. 204° (also obtained directly from dehydro-β-naphthol 1-sulphide), which with NH_2Ph yields 3-*bromo*-4-*anilinodehydro*-β-*naphthol* 1-*sulphide*, m. p. 240—241°. 3-Bromo-β-naphthol and S_2Cl_2 in $CHCl_3$ at 100° give 3 : 3′-*dibromo*-β-*naphthol* 1-*sulphide*, m. p. 192°, oxidised by warm alkaline $K_3Fe(CN)_6$ to 3 : 3′-*dibromodehydro*-β-*naphthol* 1-*sulphide*, m. p. 205° (no phenylhydrazone formed), converted by AcI in Ac_2O into 6 : 13-*dibromo*-αββ′α′-*dinaphthathioxin*, m. p. 248°, and by boiling AcCl into a ?-*Cl*-derivative, m. p. 264°, of the latter. 3-*Bromo*-β-*naphthol* 1-*sulphide*, m. p. 192° (from 3-bromo-β-naphthol and β-naphthol-1-bromothiol), gives on oxidation a mixture containing 3′-*bromodehydro*-β-*naphthol* 1-*sulphide* (II), m. p. 172—173° (*phenylhydrazone*, m. p. 196°).

R. S. Cahn.

Mechanism of the action of phosphorus aryloxy- and alkoxy-dichlorides on pyrocatechol. L. Anschütz and H. Walbrecht (J. pr. Chem., 1932, [ii], **133**, 65—80).—*o*-$C_6H_4(OH)_2$ reacts with P alkoxy- (or aryloxy-)dichlorides in C_6H_6 at room temp.—100° (bath) forming alkyl (aryl) *o*-phenylene phosphites (I), $o\text{-}C_6H_4{<}^{O}_{O}{>}P\cdot OR$, together with *o*-hydroxyphenyl *o*-phenylene phosphite, $OH\cdot C_6H_4\cdot O\cdot PO_2C_6H_4$, (II), m. p. 117—118° (cf. A., 1928, 880) (O-*Ac* derivative, b. p. 135°/0·02 mm.), and *o*-phenylene phosphite, $(C_6H_4)_3(PO_3)_2$ (III). The reactions occurring are: (i) $C_6H_4(OH)_2 + OR\cdot PCl_2 \longrightarrow (I) + 2HCl$; (*b*) $(I) + C_6H_4(OH)_2 \longrightarrow (II) + R\cdot OH$; (*c*) $(II) + (I) \longrightarrow (III) + R\cdot OH$. In accordance with (*b*), Et *o*-phenylene phosphite, *o*-$C_6H_4(OH)_2$, and dry HCl give (II) and EtCl (from EtOH). The following *alkyl* and *aryl* o-*phenylene phosphites* are prepared: *Me*, b. p. 76—77°/15 mm.; *Et*, b. p. 83—84°/11 mm.; n-*Pr*, b. p. 100—102°/13 mm.; n-*Bu*, b. p. 116—117°/12 mm.; *Ph* (IV), b. p. 152°/11 mm.; o-, b. p. 159—160°/13 mm., m-, b. p. 158—159°/11 mm., and p-*tolyl*, b. p. 164°/12 mm., m. p. 25°. Guaiacol and P pyrocatechyl chloride (*loc. cit.*) at 130° give o-*methoxyphenyl* o-*phenylene phosphite*, b. p. 137°/0·13 mm., 184°/13 mm., not obtainable by methylation of (II).

[By W. Broeker.] (IV) is also prepared from *o*-$C_6H_4(OH)_2$ and $P(OPh)_2Cl$ in warm C_6H_6 or from PhOH and P pyrocatechyl chloride at 100°. *Pyrocatechyl phenylphosphinate*, $Ph\cdot P({:}O){<}^{O}_{O}{>}C_6H_4\text{-}o$, m. p. 124—125°, is obtained from *o*-$C_6H_4(OH)_2$ and

$Ph\cdot POCl_2$ at 160—180°. The following *aryl* o-*phenylene thiophosphates*, $o\text{-}C_6H_4{<}^{O}_{O}{>}P(\colon S)\cdot OAr$; are prepared from the aryl *o*-phenylene phosphites and S at 180—190° : *Ph*, b. p. 186°/10 mm., m. p. 71—72° ; o-, b. p. 197—200°/14 mm., m. p. 87—88°, and p-*tolyl*, b. p. 206—208°/12 mm., m. p. 71—72° ; o-*methoxyphenyl*, m. p. 93—94°. H. BURTON.

Substitution in resorcinol derivatives. III. Molecular rearrangement during bromination. C. SRIKANTIA, M. S. IYENGAR, and K. SANTANAM (J.C.S., 1932, 524—527).—Nitration (I) of 2-hydroxy-4-methoxybenzaldehyde affords mainly the 5-nitro-aldehyde (cf. A., 1925, i, 675), and in small quantity, 6-nitroresorcinol 3-Me ether [*monobromo*-derivative, m. p. 117—118°, identical with the product of nitration of 5-bromo-2-hydroxy-4-methoxybenzaldehyde; Br_2-derivative, m. p. 127—128°, identical with 2 : 4-dibromo-6-nitroresorcinol 3-Me ether (II)]. Bromination of 5-nitro-2-hydroxy-4-methoxybenzaldehyde affords first 3-*bromo*-5-*nitro*-2-*hydroxy*-4-*methoxybenzaldehyde*, m. p. 129—130°, oxidised by $KMnO_4$ to an acid, m. p. 212—214°, obtained by brominating 5-nitro-2-hydroxy-4-methoxybenzoic acid. Further bromination affords (II). Another product of (I) is 3-*nitro*-2-*hydroxy*-4-*methoxybenzaldehyde*, m. p. 146—147°, which on bromination first affords 5-*bromo*-3-*nitro*-2-*hydroxy*-4-*methoxybenzaldehyde*, m. p. 126°, identical with the product of nitration of 5-bromo-2-hydroxy-4-methoxybenzaldehyde. Further bromination affords (II). As 3-nitro-2-hydroxy-4-methoxybenzaldehyde and 5-nitro-2-hydroxy-4-methoxybenzaldehyde both yield (II) with excess of Br, it is suggested that an intramol. rearrangement involving the migration of a NO_2-group has occurred. J. L. D'SILVA.

Bactericidal properties of mono-ethers of dihydric phenols. II. E. KLARMANN and others.—See this vol., 308.

Action of benzoyl chloride on dimethylpyrogallol [pyrogallol 1 : 3-dimethyl ether]. F. MAUTHNER (J. pr. Chem., 1932, [ii], **133**, 126—128).—Pyrogallol 1 : 3-Me_2 ether, BzCl, and $AlCl_3$ in $PhNO_2$ give 3 : 4-*dihydroxy*-5-*methoxybenzophenone* m. p. 168—169° (*oxime*, m. p. 169—170° after previous sintering). H. BURTON.

Quaternary ammonium halides of ephedrine. C. T. FENG (J. Amer. Pharm. Assoc., 1932, **21**, 8—15).—Methylephedrine methiodide, m. p. 208—209°, $[\alpha]_D^{22}$ − 32·3° in MeOH ($C = 5{\cdot}0$), − 22·3° in H_2O, isolated during the prep. of methylephedrine, has been used for the prep. of methylephedrine methochloride, m. p. 245° (decomp.), $[\alpha]_D^{22}$ − 45·2° in MeOH, − 31·2° in H_2O, and *methylephedrine methobromide*, m. p. 238·0°, $[\alpha]_D^{22}$ − 37·9° in MeOH, −25·8° in H_2O. The properties of these compounds and their reactions with $K_2Cr_2O_7$, H_2PtCl_6, $HAuCl_4$, and $HgCl_2$ are given. They give no biuret reaction, have equal mol. rotations, and form characteristic crystals. Bi can be detected by the methiodide in an aq. solution containing 0·001% of $Bi(NO_3)_3$. E. H. SHARPLES.

Chromic acid oxidation of *sec*.-cyclic alcohols. G. VAVON and C. ZAREMBA (Bull. Soc. chim., 1931, [iv], 49, 1853—1860).—The oxidation of *sec*. cyclic alcohols by AcOH–CrO_3 in dil. (0·005*N*) solution is approx. of the second order, the reaction const., *K*, increasing towards the end of the reaction, due to oxidation of the ketone formed. In more conc. solutions (0·05*N*) the reaction is bimol. and the const. decreases towards the end of the reaction. The concn. of the AcOH is crit. and with 0·005*N*-*cyclo*hexanol at 25° oxidation is 1000 times as fast in 100% as in 50% AcOH. For the 27 cyclanols studied the velocity of oxidation at 39° is 7 to 13 times as great in 75% as in 50% AcOH and similarly at 39° in 100% AcOH menthone is oxidised 50 times as fast as in 50% AcOH, and in 75% AcOH 6 times as fast. In eleven out of thirteen instances, the *cis*- is oxidised more rapidly than the *trans*-isomeride. The rate of oxidation increases with the mol. wt. of the alkyl group in the 2-position with respect to OH. Thus the 2-methyl*cyclo*hexanols are oxidised more slowly than the 2-ethyl-, -propyl-, or -butyl-*cyclo*hexanols and the 2-*iso*propyl*cyclo*hexanols more readily than the 2- or 4-Pr^a derivatives. Di*tert*.-butylcarbinol in 75% AcOH at 25° or 39° or in 50% AcOH at 39° is oxidised a little more rapidly than di-*n*-butylcarbinol, although with AcOH at 140° and Ac_2O in C_6H_6 at 100° it is esterified at 1/40 to 1/50 the rate of its isomeride. Similarly, di*tert*.-butylmethyl phthalate is hydrolysed at 1/140 the rate of di-*n*-butylmethyl phthalate in aq. EtOH and 1/400 in H_2O. Neither dehydration nor CrO_3 oxidation is sensitive to steric hindrance. R. BRIGHTMAN.

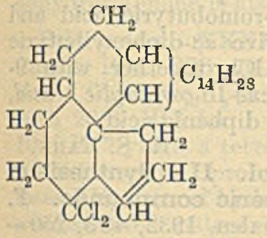
αβ-Di*cyclo*hexylethylene glycol. J. S. BUCK and W. S. IDE (J. Amer. Chem. Soc., 1932, **54**, 820—821).—αβ-Di*cyclo*hexylethylene glycol, m. p. 194° (cf. A., 1931, 1294), is prepared by catalytic reduction of dodecahydrobenzoin. Hexahydromandelonitrile and hexahydromandelamide, b. p. 104°/0·7 mm., 121°/1·8 mm., do not react with Mg *cyclo*hexyl bromide, whilst unimol. glyoxal gives iso-αβ-*di*cyclo*hexylethylene glycol*, m. p. 153° (corr.).

C. J. WEST (*b*).

Resorcyl alcohols. T. BOEHM and H. PARLASCA (Arch. Pharm., 1932, **270**, 168—183).—The dicarbomethoxy-derivative [m. p. 94—95° (lit. 154—155°)] of 3 : 5-dihydroxybenzaldehyde (α-resorcylaldehyde) [$+H_2O$, m. p. (anhyd.) 156—157° (lit. 145—146°)], when reduced catalytically (Pd–$BaSO_4$) in AcOH gives *dicarbomethoxy*-α-*resorcyl alcohol*, m. p. 75—76° (p-*nitro*- and p-*bromo-benzoyl* derivatives, m. p. 107—108° and 104—105°, respectively; α-*naphthylurethane*, m. p. 114—115°), hydrolysed by aq.-alcoholic KOH in H_2 to the phenolic alcohol, which is stable to acids. Attempts to prepare 2 : 4-dihydroxybenzyl alcohol (β-resorcyl alcohol) (I) by catalytic reduction of the corresponding aldehyde failed. The *dicarbomethoxy*-derivative, m. p. 99° (p-*nitrophenylhydrazone*, m. p. 172—173°), of the latter is reduced catalytically to the *dicarbomethoxy*-derivative, an oil (p-*nitrophenylhydrazone*, m. p. 108°), of (I), whilst the *Ac_2* derivative, m. p. 65—66° (p-*nitrophenylhydrazone*, m. p. 206—207°), affords similarly the *Ac_2* derivative, b. p. 290—293°/768 mm., 172—173°/23 mm. (p-*nitro*- and 2 : 4-*dinitro-benzoyl* derivatives, m. p. 90—91° and 109°, respectively), of

(I). Hydrolysis led, however, to red, amorphous polymerisation products, similar to "artopon." Resorcinol and CH_2O do not give 6-hydroxyfluorone (cf. A., 1925, i, 812). R. S. CAHN.

Irradiation of cholesterol. W. B. S. BISHOP (Chem. Eng. Min. Rev., 1932, **24**, 145—146).—*X*-Rays and Ra radiations have no effect on cholesterol dissolved in C_6H_6 and EtOH, but reduce its concn. in $CHCl_3$ and CCl_4 solutions. The last two solvents are, however, themselves affected by the radiations with liberation of Cl_2, so that the reaction on the cholesterol may be indirect. N. H. HARTSHORNE.



Constitution of cholesterol. VI. Reactions of cholesterol with phosphorus pentachloride. F. PIRRONE (Gazzetta, 1932, **62**, 63—80).—PCl_5 with cholesterol under various conditions does not give H_3PO_4 derivatives as with indene etc. (A., 1930, 1050), but trichlorocholestane, m. p. 106°, cholesteryl chloride, m. p. 96°, and 4 : 4-*dichlorocholestene* (annexed formula), m. p. 92° (*Br*-derivative, m. p. 108—109°); *i.e.*, it appears to react not as $PCl_4^+Cl^-$, as predicted by the octet theory of Lewis and Langmuir, but as PCl_3+Cl_2. E. E. J. MARLER.

Cholesteryl esters. XV. E. MONTIGNIE (Bull. Soc. chim., 1931, [iv], **49**, 1852—1853).—Cholesterol and acetylsalicylic acid at 150° for 2 hr. give cholesteryl acetylsalicylate, m. p. 105° (bromide, m. p. 108°), giving the Liebermann reaction. *Cholesteryl cresotate*, m. p. 158—159°, similarly obtained at 180° (*dibromide*, m. p. 112°), also gives the Liebermann reaction, but *cholesteryl acetylcresotate*, m. p. 102° (bromide, m. p. 118—119°), does not. Camphorcarboxylic acid at 130° similarly yields *cholesteryl camphorcarboxylate*, m. p. 178—179° (*phenylhydrazone*, m. p. 184°; *oxime*, m. p. 160°) (slow Liebermann reaction), together with a *substance*, m. p. 139—140° (*acetate*, m. p. 110°). R. BRIGHTMAN.

Crystalline form of anhydrous cholesterol. L. KOFLER and A. KOFLER (Z. physiol. Chem., 1932, **204**, 211—213).—Anhyd. cholesterol crystallises in needles and sublimes in rectangular plates belonging to the rhombic system. J. H. BIRKINSHAW.

Isomerisation of various ergosterol derivatives with hydrogen chloride. K. DITHMAR and T. ACHTERMANN (Z. physiol. Chem., 1932, **205**, 55—64).—HCl in $CHCl_3$ converts ergostatrienone *D* (I) into *ergostatrienone* B_1 (II), m. p. 149—150°, $[\alpha]_D^{19}$ −57·5° [*oxime*, m. p. 187—191° (decomp.)]. Hydrogenation of (II) with Na in EtOH yields *ergostatrienol* B_1, m. p. 148°, $[\alpha]_D^{19}$ −42·5° (*acetate*, m. p. 140°, $[\alpha]_D^{19}$ −54·7°). Ergosterol B_1 prepared from (I) is identical with that from ergosteryl acetate and HCl. With Pt and H_2 its acetate yields *allo*-α-ergostanyl acetate (III) at 65° in presence of HCl and α-ergostenyl acetate (IV) at room temp. HCl in $CHCl_3$ converts ergostadienone *I* into *ergostadienone* III (V), m. p. 114°, $[\alpha]_D^{18}$ −5·1 [*oxime*, m. p. 192—193° (decomp.)]. Hydrogenation of (V) with Na in EtOH affords *dihydroergosterol* III, m. p. 122°, $[\alpha]_D^{18}$ −16·7° [*acetate* (VI), m. p. 108°, $[\alpha]_D^{17}$ −25·3°]; treatment of (VI) with Pt and H_2 yields (III) at 65° (+HCl) and (IV) at room temp.

u-Ergostatrienone with HCl in $CHCl_3$ gives *u-ergostatrienone* B (VII), m. p. 120° $[\alpha]_D^{18}$ −49·1° (*oxime*, m. p. 166—168°). With Na in EtOH, (VII) gives u-*ergostatrienol* B, m. p. 163—164°, $[\alpha]_D^{18}$ −49·3° [*acetate* (VIII), m. p. 128°, $[\alpha]_D^{18}$ −35·5°]. With Pt and H_2 in AcOH at 65°, (VIII) yields *u*-ergostanyl acetate. (All rotations in $CHCl_3$.) J. H. BIRKINSHAW.

Lumisterol. A. WINDAUS, K. DITHMAR, and E. FERNHOLZ (Annalen, 1932, **493**, 259—271).—Acetylation of vitamin-D_1 (A., 1931, 1464) (convenient prep. given) with Ac_2O at 100° gives the acetate of vitamin-D_2 (this vol., 311) together with the *acetate*, m. p. 100°, $[\alpha]_D^{19}$ +130·5° in $COMe_2$, of *lumisterol* (I), $C_{27}H_{42}O$, m. p. 118°, $[\alpha]_D^{19}$ +191·5° in $COMe_2$. (I) absorbs 3O when titrated with BzO_2H, shows absorption maxima at 265 and 280 mμ, eliminates 1 mol. of H_2O when heated with NaOEt at 200°, has no antirachitic action, is non-poisonous, is unaffected by heating to 190°, forms a mol. (1 : 1) compound (=vitamin-D_1) with vitamin-D_2, and is converted into vitamin-D_2 by irradiation of a solution in Et_2O with unfiltered light from a Mg arc. (I) is reduced by Na and EtOH to *dihydrolumisterol* (II), m. p. 138—139°, $[\alpha]_D^{18}$ +50·4° in $CHCl_3$ (*acetate*, m. p. 142°, $[\alpha]_D^{19}$ +25·2° in $CHCl_3$; *benzoate*, m. p. 130°, $[\alpha]_D^{19}$ +4·8° in $CHCl_3$), converted by NaOEt at 200° into epi*dihydrolumisterol* (III), m. p. 140°, $[\alpha]_D^{18}$ +43·3° in $CHCl_3$ (*acetate*, m. p. 127°, $[\alpha]_D^{19}$ +48·6° in $CHCl_3$; *benzoate*, m. p. 151°, $[\alpha]_D^{19}$ + 35·7° in $CHCl_3$), which is pptd. by digitonin. (II) and (III) form a 1 : 1-additive *compound*, m. p. 186°, $[\alpha]_D^{19}$ +47·8° in $CHCl_3$. (I) is converted by dry HCl in $CHCl_3$ at −10° into iso*lumisterol*, m. p. 138°, $[\alpha]_D^{19}$ −103° in C_6H_6, $[\alpha]_D^{18}$ −125° in $CHCl_3$ (*acetate*, m. p. 128°), isomerised by NaOEt at 150—200° to epi-iso*lumisterol*, m. p. 165°, $[\alpha]_D^{17}$ −123° in $COMe_2$ (*acetate*, m. p. 117°, $[\alpha]_D^{19}$ −105·7° in $COMe_2$), also pptd. by digitonin. H. BURTON.

Spinasterol and some of its esters. M. C. HART and F. W. HEYL (J. Biol. Chem., 1932, **95**, 311—315).—The crude unsaponifiable matter from spinach fat crystallised from EtOH gives spinasterol, m. p. 168—169°, $[\alpha]_D^{23}$ −1·8°, and from the mother-liquor cryst. Et_2O-insol. material, m. p. 102—103°, has been isolated. The following esters of spinasterol have been obtained: *acetate*, m. p. 183—185°, $[\alpha]_D^{23}$ −4·7°; *benzoate*, m. p. 201—202°, $[\alpha]_D^{23}$ +2·25°; *phenylurethane*, m. p. 173—174°, $[\alpha]_D^{23}$ −2·25°; p-*nitrobenzoate*, m. p. 217—218°, $[\alpha]_D^{23}$ +4·5°; *trichloroacetate*, m. p. 167—169°, $[\alpha]_D^{23}$ −3·5°; *propionate*, m. p. 152—153°, $[\alpha]_D^{23}$ −5·0°; and *butyrate*, m. p. 131—132°, $[\alpha]_D^{23}$ −4·0°. With $CH_2Cl\cdot COCl$, in absence of C_5H_5N, iso*spinasteryl chloroacetate*, m. p. 155—156°, $[\alpha]_D^{23}$ −6·0°, is formed, hydrolysed to *iso*spinasterol, m. p. 148—150°, $[\alpha]_D^{23}$ +5·2°. Colorimetric tests indicate the absence of the $\Delta^{1:2}$ (or $\Delta^{1:13}$) and the inactive $\Delta^{10:19}$ linkings in spinasterol. F. R. SHAW.

Action of selenium oxide on sterols. E. MONTIGNIE (Bull. Soc. chim., 1932, [vi], **51**, 154).—In EtOH solution at 95° with 10% aq. SeO_2 ergosterol gives a red coloration or ppt. of Se-red after boiling for 1—2 min. Other sterols, particularly cholesterol, stigmasterol, and phytosterols, do not give the reaction, and ergosterol derivatives give the reaction less readily, *e.g.*, the acetate and γ-dihydroergosterol are about 2—3 times less sensitive. The limit of the reaction is about 0·0006 g. of ergosterol. The sensitivity decreases on irradiation in proportion to the time of irradiation and resin formation. R. BRIGHTMAN.

Action of hydrogen selenide on acid chlorides. I. Hydrogen selenide and benzoyl chloride. L. SZPERL and W. WIOROGÓRSKI (Rocz. Chem., 1932, **12**, 71—78).—H_2Se yields *CH_2Ph selenobenzoate* (an oil) with BzCl in boiling xylene solution; in the presence of $AlCl_3$ at room temp. the *products* are Bz_2Se, m. p. 61—62°, Bz_2Se_2, m. p. 129—130°, and *benzylidene diselenobenzoate*, m. p. 149—150°. The above compounds readily decompose in the presence of light and H_2O, with the liberation of Se. R. TRUSZKOWSKI.

Reaction of phenylacetonitrile. J. A. NIEUWLAND and L. H. BALDINGER (J. Amer. Chem. Soc., 1932, **54**, 828).—$CH_2Ph{\cdot}CN$ (1 mol.) and Na (1 mol.) in liquid NH_3 form a salt, converted by EtBr (in liquid NH_3) into $CHPhEt{\cdot}CN$; the H atom in this nitrile can be replaced by Na and the resulting salt reacts with a second mol. of alkyl bromide.

C. J. WEST (*b*).

Pinacolin deamination. I. Action of nitrous acid on amino-alcohols derived from α-aminohydratropic acid. A. MCKENZIE and J. R. MYLES (Ber., 1932, **65**, [*B*], 209—218).—α-Amino-α-phenylpropionic acid is converted by EtOH and HCl into the *Et* ester, b. p. 135—136°/15 mm. (*hydrochloride*, m. p. 121—123°), transformed by MgPhBr into r-β-*amino*-ααβ-*triphenylpropan*-α-*ol*, m. p. 114—115° (*hydrochloride*, m. p. 212—213°). Treatment of the NH_2-alcohol in dil. AcOH with $NaNO_2$ affords αα-*diphenylpropiophenone*, m. p. 91—92°, which does not yield an oxime, semicarbazone, or *p*-nitrophenylhydrazone, does not react with MgPhBr, but is converted by boiling 10% KOH–EtOH into αα-diphenylethane. (αα-*Diphenylpropionyl chloride*, m. p. 40—41°, from the acid and $SOCl_2$, is converted by C_6H_6, $AlCl_3$, and CS_2 into a *substance*, m. p. 139—140°.) Deamination yields smaller quantities of ααβ-*triphenylpropylene oxide*, m. p. 63—64°, converted by conc. H_2SO_4 into CPh_3Ac, m. p. 138—138·5°, which, with KOH–EtOH, gives $CHPh_3$ and KOAc ($CHPh_3$ is formed by the action of MgMeI on $CPh_3{\cdot}CN$). Dehydration of ααβ-triphenylpropane-αβ-diol with conc. H_2SO_4 at room temp. or boiling dil. H_2SO_4 yields acetyltriphenylmethane. (+)-α-Formamido-α-phenylpropionic acid is hydrolysed by *N*-HBr to (+)-α-*amino*-α-*phenylpropionic acid hydrobromide*, $[\alpha]_D^{14}$ +69·7° in EtOH [(−)-*isomeride*, $[\alpha]_D^{16}$ −69·1° in EtOH], which yields *Et* (+)-α-*amino*-α-*phenylpropionate*, $[\alpha]_D^{18}$ +24·70° [(−)-*isomeride*, $[\alpha]_D^{18}$ −25·5°]. The (+)-ester is converted into (+)-β-*amino*-ααβ-*triphenylpropan*-α-*ol*, m. p. 118—119°, $[\alpha]_D^{14}$ +69·4° in EtOH, de-aminated to αα-diphenylpropiophenone and a *product*, $[\alpha]_{5461}$ −13·5° in $COMe_2$, consisting of (−)-ααβ-*triphenylpropylene oxide* possibly containing a little αα-diphenylpropiophenone. r-β-*Amino*-β-*phenyl*-αα-*di*-p-*tolylpropan*-α-*ol*, m. p. 107—108°, is converted by HNO_2 into p-*tolyl* α-*phenyl*-α-p-*tolylethyl ketone*, m. p. 77—78°, and (?) 2-*phenyl*-1-p-*tolyl*-5-*methylindene*, m. p. 145—146°. The pinacolin is transformed by KOH–EtOH into *p*-toluic acid and α-phenyl-α-*p*-tolylethane. H. WREN.

Condensation of αβ-dibromocarboxylic acids with benzene in presence of aluminium halides. J. C. EARL and C. H. WILSON (J. Proc. Roy. Soc. New South Wales, 1932, **65**, 178—184).—αβ-Dibromo-β-phenylpropionic acid and C_6H_6 in presence of $AlBr_3$ or $FeCl_3$ give αββ-triphenylpropionic acid, but using $AlCl_3$ afford 9-*phenyl*-9 : 10-*dihydrophenanthrene*-10-*carboxylic acid*, m. p. 148° (*Et* ester, m. p. 116°), yielding 9-*phenyl*-9 : 10-*dihydrophenanthrene*, m. p. 121·5°, when distilled with soda-lime, a *substance*, $C_{20}H_{14}O_2$, m. p. 105—106°, when treated with CrO_3 in AcOH, and BzOH and phthalic acid when oxidised by $KMnO_4$. αβ-Dibromobutyric acid and C_6H_6 in presence of $AlBr_3$ give αβ-diphenylbutyric acid, also obtained using $AlCl_3$ together with 9-*methyl*-9 : 10-*dihydrophenanthrene*-10-*carboxylic acid*, m. p. 127°, oxidised (CrO_3) to diphenic acid.

R. S. CAHN.

Constitution of cannabinol. II. Synthesis of cannabinolactone and isomeric compounds. F. BERGEL and K. VÖGELE (Annalen, 1932, **493**, 250—258).—3-Methylphthalic anhydride (1 mol.) and MgMeI (2 mols.) give probably 3-*methyl*-αα-*dimethylphthalide*, b. p. 80—85°/0·01 mm., m. p. 58·5°, oxidised by alkaline $KMnO_4$ to αα-*dimethylphthalide*-3-*carboxylic acid* (I), m. p. 178·5° (*Et* ester, m. p. 146·5°), not identical but isomeric with cannabinolactonic acid (II). Fusion of (I) with KOH at 290—300° gives *p*-$C_6H_4(CO_2H)_2$, which probably results from a rearrangement of *o*-$C_6H_4(CO_2H)_2$. MgMeI and 4-methylphthalic anhydride give a mixture, b. p. 106°/0·5 mm., m. p. 89°, of 4- and 5-methyl-αα-dimethylphthalides; oxidation of the mixture and extraction of the mixed acids with Et_2O affords impure αα-*dimethylphthalide*-4-*carboxylic acid* (III) as the more sol. acid. *p*-Cymene-3-carboxylic acid is oxidised by CrO_3 in AcOH–$KHSO_4$ to 4-*iso*propyl*iso*phthalic acid, thymoquinone, and 4-methyl-αα-dimethylphthalide (cannabinolactone) (IV). (IV) is oxidised by alkaline $KMnO_4$ to (III), m. p. 203—204° (*Et* ester, m. p. 103—104°), which is identical with (II). H. BURTON.

3-Methylgallic acid. F. MAUTHNER (J. pr. Chem., 1932, [ii], **133**, 120—125).—4 : 5-Dihydroxy-3-methoxybenzoic (3-*O*-methylgallic) acid (*Me* ester, m. p. 112—113°) and $Cl{\cdot}CO_2Me$ in *N*-NaOH give 3-*methoxy*-4 : 5-*di*(*carbomethoxyoxy*)*benzoic acid*, m. p. 149—150°, the *acid chloride*, m. p. 101—102°, of which is reduced catalytically (Pd–$BaSO_4$) in PhMe to the 4 : 5-di-*O*-carbomethoxy-derivative (not characterised) of 4 : 5-dihydroxy-3-methoxybenzaldehyde, m. p. 130—131° (p-*nitrophenylhydrazone*).

H. BURTON.

Esters of gallic acid. B. HEPNER and L. ZYTO (Rocz. Chem., 1932, **12**, 100—102).—Pr^{α}, m. p. 150°, Bu^{α}, m. p. 143—144°, and Bu^{β}, m. p. 130—131°, *gallates* have been prepared. R. TRUSZKOWSKI.

Rotenone, the active constituent of derris root. XI. Synthetical experiments with 2-hydroxy-4 : 5-dimethoxybenzoic acid and rissic acid. Partial synthesis of derrissic acid and dehydro-

rotenone from derritol. S. Takei, S. Miyajima, and M. Ono (Bull. Inst. Phys. Chem. Res. Tokyo, 1932, **11**, 304—318; cf., this vol., 400).—3-Nitro-2 : 5-dimethoxybenzoic acid has m. p. 169°, and 2 : 5-dimethoxymandelic acid, m. p. 98—103° (cf. A., 1931, 1415). 4-*Hydroxyveratrole* (I), m. p. 78°, gives 3 : 4-dimethoxyphenoxyacetic acid, m. p. 116° (NO_2-derivative, m. p. 209°), identical with decarboxyrissic acid. (I) led to 2-*hydroxy*-4 : 5-*dimethoxybenzoic acid*, m. p. 202° (*Me* ester, m. p. 92°; *Me ether*, m. p. 143°, identical with asaronic acid), identical with the product from dehydrorotenone, and thence to 2-*carboxy*-4 : 5-*dimethoxyphenoxyacetic acid*, m. p. 255° (*Me*$_2$ ester, m. p. 85°), identical with rissic acid. Alkali fusion of hydroxyquinol or its Ac_3 derivative gives some quinol. In the prep. of derritol from derrissic acid some dehydrorotenone is also formed. R. S. Cahn.

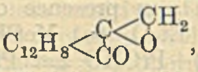
Bile acids. XXXIII. M. Schenck (Z. physiol. Chem., 1932, **205**, 76—82; cf. this vol., 159).—The α-acid, $C_{24}H_{36}O_{10}N_2$ (A., 1930, 915), loses NH_3 on boiling with 20% HCl for 1 hr. Boiling for 20 min. with 10% HCl yields a tetrabasic *acid*, $C_{24}H_{38}O_{11}N_2$, m. p. 226° (decomp.), probably an acid amide, since it loses NH_3 on acid hydrolysis. The α-acid is probably a substituted malonic acid (rupture of ring III) with the supposed nitro-N present as a CN group. J. H. Birkinshaw.

New synthesis of aromatic aldehydes. H. Wuyts, L. Berman, and (Miss) A. Lacourt (Bull. Soc. chim. Belg., 1931, **40**, 665—672).—Dithiocarboxylic acids, $R·CS_2H$, with semicarbazide hydrochloride, best in aq. pyridine, give the semicarbazones of the aldehydes, R·CHO, readily hydrolysed after removal of most of the free S. The following were thus prepared: PhCHO, *o*- and *p*-tolu-, *p*-bromobenz-, α- and β-naphth-aldehyde. R. S. Cahn.

Distyryl ketone and triphenylmethane. XIV. α-Methoxybenzyl chloride and α-methoxycinnamyl chloride. F. Straus and H. Heinze (Annalen, 1932, **493**, 191—217).—$CHPh(OMe)_2$ (0·5 mol.) with AcCl (1·1 mols.) containing a little $SOCl_2$, first at 55° and then at room temp., gives 80% of not quite pure *α-methoxybenzyl chloride* (*α-chlorobenzyl Me ether*) (I), b. p. 71—72°/0·1 mm., m. p. about −24°, hydrolysed readily by H_2O to PhCHO, MeOH, and HCl, converted by NaOMe into $CHPh(OMe)_2$, and decomposed at 110° to PhCHO and MeCl. Impure *α-methoxycinnamyl chloride* (II) is similarly prepared from cinnamaldehyde dimethylacetal. (I) and $HgCl_2$ in Et_2O give a *complex* containing 5—6 mols. of $HgCl_2$, whilst (II) similarly affords the *mercurichloride*, $[CHPh{:}CH·CH(OMe)]Cl,HgCl_2$ (III), which, like (I) and (II), is extremely sensitive to moisture. (I) and COPhMe give Ph styryl ketone; with $COMe_2$, distyryl ketone [dimethylacetal, m. p. 63—63·5° (corr.) (lit. 55—56°)] and styryl Me ketone are produced. (I) and MeCHO in absence or presence of Et_2O afford PhCHO and paracetaldehyde, but in presence of $Et_2O–HgCl_2$, (III) is gradually produced. Mol. quantities of (I) and cinnamaldehyde or of (II) and PhCHO give after about 20 hr., an equilibrium mixture of about 59% of (I) and 41% of (II), indicating the reversible reaction, $CHPhCl·OMe + CHPh{:}CH·CHO \rightleftharpoons CHPh{:}CH·CHCl·OMe + PhCHO$. In presence of 1 mol. of $HgCl_2$ (and Et_2O), equilibrium is displaced to the right and (III) results; this is the most convenient method of prep. of (III). (III) is also produced by the prolonged interaction of (I) and $Et_2O–HgCl_2$ in presence of air, owing to the oxidation of Et_2O to MeCHO. The reversible reaction, (I)+PrCHO $\rightleftharpoons$ PhCHO+CHPrCl·OMe (to be described later), also occurs; prolonged interaction leads to other condensation products. (I), Ph styryl ketone (IV), and $HgCl_2$ in Et_2O give a compound, convertible by NaOMe into the dimethylacetal of (IV). PhCHO and $CH_2Cl·OMe$ give (after treatment with NaOMe) a mixture of $CHPh(OMe)_2$ and *α-methoxybenzyl methoxymethyl ether* (V), b. p. 109—110°/12 mm.; the amount of (V) produced rises (up to 39·4%) with increased (initial) reaction time. (V) decomposes readily in air to CH_2O and PhCHO. The production of (V) involves the addition of Cl and $·CH_2·OMe$ across the C:O group of PhCHO; a similar reaction does not occur with PhCHO and MeCl. $CPh_2(OMe)_2$ and PCl_5 in C_6H_6 afford impure $CPh_2Cl·OMe$, which when heated gives MeCl and $COPh_2$, and with NaOMe yields $CPh_2(OMe)_2$. H. Burton.

Syntheses with diazomethane. VII. Reaction of aldehydes and ketones. F. Arndt, J. Amende, and W. Ender (Monatsh., 1932, **59**, 202—219; cf. A., 1929, 328).—OH-Compounds (*e.g.*, MeOH) catalyse the reaction between diazomethane and RCHO (especially when R is positive) in Et_2O and the subsequent formation of $CH_2R·CHO$ (from the hypothetical intermediate $CHR\Big<\begin{matrix}O-\\CH_2-\end{matrix}$), which results, together with COMeR, when R is an (electrically) indifferent group. When R is positive, ethylene oxide production is favoured. $CH_2R·CHO$ reacts in the same ways as RCHO, but a positive R now favours the formation of $CH_2R·COMe$. COMeR also reacts similarly; a positive R promotes the formation of an ethylene oxide and COEtR (catalysed by OH-compounds). Compounds of the type $RSO_2·CH_2·COR$ react readily with diazomethane to give $RSO_2·CH{:}CR·OMe$.

p-$NO_2·C_6H_4·CHO$ and Et_2O–diazomethane (I) in presence of a little MeOH give (contrary to previous findings) practically no p-$NO_2·C_6H_4·CH_2·COMe$, but somewhat better yields of p-$NO_2·C_6H_4·COMe$ and *p*-nitrophenylethylene oxide (cf. *loc. cit.*). The yield of o-$NO_2·C_6H_4·COMe$ from o-$NO_2·C_6H_4·CHO$ and (I) is improved by a little, and decreased by much MeOH; the amount of *o*-nitrophenylethylene oxide remains more or less const. in both cases. 2 : 4 : 6-$(NO_2)_3C_6H_2·CHO$ and (I) give a product, decomp. 80—90°, which is not 2 : 4 : 6-$(NO_2)_3C_6H_2·COMe$ (cf. Sonn and Bülow, A., 1925, i, 1267). $CH_2Cl·COMe$ and (I) give an additive compound converted by evaporation into N_2 and *α-chloroisobutylene oxide*, $\begin{matrix}CH_2\\|\\O\end{matrix}\!\!>CMe·CH_2Cl$, b. p. 124° (main product); the oxide and conc. HCl give $OH·CMe(CH_2Cl)_2$. Similarly, $CCl_3·COMe$ affords *ααα-trichloroisobutylene oxide*, $\begin{matrix}CH_2\\|\\O\end{matrix}\!\!>CMe·CCl_3$, b. p. 51°/10 mm., m. p. 53—54°, converted by conc. HCl into impure *methylchloromethyltrichloromethylcarbinol*, b. p. 93—95°/12 mm.

*epi*Chlorohydrin is not obtained from $CH_2Cl·CHO$; reaction appears to proceed by way of $CH_2Cl·COMe$. Phenanthraquinone and (I) react slowly and incompletely; in presence of a little MeOH, spiro*phenanthroylethylene oxide*,  $C_{12}H_8<\begin{matrix}C<\begin{matrix}CH_2\\ |\\ O\end{matrix}\\ CO\end{matrix}$, m. p. 166° [converted by MeOH–HCl into a *chlorohydrin*, m. p. 117° (*benzoate*, m. p. 168°)], results, whilst with 20% of MeOH the $:CH_2$ ether described by Biltz and Paetzold (A., 1923, i, 1233) is obtained. Benzil is converted into αα′-methylenedioxystilbene under all the conditions tried. 1-Hydroxyisatin and 1 mol. of (I) give 3-*hydroxy*-1-*methoxycarbostyril*, m. p. 203°; with 2 mols. of (I), 1 : 3-*dimethoxycarbostyril*, m. p. 128—129°, results.

The reaction between solid $CCl_3·CH(OH)_2$ and (I) (cf. *loc. cit.*; Meerwein *et al.*, A., 1929, 681) depends on the immediate decomp. of the additive compound at the crystal surface. The additive compound from $CCl_3·CHO$ and (I) is decomposed by Et_2O–BzOH after several min.; in presence of porous earthenware decomp. occurs immediately.

H. Burton.

Action of acetic anhydride on benzylideneanilines. J. B. Ekeley, M. C. Swisher, and C. C. Johnson (Gazzetta, 1932, 62, 81—84).—Previous work by Ekeley and collaborators on the condensation of Ac_2O with substituted benzylideneanilines is discussed and the experimental conditions are described (cf. A., 1922, i, 934). E. E. J. Marler.

Symmetrical triad prototropic systems. VIII. Analogy between symmetrical triad systems and aromatic side-chain reactivity, and the effect of *m*-substitution on mobility and equilibrium in the αγ-diphenylmethyleneazomethine system. C. W. Shoppee (J.C.S., 1932, 696—711; cf. A., 1931, 834).—*m*-Chloro-, -bromo-, -iodo-, -nitro-, and -dimethylamino-benzaldehyde, *m*-anisaldehyde, and *m*-tolualdehyde (from m-*toluanilide*, m. p. 126°) give cryst. H sulphite compounds. Reduction of *m*-tolualdoxime, m. p. 60°, b. p. 137°/17 mm., by 3% Na amalgam in AcOH affords *m*-methylbenzylamine, b. p. 96°/20 mm. [picrate, m. p. 198° (decomp.); *benzoate*, m. p. 150—150·5°; *carbamido*-derivative, m. p. 148°]. The following substituted benzylamines were prepared : *m*-chloro-, b. p. 111—112°/18 mm. [picrate, m. p. 204° (decomp.); *carbamido*-derivative, m. p. 129°] (from *m*-chlorobenzaldoxime, m. p. 70°); *m*-bromo-, b. p. 126—127°/18 mm. [*picrate*, m. p. 205° (decomp.); *benzoate*, m. p. 135·5°; *carbamido*-derivative, m. p. 132°; hydrochloride, m. p. 216—217°] (from *phthalo*-m-*bromobenzylimide*, m. p. 138—139°, by N_2H_4,H_2O); *m*-iodo-, b. p. 132°/8 mm. [*picrate*, m. p. 210° (decomp.); *benzoate*, m. p. 132°; *Ac* derivative, m. p. 114·5°; *carbamido*-derivative, m. p. 170—171°] [from *phthalo*-m-*iodobenzylimide*, m. p. 143·5°, which, with a *substance*, m. p. 228°, was prepared from m-*iodobenzyl bromide*, m. p. 49—49·5° (obtained from *m*-iodotoluene and Br at 180°)]; *m*-methoxy-, b. p. 103—104°/6 mm. (*picrate*, m. p. 181°; *benzoate*, m. p. 95°; p-*nitrobenzoyl* derivative, m. p. 124°) (from m-*anisaldoxime*, b. p. 170°/26 mm., and, less well, by electrolytic reduction of m-*methoxybenzamide*, m. p. 133°); *m*-dimethylamino-, b. p. 134—135°/10 mm. [*monopicrate*, m. p. 206° (decomp.); *dipicrate*, m. p. 170°; *benzoate*, m. p. 111·5°] (from the oxime); *m*-nitro- (picrate, m. p. 202°) (from the phthalo-derivative, m. p. 160·5°). Reduction of (*a*) *m*-bromo- and (*b*) *m*-iodo-benzaldoxime by 3% Na amalgam and AcOH gives benzylamine in (*a*) 34—35% and (*b*) 100% yield. The following were prepared : m-*methyl*-, b. p. 187°/12 mm.; m-*chloro*-, b. p. 190°/10 mm.; m-*bromo*-, b. p. 200°/10 mm., m. p. 38°; m-*iodo*-, m. p. 73°; m-*methoxy*-, b. p. 206°/15 mm.; m-*dimethylamino*-, b. p. 233°/10 mm. -*benzylidenebenzylamines*; also *benzylidene*-m-*methyl*-, b. p. 170°/7 mm.; -m-*chloro*-, b. p. 175°/5·5 mm.; -m-*bromo*-, b. p. 217—218°/15 mm.; -m-*iodo*-, b. p. 220—221°/12 mm.; -m-*methoxy*-, b. p. 186°/6 mm., m. p. 37°; -m-*dimethylamino*-, b. p. 200°/5 mm.; and -m-*nitro-benzylamine*, m. p. 32·5—32·7° (lit. 42°). ω-*Benzylimino*- (I) and ω-*benzylideneamino*- (II) -m-*tolyltrimethylammonium iodide* have m. p. 128—129° and 145—146°, respectively. The above compounds with *p*-nitrophenylhydrazine (III) yield the following substituted *benzaldehyde*-p-*nitrophenylhydrazones*: m-*methyl*-, m. p. 157°; m-*chloro*-, m. p. 214°; m-*bromo*-, m. p. 220·5°; m-*iodo*-, m. p. 208°; m-*methoxy*-, m. p. 171°; m-*dimethylamino*-, m. p. 190°; m-*nitro*-, m. p. 248°. (I) and (II) are stable to 0·145*N*-NaOEt at 82°; with (III), followed by H_2PtCl_6, (I) gives the impure *salt* $[(p\text{-})NO_2·C_6H_4·NH·N:CH·C_6H_4·NMe_3(m)]_2PtCl_6$, m. p. 207—208° (decomp.). Interconversion of the above tautomerides by 0·145*N*-NaOEt at 82° and thermal analysis of the hydrazones obtained on treating the resulting mixture with (III) indicates the following sequence for *m*-substituents, the figures in parentheses representing the mobilities conferred by the substituent, and those in brackets the percentage of isomeride $C_6H_4R·CH:N·CH_2Ph$: NMe_2 (0·606) [63], Me (1·10) [60], OMe (2·51) [54·7], I (7·33) [42·5], Br (9·47) [36·5], Cl (10·7) [35·5], NO_2 (147) [68]. The relation between these results and those in the *p*-series and dipole moments is discussed in the light of current electronic theories. m-*Bromobenzaldehydesemicarbazone* has m. p. 228° (decomp.).

R. S. Cahn.

Alkyloxyaldehydes. S. Sabetay and D. N. Mira (Compt. rend., 1932, 194, 617—620).—By the action of the appropriate halogenoacetal, in the presence of Cu, on the Na or K derivatives of various alcohols and subsequent hydrolysis of the product with 15% H_2SO_4 in AcOH, the following alkoxyaldehydes are obtained (cf. A., 1930, 323) : *benzyloxy*-, b. p. 110—112°/13 mm. (*acetal*, b. p. 143—144°/15 mm.; *semicarbazone*, m. p. 118°); β-*phenylethoxy*-, b. p. 119—121°/13 mm. (*acetal*, b. p. 153—154°/16 mm.; *semicarbazone*, m. p. 88°); and *cinnamyloxy*-, b. p. 139—141°/16 mm. (*acetal*, b. p. 155—157°/16 mm.; *semicarbazone*, m. p. 120°), -*acetaldehyde*.

J. W. Baker.

Preparation of 3 : 4 : 5-trimethoxybenzaldehyde. K. H. Slotta (J. pr. Chem., 1932, [ii], 133, 129—130).—3 : 4 : 5-Trimethoxybenzaldehyde is prepared in 80% yield by reduction of carefully purified 3 : 4 : 5-trimethoxybenzoyl chloride (from the acid and PCl_5, not $SOCl_2$) with H_2 and Pd–$BaSO_4$ in dry xylene (cf. A., 1925, i, 951; 1931, 213). H. A. Piggott.

Nitro-derivatives of dehydrodivanillin. J. M. Gulland and G. U. Hopton (J.C.S., 1932, 439—443).—Dehydrodivanillin, m. p. 312° (lit., m. p. 305°), with Me_2SO_4 and NaOH affords the Me_2 ether and sometimes also *dehydrodivanillin Me ether*, m. p. 196°. Nitration of the Me_2 ether with cold HNO_3 (*d* 1·42) affords 3 : 3′-*dinitro*-5 : 6 : 5′ : 6′-*tetramethoxydiphenyl*, m. p. 215°, whilst with mixed H_2SO_4 and fuming HNO_3 at −18° it affords 2 : 3 : 2′ : 3′-*tetranitro*-5 : 6 : 5′ : 6′-*tetramethoxydiphenyl* (I), m. p. 242°, which, after reduction to the $(NH_2)_4$-compound, condenses with phenanthraquinone to give 5 : 6 : 5′ : 6′-*tetramethoxydiphenyl*-2 : 3 : 2′ : 3′-*bisphenanthraphenazine*, m. p. above 300°. The strong violet fluorescence of the phenazine in C_6H_6 supports the structure assigned to the $(NO_2)_4$-compound. Contrary to Elbs and Lerch (A., 1916, i, 315), diacetyldehydrodivanillin and HNO_3 (*d* 1·5) at −18° affords 4 : 4′-*dinitrodiacetyldehydrodivanillin*, m. p. 168—169° (+2·5EtOH, m. p. 85—90°), which on alkaline hydrolysis affords 4 : 4′-*dinitrodehydrodivanillin*, m. p. 230° (decomp.) [*Me_2 ether*, m. p. 176—177°]. Nitration of this Me_2 ether with HNO_3 (*d* 1·48) and H_2SO_4 at 50° affords 2 : 3 : 4 : 3′ : 4′-*pentanitro*-5 : 6 : 5′ : 6′-*tetramethoxydiphenyl*, m. p. 175°, but at 0°, the product is 3 : 4 : 3′ : 4′-*tetranitro*-5 : 6 : 5′ : 6′-*tetramethoxydiphenyl*, m. p. 197°, isomeric with (I).

J. L. D'Silva.

Thiolacetic acid lignin of pine wood. VI. B. Holmberg [with S. Haglund] (Svensk Pappers-Tidn., 1930, **33**, 679—686; Chem. Zentr., 1931, ii, 420—421).—The aq. extract, after evaporation, was treated with thiolacetic acid in 2*N*-HCl, affording lignothiolacetic acid; 17 samples of pine wood were so treated, the results being tabulated. Purified samples of lignothiolacetic acid contained (1) C 53·16, H 5·20, S 13·27%, corresponding with the formula $C_{40}H_{38\cdot81}O_{10\cdot50}$,4·60HS·$CH_2$·$CO_2$H; (2) C 55·29, H 5·27, O 24·49, S 9·95, OMe 11·46, corresponding with $C_{40}H_{40\cdot01}O_{21\cdot26}$,3·11HS·$CH_2$·$CO_2$H; (3) C 55·00, H 5·34, S 9·98, OMe 11·56%. A. A. Eldridge.

Preparation of *cyclo*pentanone and glutaric acid. M. E. Bœdtker (J. Pharm. Chim., 1932, [viii], **15**, 225—228).—A detailed account of the prep. of *cyclo*pentanone by distillation of Ba adipate (yield 94% of theory) and its oxidation to glutaric acid by boiling aq. HNO_3 (*d* 1·084). Adipic acid has b. p. 320°/752 mm. (corr.; slight decomp.).

H. A. Piggott.

Additive reactions of phenyl vinyl ketone. II. Deoxybenzoin. C. F. H. Allen and W. E. Barker (J. Amer. Chem. Soc., 1932, **54**, 736—748; cf. A., 1929, 1071).—*αε-Diketo-αβε-triphenylpentane* (I), m. p. 95° (*monoxime*, m. p. 131°; *dioxime*, m. p. 162°; *mono*-2 : 4-*dinitrophenylhydrazone*, m. p. 221°), prepared from Ph β-chloroethyl ketone, deoxybenzoin, and KOAc in MeOH–NaOMe, gives with NH_2OH,HCl in MeOH 2 : 3 : 6-*triphenylpyridine*, m. p. 115° (*picrate*, m. p. 163°), and with Ac_2O and $FeCl_3$ the *pyrylium* salt, $C_{23}H_{17}OCl_4Fe$, m. p. 189°. *αε-Diketo-βε-diphenyl-α-*p-*diphenylylpentane* (II), m. p. 104° (*dioxime*, m. p. 79—80°), prepared similarly, gives a *pyrylium* salt, $C_{29}H_{21}OCl_4Fe$, m. p. 191—193°, and 2 : 3-*diphenyl*-6-p-*diphenylylpyridine*, m. p. 193°, whilst *αε-diketo-αβ-diphenyl*-ε-p-*diphenylylpentane* (III), m. p. 115° (*dioxime*, m. p. 214—215°), affords a *pyrylium* salt, m. p. 203°. Monobromination of (I) gives (probably) the δ-*Br* derivative, m. p. 152° (50—55% yield); a *stereoisomeride*, m. p. 150°, of this is produced during the dibromination of (I), whereby two *Br_2* derivatives, probably the βδ-stereoisomerides (not interconvertible), m. p. 127° and 180°, are produced. Bromination of both Br compounds gives the Br_2 derivative, m. p. 127°, converted by Hg and aq. MeOH–KI into 1 : 2-*dibenzoyl*-1-*phenyl*cyclo*propane* (IV), m. p. 123°; the less fusible Br_2 derivative is unchanged by this treatment. (IV) is converted by 1% EtOH–KOH into an *isomeride* (V), m. p. 126°, also formed from the Br derivative, m. p. 150°, and 8—10% EtOH–KOH. (IV) and (V) give the same *dioxime*, m. p. 212°, and the same *monophenylhydrazone*, m. p. 169°. (IV) is much more reactive than (V); (IV) is reduced by Zn and EtOH or AcOH to (I), whilst (V) is unaffected by Zn and EtOH. (IV) and HBr give the Br derivative, m. p. 152°, whilst (V) is unaffected. (IV) and Br give mainly the Br_2 compound, m. p. 127°, and a little of its isomeride [also formed in small amount by prolonged treatment of (V)]. (IV) and MgPhBr give 40% of 1-*phenyl*-1 : 2-*di*(*hydroxydiphenylmethyl*)cyclo*propane*, m. p. 168°; with MgMeI, 1-*phenyl*-1 : 2-*di*(*α-hydroxy-α-phenylethyl*)cyclo*propane*, m. p. 196° (45% yield), results. In all reactions involving opening of the *cyclo*propane ring, fission occurs in the 1 : 2-position (*i.e.*, the point of ring closure), regardless of the nature of the reagent. C. J. West (*b*).

Abnormal reactions of magnesium benzyl chloride. P. R. Austin and J. R. Johnson (J. Amer. Chem. Soc., 1932, **54**, 647—660).—$CH_2Ph{\cdot}MgCl$ (I) and $ClCO_2Et$ give mainly *o*-$Me{\cdot}C_6H_4{\cdot}CO_2Et$ and $C(CH_2Ph)_3{\cdot}OH$; it is suggested that the formation of these products depends on a selective action of the Grignard reagent on the initial products of the reaction. $ClCO_2Me$ gives an ester fraction from which *o*-$Me{\cdot}C_6H_4{\cdot}CO_2H$ is obtained; $CH_2Ph{\cdot}CO_2H$ could not be isolated, but microscopical examination showed its presence. The main product from (I) and Et_2CO_3 is $C(CH_2Ph)_3{\cdot}OH$, whilst *o*-$Me{\cdot}C_6H_4{\cdot}CO_2Et$ and (I) give (probably) *o*-$Me{\cdot}C_6H_4{\cdot}CO{\cdot}CH_2Ph$, b. p. 225—227°/7 mm. (I) and solid CO_2 give 40% of $CH_2Ph{\cdot}CO_2H$, whilst *o*-$Me{\cdot}C_6H_4{\cdot}MgBr$ (II) affords similarly 62% of *o*-$Me{\cdot}C_6H_4{\cdot}CO_2H$. (II) and $CO(CH_2Ph)_2$ give a *compound*, $C_{30}H_{30}O_2$(?), m. p. 157—158°, which may be tetrabenzylethylene glycol. (I) and Ac_2O afford 30% of *o*-$Me{\cdot}C_6H_4Ac$; with $(CH_2Cl{\cdot}CO)_2O$, 42% of o-*tolyl chloromethyl ketone*, b. p. 129—130°/11 mm. (*semicarbazone*, m. p. 103—105°), results.

o-$Me{\cdot}C_6H_4Ac$ (24%) and *o*-$Me{\cdot}C_6H_4{\cdot}COPh$ are obtained from (I) and AcCl and BzCl, respectively. (I) reacts normally with paracetaldehyde, alkyl and aryl ketones, acetals, Et orthoformate, AcOEt, BzOEt, Et_2CO_3, CO_2, *epi*chlorohydrin, $ClCH_2Ac$, allyl iodide, $HgCl_2$, PhNCO, and alkyl *p*-toluenesulphonates. *o*-$C_6H_4Cl{\cdot}CH_2{\cdot}MgCl$ and CO_2 (gas) give *o*-$C_6H_4Cl{\cdot}CH_2{\cdot}CO_2H$ (also formed using $ClCO_2Me$); with Ac_2O or AcCl, a ketone, oxidised to 6-chloro-*o*-toluic acid, is produced. The Grignard reagent from 2 : 6-*dichlorobenzyl chloride*, b. p. 135°/25 mm., m. p. 39—40°, and CO_2 or $ClCO_2Me$ give 2 : 6-*dichloro*-

phenylacetic acid, m. p. 156—157°; with Ac_2O, a product containing 2 : 6-dichlorophenylacetone is produced, whilst with AcCl, a product containing 3 : 5-dichloro-4-methylacetophenone results. The mechanism of the rearrangement process in abnormal reactions of (I) is discussed. C. J. West (*b*).

Structure of metal ketyls. C. B. Wooster (J. Amer. Chem. Soc., 1932, 54, 834—835).—The metal ketyl from $COPh_2$ conducts an electric current in liquid NH_3, suggesting that $CPh_2{\cdot}ONa$ is ionised to Na^+ and CPh_2O^-. The constitution of metal ketyls is being studied. C. J. West (*b*).

Condensation of benzanilides and *p*-dialkylanilines with phosphoryl chloride as condensing agent. Mechanism of the reaction. R. C. Shah, R. K. Deshpande, and J. S. Chaubal (J.C.S., 1932, 642—650).—NHPhBz and $POCl_3$, when heated, give HCl and undistillable P compounds, which with $NPhMe_2$ (I) at 100° yield *p*-dimethylaminobenzophenone (II). Benzanilide imidochloride (III) does not react with (I) at 100° and is thus not, as hitherto assumed, an intermediate in the formation of (II). (III) and (I) at 160—180° give a *base*, m. p. 148—150° [*hydrochloride*, m. p. 282° (decomp.); *picrate*, m. p. 218°], believed to be a stereoisomeride of *diphenyl*-N-*methylbenzamidine*, an oil (*hydrochloride*, m. p. 250°; *picrate*, m. p. (189—190°) [prepared from (III), NHPhMe, and $NPhEt_2$ (IV) at 100°]. (III) and (IV) similarly yield a *base*, m. p. 150° [*hydrochloride*, m. p. 289—290° (decomp.)], believed to be stereoisomeric with *diphenyl*-N-*ethylbenzamidine*, m. p. 81° (*hydrochloride*, m. p. 189—190°) (similarly prepared). NPhMeBz, (I), and $POCl_3$ at 100° give (II) and NHPhMe. The first stage of the above reactions is considered to be formation of $CPh(NPhR){:}CCl{\cdot}O{\cdot}POCl_2$ (R=Me or H), which on further heating loses HCl if R=H, or with (I) gives $CClPh(NRPh){\cdot}C_6H_4{\cdot}NMe_2$, which is subsequently hydrolysed. The following *benzophenones* were prepared by heating the appropriate anilide with the necessary alkylaniline and $POCl_3$ at 100°: 4-*dimethylamino*-2′-*methoxy*-, m. p. 74°; *p*-diethylamino- (*oxime*, m. p. 143—144°); *p*-dimethylamino-, m. p. 92—93° (lit. 90°) (*oxime*, m. p. 152°); 4′-*bromo*-4-*dimethylamino*-, m. p. 128—129° (*oxime*, m. p. 185°); 2′-*chloro*-2-*diethylamino*-, m. p. 79°; 4-dimethylamino-3′-methoxy-, m. p. 72—73° (lit. 67°) (*oxime*, m. p. 185°); 4-dimethylamino-4′-methoxy-; 4-*diethylamino*-4′-*methoxy*-, m. p. 92°; 4-*dimethylamino*-3′-*hydroxy*-, m. p. 185—187°; 4-*dimethylamino*-4′-*hydroxy*-, m. p. 199—200° (from p-*methylcarbonatobenzanilide*, m. p. 179—181°). The following were similarly prepared at 110—115°: 3′-*nitro*-4-*diethylamino*-, m. p. 84°; 4′-*nitro*-4-*dimethylamino*-, m. p. 206—207°; 4′-*nitro*-4-*diethylamino*-, m. p. 116—117° (*oxime*, m. p. 156°), and 2′-*nitro*-4-*dimethylamino-benzophenone* (prepared by long heating at 60°), m. p. 251—253°, accompanied by a *substance*, m. p. 93°. *p*-Dimethylaminophenyl 1- and 2-naphthyl ketone, new m. p. 115—116° and 128—129°, respectively, were similarly prepared at 100°. The following N-*methyldiphenylbenzamidines* were prepared (m. p. of the hydrochloride in parentheses): o- [m. p. 141° (m. p. 225—227°)], m- [an oil (m. p. 230°)], and p- [m. p. 94° (m. p. 213°)] -*nitro*-; m-*methoxy*-, m. p. 83° (m. p. 214—215°); o-*chloro*-, m. p. 106° (m. p. 230—235°); p-*bromo*-, m. p. 121—123° (m. p. 290—295°). The following N-*ethyldiphenylbenzamidines* were prepared: o- [m. p. 99—100° (m. p. 160—161°)], m- [m. p. 174—175° (m. p. 247°)], and p- [m. p. 112° (m. p. 179—180°)] -*nitro*-; m-*methoxy*-, m. p. 175° (m. p. 248°); o-*chloro*-, m. p. 70—71° (m. p. 250°). R. S. Cahn.

Direct synthesis of *p*-dialkylaminobenzophenones. R. C. Shah and J. S. Chaubal (J.C.S., 1932, 650—652).—By condensing $NPhMe_2$ or $NPhEt_2$ with the appropriate benzanilide imidochloride in cold CS_2 in presence of $AlCl_3$ the following benzophenone derivatives were prepared in good yield: *p*-dimethyl- (I) and -diethyl-amino-; 4′-nitro-4-dimethyl- and -diethyl-amino-; 4′-bromo-4-dimethylamino-; 4′-*bromo*-4-*diethylamino*-, m. p. 99—100°; 2′-*chloro*-4-*dimethylamino*-, m. p. 68°. p-*Bromobenzanilide imidochloride* has m. p. 85—86°; the corresponding o-*chloro*-compound is an oil, b. p. 182—183°/10 mm. $NPhMe_2$, BzCl, and $AlCl_3$ in hot CS_2 give a poor yield of (I). R. S. Cahn.

4′-Dimethylaminobenzophenone-2-sulphonic acid. R. T. K. Cornwell (J. Amer. Chem. Soc., 1932, 54, 819—820).—*o*-Sulphobenzoic anhydride (1 mol.) and $NPhMe_2$ (3 mols.) at 110° give 43% of 4′-*dimethylaminobenzophenone*-2-*sulphonic acid* (+$2H_2O$), decomp. slowly at 230—235° to a green liquid [*Ba* (+$3H_2O$) and NH_4 salts]. An Ac derivative could not be prepared. C. J. West (*b*).

Preparation of substituted fluorenones. E. H. Huntress and I. S. Cliff (J. Amer. Chem. Soc., 1932, 54, 826—828).—Langecker's statement (this vol., 163) that nitration of 9-acetamidofluorene gives 2-nitrofluorenone as the only recognisable product is confirmed; more vigorous nitration affords 30% of the 2 : 7- and 13% of a new $(NO_2)_2$-derivative, m. p. 213—214°. 2-Nitrofluorenoneoxime is described with m. p. 249° (*loc. cit.*) and 262·5—263° (A., 1927, 1201); these may be stereoisomeric forms. C. J. West (*b*).

Beckmann rearrangement. VI. Unsaturated ketoximes. II. K. von Auwers and H. Brink (Annalen, 1932, 493, 218—240).—In part a reply to Blatt (A., 1931, 621; this vol., 163). Oximation of Ph *o*-methoxystyryl ketone (*dibromide*, m. p. 132°) in acid solution (cf. A., 1931, 223) gives mainly the *oxime* (I), m. p. 135—145° (*Bz* derivative, m. p. 133—134°), and a little 3-*phenyl*-5-o-*methoxyphenyl*iso*oxazoline* (II), m. p. 103—104°. (I) is unaffected by boiling NaOH, is probably sulphonated by conc. H_2SO_4, and is converted by PCl_5 in Et_2O into o-*methoxycinnamanilide*, m .p. 161—162°. Oximation of the ketone in aq. NaOH (cf. *loc. cit.*) gives mainly (II) and an alkali-sol. hydroxylamino-oxime. Ph *m*-methoxystyryl ketone is oximated in acid or alkaline solution to the oxime, m. p. 75—95° (small yield in alkali) (*Bz* derivative, m. p. 144—145°, hydrolysed in one case to the *oxime*, m. p. 94—97°), rearranged to m-*methoxycinnamanilide*, m. p. 107—108°, and converted by conc. H_2SO_4 into a sulpho-derivative, m. p. 169—170°. Ph *p*-methoxystyryl ketone affords mainly 3-phenyl-4-anisyl*iso*oxazoline (III), m. p. 103—104° (oxidised by CrO_3 in AcOH to the *iso*oxazole), and a little oxime(?) in acid, whilst in alkali, (III), a substance, m. p. 184—186° (decomp.), and (mainly) a *hydroxylamino-oxime*, $C_{16}H_{18}O_3N_2$, m. p. 118—119° (decomp.), are produced. o-*Methoxyphenyl styryl ketone*, b. p. 226°/11·5 mm., prepared from *o*-OMe·C_6H_4Ac and PhCHO in aq. EtOH–NaOH, is oximated in acid to the *oxime*, m. p. 135—145° (*Bz* derivative, m. p. 140—141°), rearranged to *cinnam*-o-*anisidide*, m. p. 136—138°, and sulphonated by conc. H_2SO_4 at room temp. Oximation in alkali gives (mainly) a *hydroxylamino-oxime*, m. p. 162°, and small amounts of the oxime and 5-*phenyl*-3-o-*methoxylphenyl*isoo*xazoline*, m. p. 50—52°. m-*Methoxyphenyl styryl ketone*, b. p. 236—238°/12 mm., m. p. 41—43°, is oximated in acid to the *oxime*, m. p. 132—137° (*Bz* derivative, m. p. 127—128°), rearranged to *cinnam*-m-*anisidide*, m. p. 121—122°, and unaffected by conc. H_2SO_4; in alkaline solution, a *hydroxylamino-oxime*, m. p. 127—128° (about 66%), and a *dioxime*, $C_{16}H_{16}O_3N_2$, m. p. 156—158° (about 33%), are produced. These results afford no evidence for the configurations of the various oximes. The position of the OMe group in the ketones studied does exert some influence on the oximation [but not in the manner indicated by the work of Meisenheimer *et al.* (A., 1928, 1136)], but has no influence on the Beckmann rearrangement (since a derivative of cinnamic acid is produced in each case). None of the above oximes is converted by conc. H_2SO_4 into an *iso*oxazoline as are the oximes of Ph and anisyl styryl ketones (cf. *loc. cit.*).

Oximation of Ph β-chloro-β-phenylethyl ketone (IV) in acid solution gives Ph styryl ketoxime, the dibromide of which undergoes the Beckmann rearrangement yielding *r*-αβ-dibromo-β-phenylpropionanilide. Prolonged interaction of (IV) and NH_2OH in MeOH–AcOEt at room temp. affords 3 : 5-diphenyl*iso*oxazoline as the main product.

H. BURTON.

Beckmann rearrangement. VII. Unsaturated ketoximes. III. K. VON AUWERS and H. BRINK (J. pr. Chem., 1932, [ii], 133, 154—172).—Distyryl ketoxime (A., 1898, i, 194; 1900, i, 237) is unchanged by hot 20% NaOH, but is converted by cold conc. H_2SO_4 into 5-phenyl-3-styryl*iso*oxazoline, m. p. 110—111° (*loc. cit.*), identified by oxidation with CrO_3 in AcOH to 5-phenyl*iso*oxazole-3-carboxylic acid, m. p. 162°, and BzOH; formation of the *iso*oxazoline is regarded as due to addition of H_2SO_4 at the double linking and subsequent elimination. 5-*Phenyl*-3-*styryl*isoo*xazole*, m. p. 144°, is obtained by the action of NH_2OH and NaOH on distyryl ketone dibromide or on α-bromodistyryl ketone; it was not formed by oxidation of the *iso*oxazoline. Rearrangement of distyryl ketoxime with PCl_5 gives *cinnamostyrylamide*, m. p. 213°, identified by hydrolysis with 25% H_2SO_4 to CHPh:CH·CO_2H, NH_3, and CH_2Ph·CHO(?). Styryl Me ketone yields the oxime, m. p. 116° (*Bz* derivative, m. p. 145—147°), both under acid (NH_2OH,HCl and EtOH) and alkaline (aq.) conditions, and, although obtained purer in the latter case, no isomeride was isolated in the former. The oxime with HCl in Et_2O, AcOH, or C_6H_6 gives the *hydrochloride*, m. p. 140—145°, which is slowly isomerised in EtOH to the *hydrochloride*, m. p. 157—160°, of an oxime, m. p. 75—88° (crude) (*Bz* derivative, m. p. 94—96°). A Beckmann rearrangement of the oxime, m. p. 116°, gives β-*acetostyrylamide*, m. p. 105—106°, identified by its non-identity with cinnamomethylamide, its hydrolysis by 25% H_2SO_4 to AcOH, NH_3, NH_2Me, and CH_2Ph·CHO(?), and its synthesis from β-acetoxystyrene and NH_2Ac or, better, from CH_2Ph·CHO and NH_2Ac. Styryl Me ketone dichloride (I) gives no definite product with NH_2OH,HCl in acid solution; in alkaline medium α-chlorostyryl Me ketoxime, m. p. 132—133°, and 5-phenyl-3-methyl*iso*oxazole, m. p. 64°, are formed, the former in preponderating amount in low concn. of alkali. α-*Chlorostyryl Me ketone*, b. p. 140°/11 mm., is prepared by action of NaOAc on (I) in anhyd. EtOH, and is converted into its oxime in acid medium; this is stable to NaOAc in anhyd. EtOH, and does not give an *iso*oxazoline with H_2SO_4. The product of the action of PCl_5 on this oxime is a viscous yellow oil which continuously evolves HCl on keeping and forms *acetophenylacetamide*, CH_2Ph·CO·NHAc, m. p. 129—130°, hydrolysed by NaOH in EtOH to NH_3, AcOH, and CH_2Ph·CO_2H. α-*Bromostyryl Me ketone*, b. p. 152°/11 mm. (hitherto incorrectly designated "β-," cf. J.C.S., 1904, 85, 464), and its *oxime*, m. p. 130—131°, are similarly prepared, and the latter behaves on rearrangement with PCl_5 analogously to the Cl-compound.

H. A. PIGGOTT.

Isomerisation of aldehydes to ketones. (MME.) P. RAMART-LUCAS and J. P. GUERLAIN (Bull. Soc. chim., 1931, [iv], 49, 1860—1874).—In confirmation of previous work (A., 1929, 815, 1166; 1930, 86) it has now been shown that α-disubstituted aldehydes, CHRAr·CHO (R=alkyl), isomerise to ketones. CH_2Ar·CO·R under the influence of heat, in presence of kieselguhr, but at higher temp. than with the diarylacetaldehydes. The isomeric ketone Ar·CO·CH_2R is not formed, and it is concluded that either the two ketones cannot be transformed one into the other or the temp. of isomerisation is higher than that of dissociation. The aldehydes are accordingly considered the intermediate stage in the conversion of glycols or ethylene oxides into ketones and in the dehydration of hydrobenzoin glycols the proportions of isomeric ketones formed can be varied only by varying the temp. or concn. of the acid if both ketones are formed and can be isomerised.

α-p-*Tolyl*-n-*valeraldehyde*, b. p. 132—133° (*semicarbazone*, m. p. 150—151°), obtained in 45% yield by distilling *p*-tolylpropylglycidic acid, with kieselguhr at 450°/10 mm. is converted into p-*tolylmethyl* Pr^α *ketone* (*semicarbazone*, m. p. 145°). α-p-*Tolyl*-γ-*methylvaleraldehyde*, b. p. 138—139°/15 mm. (*semicarbazone*, m. p. 230°), similarly obtained (yield 65%) is similarly converted at 450°/15 mm. into p-*tolylmethyl* Bu^β *ketone* (*semicarbazone*, m. p. 160°). CH_2Ph·COMe and CH_2Ph·COEt are obtained in 60% and 40% yields, respectively, from $CHPh_2$·CN and MgMeI or MgEtI, but *p*-tolylacetonitrile does not afford the homologous ketones. p-*Tolyl isoamyl ketone*, b. p. 156—157°/14 mm. (*semicarbazone*, m. p. 178—179°), is obtained from *iso*butylacetic acid, b. p. 185—190°, by condensing the chloride with PhMe. CHPhMe·CHO in presence of kieseleguhr at 600°/15 mm. affords about 60% of CH_2Ph·COMe; α-phenylbutaldehyde similarly yields $CH_2Ph{\cdot}COEt$, and α-*p*-tolylbutaldehyde at 500/15 mm. yields *p*-methylbenzyl Et ketone.

The ultra-violet absorption spectra of the aldehydes and ketones are described. R. Brightman.

Synthesis of chalkone homologues and related compounds. I. Methoxyacetophenone, methoxychalkone, and some related compounds. (Miss) C. Kuroda and (Miss) T. Matsukuma. **II. Some homologues of methoxychalkone and their related compounds.** (Miss) C. Kuroda and (Miss) T. Nakamura (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, **18**, 51—60, 61—76).—I. Careful addition of $AlCl_3$ to PhOMe or the appropriate polymethoxybenzene in cold AcCl gives the following acetophenone derivatives (m. p. in parentheses), which with anisaldehyde and KOH in MeOH at 50—60° yield the chalkones (m. p. in brackets): 4-methoxy- (I) [m. p. 100°]; 2 : 4- (II) [m. p. 80—81°], 3 : 6- (oxime, m. p. 106°) [m. p. 93°] -dimethoxy-; 2 : 3 : 4- (an oil; oxime, m. p. 91°) [94—95°], 1 : 2 : 4- (m. p. 99°), 1 : 3 : 5- [m. p. 119°] -trimethoxy-. In the prep. of (I) and (II) *substances*, m. p. 135° and 145°, respectively, were also obtained. The prep. of 4 : 5-dinitro- and -diamino-veratrole is modified. Halochromy in 30% HCl, conc. H_2SO_4, and 90% H_3PO_4 increases with increasing no. of MeO groups. Anisaldehyde, but not *p*-hydroxy-, *p*-hydroxy-*m*-methoxy-, or *m*-methoxy-*p*-ethoxy-benzaldehyde, shows halochromy. The above method of synthesis failed with 1 : 2 : 4 : 5-tetramethoxybenzene.

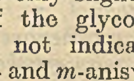
II. Thymol Me ether gives (above method) 4-*methoxy*-2-*methyl*-5-iso*propylacetophenone*, b. p. 236°, 157—158°/8 mm. (*oxime*, m. p. 157°; *semicarbazone*, m. p. 113°), which yields 4-*methoxy*-2-*methyl*-5-iso*propylchalkone*, m. p. 70°, and the following derivatives of the last substance: 2′- (m. p. 138°), 4′- (m. p. 163°) -*hydroxy*-; 4′-*methoxy*-, m. p. 77°; 3′-*methoxy*-4′-*ethoxy*-, m. p. 94—96°; 3′ : 4′-*methylenedioxy*-, m. p. 97°; 3′ : 4′-*dimethoxy*-6′-*methyl*-, m. p. 119°. The same method yields also the following chalkone derivatives: 3 : 4 : 3′ : 4′-*tetramethoxy*-6 : 6′-*dimethyl*-, m. p. 132°; 3-*hydroxy*-4 : 3′ : 4′-*trimethoxy*-6 : 6′-*dimethyl*-, m. p. 197—198°; 4 : 3′ : 4′-*trimethoxy*-6′-*methyl*-, m. p. 169°; 2-*hydroxy*-3′ : 4′-*dimethoxy*-6′-*methyl*-, m. p. 150—151°; 2 : 3 : 4 : 6 : 3′ : 4′-*hexamethoxy*-6′-*methyl*-, m. p. 132°; 4′-*hydroxy*-3 : 4-*dimethoxy*-6 : 3′-*dimethyl*-, m. p. 144—145°; 3 : 4 : 3′-*trimethoxy*-4′-*ethoxy*-6-*methyl*-, m. p. 136°; 2 : 3 : 4 : 6 : 2′ : 3′ : 4′ : 6′-*octamethoxy*-, m. p. 96—97°. 2 : 3 : 4 : 6-Tetramethoxyacetophenone with alkaline $KMnO_4$ affords 2 : 3 : 4 : 6-*tetramethoxybenzoylformic acid*, decomp. 126°, the NH_2Ph salt (m. p. 96°) of which in boiling xylene affords 2 : 3 : 4 : 6-*tetramethoxybenzanil*, m. p. 86° after softening at 83°, hydrolysed to the corresponding *aldehyde*, m. p. 86·5—87°. Pyrogallol Me_3 ether gives gallacetophenone, b. p. 140°/10 mm., which led similarly to 2 : 3 : 4-*trimethoxybenzoylformic acid*, m. p. 136° (NH_2Ph salt), and 2 : 3 : 4-*trimethoxybenzanil*, m. p. 76° after sintering at 74°. R. S. Cahn.

Affinity capacity and migratory power. II. Mechanism of dehydration of glycols and their transformation into aldehydes or ketones; reality of the semipinacolic transformation and vinyl dehydration; non-necessity of intermediate aldehyde–ketone transposition. M. Tiffeneau, (Mme.) J. Lévy, and P. Weill (Bull. Soc. chim., 1931, [iv], 49, 1606—1617).—From a review of the transformations of di-*tert.* and di-*sec.* glycols and of *sec.*-*tert.*-glycols the following evidence is advanced in support of actual semipinacolic transformation in the dehydration of aryldialkylethylene glycols, and against aldehyde formation as an intermediate stage: (1) the non-identity of the ketones obtained by dehydration with H_2SO_4 of *o*- and *m*-anisyldimethyl- and of *p*-anisylmethylethyl-ethylene glycol with those similarly obtained from the corresponding trisubstituted acetaldehydes: (2) the formation of active αγδ-triphenylbutan-β-one by dehydration of active phenyldibenzylethylene glycol with cold H_2SO_4, when the formation of an inactive intermediate aldehyde must lead to an inactive ketone; and (3) differences produced by varying experimental conditions, *e.g.*, concn. of H_2SO_4, and temp., on the dehydration of arylalkylethylene glycols and the isomerisation of aryldialkylacetaldehydes. Thus whilst numerous glycols yield only ketones on distillation, most of the corresponding trisubstituted aldehydes are unchanged at the same temp. and isomerise only at higher temp. α-Anisyl-α-methylbutaldehyde is converted into the ketone at 450° only in presence of kieselguhr, but the latter is readily obtained by dehydration of anisylmethylethylethylene glycol at 260°. The occurrence of vinyl dehydration is similarly established by the conversion of di-*p*-anisylpropylene glycol with H_2SO_4 into anisoylanisylethane by vinyl dehydration without transposition, whilst αα-di-*p*-anisylpropaldehyde is similarly converted by aldehydo–ketone isomerisation with migration of Me into αα-di-*p*-anisylpropan-β-one. Accordingly, it is concluded that comparisons of the affinity capacity of cyclic radicals can safely be based on their migratory powers. R. Brightman.

Affinity capacity and migratory power. III. General study of affinity capacity. M. Tiffeneau and (Mme.) J. Lévy (Bull. Soc. chim., 1931, [iv], 49, 1617—1661).—Since "affinity capacity" is directly proportional to the effect of the radicals on various additive or elimination reactions, it is considered to be of use in interpreting the mechanism of reactions or in predicting their course. The following conclusions are reached from direct and indirect comparisons of the radicals by dehydration of glycols, isomerisation of the corresponding ethylene oxides, or addition of HOI to the analogous olefines, in the types $CHR{:}CH_2$, $CRR'{:}CH_2$, $CHR{:}CHR'$, $CRR'{:}CHR''$, and $CRR'{:}CR''R'''$: the affinity capacities of the aryl radicals are without exception higher than those of alkyl groups or than that of H, being approx. equal to that of two alkyl radicals. The affinity capacity of the Ph radical is slightly less than that of two Me groups, but is approx. equal to that of Me+Et or Me+Pr^a and is greater than Me+CH_2Ph. The radicals are thus classified in two broad groups of strong and weak affinity capacity, within which groups minor variations exist. The aryl groups may be arranged in the following order of decreasing affinity capacity: *p*-anisyl>piperonyl, *p*-tolyl, *o*-anisyl>*m*-anisyl>Ph. The effect of Me is not identical with that of OMe substitution and for the tolyl groups the order of affinity capacity is *o*->*p*->*m*-. For the alkyl groups the order is : Me>Pr^α^>Bu>Et, the affinity capacity being generally greater than that of H, especially for Me, amyl, and *iso*amyl. Pr$^{\alpha}$ and Pr$^{\beta}$ approx. to, and CH_2Ph is lower than, H. R. BRIGHTMAN.

Affinity capacity and migratory power. IV. General study of migratory powers. M. TIFFENEAU and (MME.) J. LÉVY (Bull. Soc. chim., 1931, [iv], 49, 1661—1709).—From mol. transpositions which occur in the dehydration of α-glycols, isomerisation of the corresponding ethylene oxides, dehalogenation of the glycol iodohydrins, and the deamination of NH_2-alcohols, derived from the types, ·CHR·CHR′·, ·CRR′·CH_2·, ·CRR′·CHR″·, ·CRR′·CRR′·, ·CRR·CRR′·, and CRR·CR′R″, the following general conclusions are reached. For aryl radicals the migratory powers are generally but not rigorously, parallel with the affinity capacities, and except in the dehydration of *p*-tolylhydrobenzoin when Ph migrates in place of *p*-tolyl, and the deamination of the NH_2-alcohols CArAr′(OH)·CHX·NH_2, when Ph has a greater migratory power than anisyl, $C_{10}H_7$, or *p*-tolyl, the comparative migratory powers of aryl groups are relatively const. and the radicals can be arranged in the following groups of decreasing migratory power: (1) *p*-anisyl, *p*-tolyl, *p*-diphenylyl, α-naphthyl, 3 : 4-veratryl, 2 : 4-veratryl, (2), *p*-ethoxyphenyl, *p*-*iso*propylphenyl, *p*-ethylphenyl, *p*-fluorophenyl, (3) Ph, *p*-iodophenyl, *o*-anisyl, *o*-ethoxyphenyl, (4) *m*-tolyl, *m*-anisyl, 2 : 5-veratryl, *o*-, *m*-, and *p*-chloro- and -bromo-phenyl. Normally *p*-substituted Ph groups, including 2 : 4-dimethoxy- and 3 : 4-dimethoxy-phenyl as well as α- and β-$C_{10}H_7$, are markedly greater in migratory power than Ph, whilst *m*-substituted Ph groups are definitely greater. Aryl groups are invariably above H and alkyl groups in migratory power, H is above Me and about equal to CH_2Ph and Et. The migratory power of the alkyl groups varies inversely with their affinity capacity, and the radicals can be arranged in the following order of decreasing migratory power: Bu$^{\alpha}$ and CH_2Ph (fairly strong); Et and *iso*amyl; Pr$^{\alpha}$ and Me (weak); Bu$^{\beta}$ and Pr$^{\alpha}$ afford an exception to the general rule that affinity capacity and migratory power vary universely. In aldehyde–ketone transposition the migration of radicals is irregular and no rules have been established. R. BRIGHTMAN.

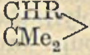
Affinity capacity and migratory power. V. Affinity capacity of the anisyl radical from the dehydration of anisyldialkyl glycols and isomerisation by heat of the corresponding ethylene oxides. M. TIFFENEAU, (MME.) J. LÉVY, and P. WEILL (Bull. Soc. chim., 1931, [iv], 49, 1709—1721).—Since the action of dry KOH on the iodohydrin of α-anisyl-ββ-dimethylethylene affords α-anisyl-α-methylpropaldehyde, b. p. 140—145°/18 mm. (*oxime*, m. p. 104—105°, converted into anisyldimethylacetonitrile, b. p. 165—170°/20 mm. by Ac_2O), and not β-anisylbutan-γ-one (cf. A., 1926, 818), whilst isomerisation of α-anisyl-β-methyl-αβ-propylene oxide yields β-anisylbutan-γ-one, also obtained by dehydration of the glycol, the affinity capacity of anisyl is greater than that of two Me groups and consequently than that of Ph. Similarly *α-anisyl-β-ethyl-αβ-butylene oxide*, b. p. 156—158°/16 mm., obtained from *α-anisyl-β-ethyl-Δ$^{\alpha}$-butylene*, b. p. 134°/15 mm., d_0^4 0·98 (from Mg anisyl bromide and α-ethylbutaldehyde, and dehydration), on distillation in presence of kieselguhr etc., affords only *α-anisyl*-n-*propyl Et ketone* (I), b. p. 160—162°/22 mm., d_0^4 1·034 (*semicarbazone*, m. p. 138°), also obtained in 40% yield from EtBr and α-anisylbutan-β-one in Et_2O in presence of $NaNH_2$. Dehydration of α-anisyl-ββ-diethylethylene glycol similarly yields (I). *α-Anisyl-β-propyl-αβ-amylene oxide*, d^0 0·995, b. p. 162—165°/13 mm., from BzO_2H and *α-anisyl-β-propyl-Δ$^{\alpha}$-amylene*, b. p. 162—165°/16 mm., d_4^0 0·953 (by dehydration of α-anisyl-β-propylpentan-α-ol at 160° in presence of sulphuric-pumice), on distillation in presence of kielselguhr etc. similarly yields *α-anisyl*-n-*butyl Pr$^{\alpha}$ ketone*, b. p. 278—282°, d_0^4 0·986, also obtained from PrBr, $NaNH_2$, and α-anisylbutan-β-one, or by dehydration of *α-anisyl-β-propylpentane-αβ-diol*, m. p. 93—94° (obtained in 50% yield from MgPrBr and Et anisylglycollate), at 280—290° or with 50% H_2SO_4. *γ-Phenyl-α-anisyl-β-benzyl-αβ-propylene oxide*, similarly obtained from *γ-phenyl-α-anisyl-β-benzyl-Δ$^{\alpha}$-propene*, b. p. 250—260°/40 mm., isomerises to *benzyl β-phenyl-α-anisylethyl ketone*, m. p. 75° {*oxime*, m. p. 95° [*Ac* derivative, m. p. 61—62°, yielding on distillation a *substance* (? the amide), m. p. 134—135°], *oximino*-derivative, m. p. 153—154°}, which with CH_2Ph·MgCl affords α-anisyl-βββ-tribenzylethyl alcohol, and is also obtained by dehydration of α-anisyl-ββ-dibenzylethylene glycol. *ωω-Dibenzyl*-p-*methoxyacetophenone*, m. p. 93—95° (*semicarbazone*, m. p. 179—180°), is obtained from *p*-methoxyacetophenone and CH_2PhCl in presence of K. R. BRIGHTMAN.

Affinity capacity and migratory power. VI. Affinity capacity of *o*- and *m*-methoxyphenyl radicals compared with that of two methyl radicals. (MME.) J. LÉVY and R. PERNOT (Bull. Soc. chim., 1931, [iv], 49, 1721—1730).—In the isomerisation of the ethylene oxides  $\begin{array}{l}CHAr\\CMe_2\end{array}\!>\!O$ by distillation with kieselguhr, the oxide ring is ruptured on the side of the Ar group when Ar=*o*-anisyl and on the Me_2 side when Ar=*m*-anisyl. Similarly, addition of HOI to CHAr:CMe_2 yields CHArI·CMe_2·OH when Ar=*o*-anisyl and OH·CHAr·CMe_2I when Ar=*m*-anisyl. Accordingly it is concluded that in affinity capacity *o*-anisyl is superior to *m*-anisyl and approximates to *p*-anisyl, whereas *m*-anisyl is only slightly superior to Ph. The dehydration of the glycols, OH·CHAr·CMe_2·OH, with H_2SO_4 did not indicate differences in affinity capacity between *o*- and *m*-anisyl, but showed that they were inferior to *p*-anisyl.

α-o-*Anisyl-β-methylpropan-α-ol* has b. p. 133°/14 mm., *α-o-anisyl-β-methyl-Δ$^{\alpha}$-propylene*, b. p. 109°/14 mm. (dimeride, b. p. 212—215°/14 mm.; *oxide*, b. p. 115°/14 mm.); α-m-*anisyl-β-methylpropan-α-ol*, b. p. 130°/12 mm., and α-m-*anisyl-β-methyl-Δ$^{\alpha}$-propylene*, b. p. 110°/12 mm. (*oxide*, b. p. 127°/17 mm.); α-o-*anisyl-β-methyl-αβ-propylene glycol*, b. p. 162—164°/14 mm. (yield 70—80% from *Et* o-*anisylglycollate*, b. p. 168°/14 mm.), on dehydration by heat or H_2SO_4 affords α-o-*anisylethyl Me ketone*, b. p. 127—128°/14 mm. (*semicarbazone*, m. p. 222°); with boiling 20%

H_2SO_4, α-o-*anisyl-α-methylpropaldehyde*, b. p. 125—126°/14 mm. (*semicarbazone*, m. p. 192°), is obtained together with (probably) a little diethylene oxide. α-m-*Anisyl-β-methyl-αβ-propylene glycol*, b. p. 129—130°/14 mm. (from *Et* m-*anisylglycollate*, b. p. 169°/14 mm.), similarly yields on distillation at 15 mm. α-m-*anisyl-α-methylpropaldehyde*, b. p. 128—129°/14 mm. (*semicarbazone*, m. p. 162°), together with resinous products; with 20% sulphuric acid a *substance*, b. p. 222—228°/13 mm., probably the diethylene oxide which in presence of sulphuric-pumice is converted into α-*m*-anisyl-α-methylpropaldehyde is also produced. With H_2SO_4, *d* 1·84, α-m-*anisylethyl Me ketone*, b. p. 135—136°/16 mm. (*semicarbazone*, m. p. 145°), is obtained. *o*-Anisyl Pr$^{\beta}$ ketone has b. p. 125—126° (? at 12 mm.) (semicarbazone, m. p. 118°), and *m*-anisyl Pr$^{\beta}$ ketone, b. p. 130°/12 mm. (*semicarbazone*, m. p. 112°). R. BRIGHTMAN.

Affinity capacity and migratory power. VII. Migratory powers of *o*- and *m*-methoxyphenyl compared with those of phenyl and anisyl radicals. (MME.) J. LÉVY and R. PERNOT (Bull. Soc. chim., 1931, [iv], 49, 1730—1738).—The elimination of HI from the *iodohydrin* of *α-phenyl-α*-o-*anisylethylene*, m. p. 37°, d_{17}^{17} 1·08, with $AgNO_3$ yields *Ph* o-*methoxybenzyl ketone*, b. p. 207—210°/16 mm., d_{25}^{25} 1·13 (*semicarbazone*, m. p. 179—180°), by migration of the *o*-anisyl group; the *iodohydrin* of *α-phenyl-α*-m-*methoxyphenylethylene*, b. p. 169—170°/12 mm., d_{15}^{15} 1·08, yields m-*methoxyphenyl* CH_2Ph *ketone*, b. p. 208—212°/16 mm. (*semicarbazone*, m. p. 141°), the *iodohydrin* of α-o-*anisyl-α*-p-*anisylethylene*, m. p. 75°, b. p. 198°/14 mm., yields p-*anisyl* o-*methoxybenzyl ketone*, b. p. 230—232°/13 mm. (*semicarbazone*, m. p. 180°), by migration of the *o*-anisyl group; and α-m-*anisyl-α*-p-*anisylethylene*, b. p. 215—216°/19 mm., d_{18}^{18} 1·10, yields m-*anisyl* p-*methoxybenzyl ketone* (I), m. p. 61° (*semicarbazone*, m. p. 145—146°), by migration of the anisyl group. (I) with MeI or CH_2PhCl in NaOEt affords m-*anisyl α*-p-*anisylethyl ketone*, b. p. 222—224° (*semicarbazone*, m. p. 185—186°; *oxime*, m. p. 82—83°), and m-*anisyl β-phenyl-α*-p-*anisylethyl ketone*, m. p. 109—110°. Accordingly, the four radicals are arranged in the following order of decreasing migratory power: *o*-anisyl, *p*-anisyl, Ph, *m*-anisyl, whereas the affinity capacities are in the decreasing order: *p*-anisyl, *o*-anisyl, *m*-anisyl, Ph. α-Phenyl-α-*o*-anisylethylene is obtained from MgMeI and *o*-methoxybenzophenone, m. p. 79°, by distillation of the *α-phenyl-α*-o-*anisylethanol*, m. p. 76°, first formed. 2 : 4′-*Dimethoxybenzophenone*, m. p. 99° (yield 30%), and α-o-*anisyl-α*-p-*anisylethanol*, m. p. 99°, are similarly obtained. m-*Methoxybenzophenone*, m. p. 37°, and 3 : 4′-*dimethoxybenzophenone*, m. p. 54—55°, obtained from *m*-methoxybenzoyl chloride in presence of $AlCl_3$, yield the ethylene direct with MgMeI. α-*o*-Anisyl-α-*p*-anisylethylene and α-*m*-anisyl-α-*p*-anisylethylene react violently with BzO_2H, but at low temp. the latter gives 80% of a *substance*, m. p. 99°, probably α-*m*-anisyl-α-*p*-anisylethylene glycol monobenzoate, since on distillation it affords BzOH and 3 : 4′-*dimethoxydiphenylacetaldehyde*, b. p. 216—222°/19 mm. (*semicarbazone*, m. p. 130°). *Phenyl*-o-*anisylacetaldehyde*, b. p. 202—206°/16 mm. (*semicarbazone*, m. p. 167—168°), *phenyl*-m-*anisylacetaldehyde*, b. p. 205—208° (*semicarbazone*, m. p. 181°), and 2 : 4′-*dimethoxydiphenylacetaldehyde*, b. p. 230—234°/14 mm. (*semicarbazone*, m. p. 183°), similarly obtained by isomerisation of the ethylene oxides or glycol benzoates, are readily resinified on distillation even under reduced pressure. R. BRIGHTMAN.

Affinity capacity and migratory power. VIII. Relative affinity capacities of *p*-tolyl and piperonyl radicals in direct or indirect comparison with other aryl radicals. M. TIFFENEAU and (MME.) J. LÉVY (Bull. Soc. chim., 1931, [iv], 49, 1738—1753).—Direct comparison of the affinity capacity of *p*-tolyl and piperonyl with that of other aryl groups in the type CHR:CHPh yields no definite conclusions, except that, since *o*-phenylpiperonylethylene oxide is ruptured on the side of the piperonyl group, the piperonyl radical has a higher affinity capacity than Ph. The other ethylene oxides isomerise to the disubstituted aldehydes and dehydration of the glycols yields the same products. Indirect comparison, by isomerisation of the ethylene oxides,  $\genfrac{}{}{0pt}{}{\mathrm{CHR}}{\mathrm{CMe_2}}\!>\mathrm{O}$, in which, when R=*p*-tolyl or piperonyl, rupture occurs on the side of the cyclic radical, indicates that *p*-tolyl and piperonyl, like *p*- and *o*-anisyl, are superior in affinity capacity to Ph and *m*-anisyl. Similarly, addition of HOI to the corresponding ethylenes yields $OH\cdot CHR\cdot CMe_2I$ when R=*p*-tolyl and piperonyl, and dehydration of the glycols yields $CRMe_2\cdot CHO$, also indicating that *p*-tolyl and piperonyl are superior to two Me groups in affinity capacity. Since under the same conditions (dil. H_2SO_4) when R=*p*-anisyl the ketone, CHRMe·COMe, is obtained, it is concluded that the order of decreasing affinity capacity is *p*-anisyl; *o*-anisyl, *p*-tolyl, and piperonyl; *m*-anisyl; Ph.

The following are described: *β-phenyl-α*-p-*tolylethanol*, m. p. 107—108° [from p-*tolyl benzyl ketone*, m. p. 107·5° (*oxime*, m. p. 131°)], giving on distillation or dehydration with 20% H_2SO_4, *β-phenyl-α*-p-*tolylethylene*, m. p. 69°, converted by BzO_2H in $CHCl_3$ into the *oxide*, m. p. 59—60°, b. p. 190—192°/22 mm., isomerising in presence of $ZnCl_2$ to *phenyl*-p-*tolylacetaldehyde*, b. p. 180—185°/14 mm. (*semicarbazone*, m. p. 157—158°), and *Ph* p-*methylbenzyl ketone*, m. p. 94—95° (*semicarbazone*, m. p. 128—129°; *oxime*, m. p. 109°). β-*Phenyl-α-piperonylethanol*, m. p. 156—157° (in 90% yield from $CH_2Ph\cdot MgCl$ and piperonal), and β-*phenyl-α-piperonylethylene*, m. p. 93—94°, yielding the *oxide* (in Et_2O) isomerised to *Ph piperonylmethyl ketone*, m. p. 70° (*semicarbazone*, m. p. 187°), and *phenylpiperonylacetaldehyde*, b. p. 214—215°/14 mm. (*semicarbazone*, m. p. 172—173°, are similarly obtained. *Piperonyl* CH_2Ph *ketone* has m. p. 91—92°, b. p. 222—223° (*semicarbazone*, m. p. 172°). α-*Phenyl*-β-p-*tolylethylene glycol*, m. p. 94—95° and 128—129°, is obtained in two stereoisomeric forms by converting the corresponding *dibromide*, m. p. 173—174°, into the stereoisomeric *diacetates*, liquid and m. p. 79—80°, and hydrolysis, both of which on dehydration with 20% H_2SO_4 afford phenyl-*p*-tolylacetaldehyde. β-*Phenyl-α-piperonylethylene glycol*, m. p. 92—93°, similarly obtained from the corresponding *dibromide*, b. p. 185—187°, and *diacetate*, b. p. 235—242°/23 mm., yields phenylpiperonylacetaldehyde and ω-piperonylacetophenone on dehydration. Dehydration of α-p-*tolyl*-β-*methylpropan*-α-*ol*, b. p. 145—147°/35 mm., by distillation alone or in presence of sulphuric-pumice, affords α-p-*tolyl*-β-*methyl*-Δ^{α}-*propylene*, b. p. 208—210°, giving an *oxide*, b. p. 120—125°/17 mm., which isomerises only in presence of $ZnCl_2$, yielding α-p-*tolylethyl Me ketone*, b. p. 114—118°/15 mm. (*semicarbazone*, m. p. 183—184°; *oxime*, m. p. 58—70°), which yields an iodohydrin converted by $AgNO_3$ into α-p-*tolyl*-α-*methylpropaldehyde* (I), b. p. 192°/14 mm. (*semicarbazone*, m. p. 171—172°). α-p-*Tolyl*-β-*methyl*-αβ-*propylene glycol*, m. p. 55—60°, obtained in 60—80% yield from *Et* p-*tolylglycollate*, m. p. 76°, b. p. 155—158°/18 mm., and 4 mols. of MgMeI, on dehydration with 20% H_2SO_4 affords (I), and a *substance*, m. p. 62°, b. p. 180°/20 mm., probably the diethylene oxide, since H_2SO_4 converts it into β-*p*-tolylbutan-γ-one; the latter is also obtained by dehydration of the glycol with H_2SO_4, *d* 1·84, at 0—5°. α-*Piperonyl*-β-*methylpropyl alcohol*, α-*piperonyl*-β-*methyl*-Δ^{α}-*propylene*, b. p. 134—135°/10 mm. (*dimeride*, m. p. 127—128°; *oxide*, b. p. 140—145°/12 mm.), *Et piperonylglycollate*, m. p. 70—71°, and α-*piperonyl*-β-*methyl*-αβ-*propylene glycol*, m. p. 107—108°, are similarly obtained, the last-named yielding with 20% H_2SO_4 α-*piperonyl*-α-*methylpropaldehyde*, b. p. 148—150°/12 mm. (*semicarbazone*, m. p. 184—185°; *oxime*, m. p. 90—91°), together with a *substance*, b. p. 250—260°/12 mm., converted into α-*piperonylethyl Me ketone* (II), b. p. 150°/12 mm. (*semicarbazone*, m. p. 179—180°), on distillation. With H_2SO_4, *d* 1·84, even at —20°, piperonylmethylpropylene glycol is resinified. Isomerisation of the ethylene oxide by distillation at the ordinary pressure also affords (II), which is also obtained by oxidation of *iso*safrole in $CHCl_3$ with BzO_2H, and methylation of the piperonylacetone, b. p. 158°/15 mm. (*semicarbazone*, m. p. 157°), in Et_2O with $NaNH_2$. Further methylation affords α-*piperonyl*-α-*methylethyl Me ketone*, b. p. 164°/17 mm. (*semicarbazone*, m. p. 217°), also obtained directly from piperonylacetone. The iodohydrin of α-piperonyl-β-methyl-Δ^{α}-propylene with $AgNO_3$ is converted into α-piperonyl-α-methylpropaldehyde, elimination of HI being thus accompanied by migration of piperonyl. *p*-Tolyl Pr^{β} ketone has m. p. 235—236° (oxime, m. p. 92°). *p*-Tolylglycollic acid, m. p. 144—145°, is obtained together with a *substance*, m. p. 75—77°, in 40—45% yield by Na_2CO_3 hydrolysis of *p*-tolyltrichloromethylcarbinol (acetate, m. p. 107°), obtained in 12—15% yield from chloral, PhMe, and $AlCl_3$. Et piperonylglycollate is obtained from piperonal cyanohydrin through the NH_2-ester hydrochloride obtained with HCl in Et_2O–EtOH solution.

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Affinity capacity and migratory power. IX. Migratory power of cyclic radicals deduced from the dehydration reactions of pinacols. A. Orékhov and M. Roger (Bull. Soc. chim., 1931, [iv], 49, 1754—1756).—Since the pinacols, $(OH{\cdot}CPhR{\cdot})_2$, where R=veratryl or 3 : 4-dimethoxyphenyl, with 20% alcoholic KOH yield the pinacolins, $CPhR_2{\cdot}COPh$, it is concluded that the migratory powers of 2 : 4- or 3 : 4-dimethoxyphenyl are superior to that of Ph. Reduction of 2 : 4-dimethoxybenzophenone affords αβ - 2 : 4 : 2′ : 4′- *tetramethoxydiphenyl* - αβ - *diphenylethylene glycol*, m. p. 192—193°, also obtained from benzil and Mg 2 : 4-dimethoxyphenyl iodide, and *Ph* 2 : 4 : 2′ : 4′-*tetramethoxytriphenylmethyl ketone*, m. p. 148—149°, the latter being obtained by dehydration of the pinacol, and yielding on scission 2 : 4 : 2′ : 4′-tetramethoxytriphenylmethane, m. p. 122°. Reduction of 3 : 4-dimethoxybenzophenone affords only *Ph* 3 : 4 : 3′ : 4′-*tetramethoxytriphenylmethyl ketone*, m. p. 120—121°, yielding on scission 3 : 4 : 3′ : 4′-*tetramethoxytriphenylmethane*, m. p. 121—124°. 2 : 4-Dimethoxytriphenylmethane has m. p. 124°.

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Affinity capacity and migratory power. X. Comparative migratory powers of cyclic radicals deduced from the deamination of amino-alcohols. M. Tiffeneau, A. Orékhov, and M. Roger (Bull. Soc. chim., 1931, [iv], 49, 1757—1765).—The comparative migratory powers of *o*- and *p*-anisyl, *o*- and *p*-ethoxyphenyl, and 2 : 4-, 2 : 5-, and 3 : 4-dimethoxyphenyl have been compared with that of Ph by observing the structure of the ketone $COPh{\cdot}CH_2R$ or $COR{\cdot}CH_2Ph$ produced by the action of 50% $NaNO_2$ on the NH_2-alcohols, $OH{\cdot}CRPh{\cdot}CH_2{\cdot}NH_2$, in AcOH. 2 : 5-Dimethoxyphenyl migrates less readily than Ph or *o*-anisyl. but the other radicals examined migrate more readily than Ph. In opposition to the results of Lévy and Pernot for *o*- and *p*-anisyl, *o*-anisyl migrates in preference to *p*-anisyl, although *p*-anisyl migrates in preference to Ph, and Ph and *o*-anisyl appear equal in migrating power. Accordingly, it is concluded that the migratory power of a radical is not invariable for different reactions.

β-*Hydroxy*-β-*phenyl*-β-p-*anisylethylamine*, m. p. 134—135° (*hydrochloride*, m. p. 164—165°), affording ω-*p*-anisylacetophenone, m. p. 98—99°, on deamination, is obtained from MgPhBr and ω-*amino*-p-*methoxyacetophenone hydrochloride*, m. p. 195—196°, prepared by reduction of oximino-*p*-methoxyacetophenone. β-*Hydroxy*-β-*phenyl*-β-p-*ethoxyphenylethylamine*, m. p. 135—136° (*hydrochloride*, m. p. 170—175°), similarly obtained from ω-*amino*-p-*ethoxyacetophenone hydrochloride*, m. p. 194—195°, affords a mixture of p-*ethoxyphenyl* CH_2Ph *ketone*, m. p. 103—104° (*semicarbazone*, m. p. 156°; *oxime*, m. p. 103—104°), and (mainly) *Ph* p-*ethoxybenzyl ketone*, m. p. 110—111·5° (*oxime*, m. p. 121—122°); β-*hydroxy*-β-*phenyl*-β-*veratrylethylamine*, m. p. 93—94°, from ω-*amino*-3 : 4-*dimethoxyacetophenone hydrochloride*, m. p. 212°, yields *Ph* 3 : 4-*dimethoxybenzyl ketone*, m. p. 61·5—62·5° (*oxime*, m. p. 105—106°), and β-*hydroxy*-β-p-*anisyl*-β-o-*anisylethylamine*, m. p. 109—110° (*hydrochloride*, m. p. 182°), *o*-anisyl *p*-methoxybenzyl ketone, m. p. 178°. β-*Hydroxy*-β-*phenyl*-o-*anisylethylamine*, m. p. 107—108° (*hydrochloride*, m. p. 175—176°), similarly obtained from Mg ω-anisyl halide and ω-aminoacetophenone in HCl, on deamination yields a mixture of *o*-anisyl CH_2Ph ketone, b. p. 198—202°(?)/14 mm. (semicarbazone, m. p. 214°), and *Ph* o-*methoxybenzyl ketone*, b. p. 198—202°/14 mm. (*semicarbazone*, m. p. 183°), on deamination. β-*Hydroxy*-β-*phenyl*-β-o-*ethoxyphenyl*-

ethylamine, m. p. 124—125° (*hydrochloride*, m. p. 183°), yields a mixture of o-*ethoxyphenyl* CH_2Ph *ketone*, b. p. 197—198°/14 mm. (*semicarbazone*, m. p. 118—119°), and mainly *Ph* o-*ethoxybenzyl ketone*, m. p. 110—111·5° (*semicarbazone*, m. p. 172°); β-*hydroxy*-β-*phenyl*-β-2 : 4-*dimethoxyphenylethylamine*, m. p. 108—109° (*hydrochloride*, m. p. 198°), yields a mixture of 2 : 4-dimethoxyphenyl CH_2Ph ketone, m. p. 47—48° (oxime, m. p. 120—121°), and mainly *Ph* 2 : 4-*dimethoxybenzyl ketone*, m. p. 99—100° (*oxime*, m. p. 92—93°); and β-*hydroxy*-β-*phenyl*-β-2 : 5-*dimethoxyphenylethylamine*, m. p. 131—132° (*hydrochloride*, m. p. 141°), yields 2 : 5-*dimethoxyphenyl* CH_2Ph *ketone*, m. p. 40° (*oxime*, m. p. 93°). 3 : 4-*Dimethoxyphenyl* CH_2Ph *ketone* has m. p. 91—93° (*oxime*, m. p. 128—129°; CH_2Ph derivative, m. p. 78—79°).

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Affinity capacity and migratory power. XI. Comparative affinity capacities of aryl and alkyl radicals. (Mme.) J. Lévy and (Mme.) Dvoleitzka-Gombinska (Bull. Soc. chim., 1931, [iv], 49, 1765—1776).—Dehydration of the glycols OH·CHAr·CHR·OH, where Ar=Ph or *p*-anisyl and R=Me, Et, Pr^{α}, Pr^{β}, CH_2Ph, with 20% H_2SO_4, and isomerisation of the corresponding oxides always yields the ketone $CH_2Ar·CO·R$, and accordingly the affinity capacity of the aryl groups is superior to that of the alkyl or aralkyl. Similarly, addition of HOI to the corresponding ethylenes always yields OH·CHAr·CHRI, but in the elimination of HI with $AgNO_3$ the semihydrobenzoin transposition is accompanied by vinyl dehydration with migration of H, affording $Ar·CO·CH_2R$ to an extent depending on the nature of Ar and R. When Ar=anisyl and R=Et, the aldehyde, CHRAr·CHO, is exclusively formed, but $Ar·CO·CH_2R$, alone is formed when Ar=Ph and R=Et or Pr^{β}. The two reactions are simultaneous when Ar=anisyl and R=Me or Pr^{α} and when Ar=Ph and R=CH_2Ph. Hence the elimination of HI is influenced by the nature of both the aryl and alkyl radicals. With HgO α-phenyl-Δ^{α}-butylene iodohydrin is converted into $COPhPr^{\alpha}$. α-Phenyl-Δ^{α}-amylene iodohydrin with $AgNO_3$ affords α-*phenylvaleraldehyde*, b. p. 122—123°/28 mm. (*semicarbazone*, m. p. 108°), and α-phenyl-γ-methyl-Δ^{α}-butylene iodohydrin (with HgO), $COPhBu^{\beta}$. αγ-Diphenyl-Δ^{α}-propylene iodohydrin similarly affords *phenylbenzylacetaldehyde*, b. p. 186—188°/23 mm., and Ph β-phenylethyl ketone; α-anisyl-Δ^{α}-propylene iodohydrin, α-anisylpropaldehyde, and a little anisyl Et ketone; α-anisyl-Δ^{α}-amylene iodohydrin, anisyl Bu^{α} ketone, and α-*anisylvaleraldehyde*, b. p. 157—158°/17 mm. (*semicarbazone*, m. p. 97°), and α-anisyl-Δ^{α}-butylene iodohydrin, α-*anisylbutaldehyde*, b. p. 145—146°/17 mm. (*semicarbazone*, m. p. 147°).

α-*Phenyl*-Δ^{α}-*propylene oxide*, b. p. 87—90°/13 mm., in presence of 50% H_2SO_4 or $ZnCl_2$ isomerises to $CH_2Ph·COMe$; α-*phenyl*-Δ^{α}-*butylene oxide*, b. p. 110—111°/21 mm., similarly yields $CH_2Ph·COEt$; α-*phenyl*-Δ^{α}-*amylene oxide*, b. p. 114—115°/13 mm., $CH_2Ph·COPr^{\alpha}$, and α-*phenyl*-γ-*methyl*-Δ^{α}-*butylene oxide*, b. p. 108—110°/17 mm., $CH_2Ph·COPr^{\beta}$. α-*Diphenyl*-Δ^{α}-*propylene oxide*, b. p. 162—165°/6 mm., commences to isomerise when distilled under reduced pressure, affording $CO(CH_2Ph)_2$, m. p. 34—35°. The ethylene oxides containing the anisyl radical are unstable and isomerise during distillation or in preparation, affording *p*-methoxybenzyl Me ketone, p-*methoxybenzyl Et ketone*, b. p. 265—270° (*semicarbazone*, m. p. 131—132°), and p-*methoxybenzyl* Pr^{α} *ketone*, b. p. 280—285° (*semicarbazone*, m. p. 142°). α-Phenyl-αβ-propylene glycol has m. p. 52—53° (α-) and 92—93° (β-form), α-*phenyl*-αβ-*butylene glycol*, m. p. 40—41° (α) and b. p. 205—208°/72 mm. (β); α-*phenyl*-αβ-*amylene glycol*, b. p. 160—170°/14 mm. (α), and m. p. 36—38° (β); α-*phenyl*-γ-*methyl*-αβ-*butylene glycol*, m. p. 81—82° (α), m. p. 108° (β); αγ-*diphenyl*-αβ-*propylene glycol*, m. p. 63—64°, α-*anisyl*-αβ-*propylene glycol*, m. p. 116°, α-*anisyl*-αβ-*butylene glycol*, m. p. 75—76° (α) and 220—240° (β), and α-*anisyl*-αβ-*amylene glycol*, m. p. 42—43°.

R. Brightman.

Affinity capacity and migratory power. XII. Isomerisation of phenyldialkylethylene oxides. (*a*). Affinity capacity of phenyl compared with that of two acyclic radicals. (*b*) Comparative migratory power of some acyclic radicals. (Mme.) J. Lévy and A. Tabart (Bull. Soc. chim., 1931, [iv], 49, 1776—1788).—In the ββ-dialkylstyrene oxides,  $\begin{matrix}\mathrm{CHPh}\\ |\\ \mathrm{CRR'}\end{matrix}\!\!>\!\mathrm{O}$, when R and R′=Me, on isomerisation by heat, the O-linking is ruptured on the side of Me; when R and R′=CH_2Ph, the rupture occurs on the Ph side. Accordingly, the affinity capacity of Ph is inferior to that of two Me groups, but superior to two CH_2Ph groups. Similarly, when R=CH_2Ph and R′=Me, Et, Pr^{α}, or Pr^{β}, the ketone, CHPhR·COR′, alone is produced, whereas when R=Me and R′=Et or Pr^{α} and when R and R′ =Et, a mixture of aldehyde and ketone is obtained. Thus whilst the affinity capacity of Ph+H is approx. equal to that of two Et groups, Me +Et, or Me+Pr^{α}, it is superior to that of CH_2Ph and any other radical. Since, moreover, when R=Me and R′=Et, the Et group alone migrates, whilst when R′=Pr^{α} Me migrates, the order of decreasing migratory power is Et, Me, Pr^{α}, observations when R=CH_2Ph, including R′=Pr^{β}, similarly indicating that CH_2Ph is superior to Et and Pr^{α} about equal to Pr^{β}.

ββ-*Diethylstyrene*, b. p. 216—218° (*oxide*, b. p. 113—114°), is obtained by dehydration of α-phenyl-β-ethylbutan-α-ol by distillation at 760 mm., or in presence of sulphuric-pumice, or of α-*phenyl*-β-*ethylbutan*-β-*ol*, b. p. 135—136°/15 mm., obtained in 80—90% yield from Et phenylacetate and MgEtX. When heated to its b. p. the oxide isomerises to a mixture of α-*phenyl*-α-*ethylbutaldehyde*, b. p. 119—121°/14 mm. (*semicarbazone*, m. p. 181°), and α-*phenylpropyl Et ketone*, b. p. 114—116°/13 mm. (*semicarbazone*, m. p. 144°). *Ph* α-*ethyl*-n-*propyl ketone* has b. p. 246—247° (*semicarbazone*, m. p. 172—173°). The following dialkylstyrenes, similarly obtained by dehydration of the appropriate *tert.*-alcohols, are converted into oxides in 70—90% yield with BzO_2H in $CHCl_3$ or Et_2O at 18—20°: α-*phenyl*-β-*methyl*-Δ^{α}-*butylene*, b. p. 201—202° [*oxide*, b. p. 137—138°/33 mm., affording when heated α-*phenyl*-α-*methylbutaldehyde*, b. p. 228—230° (*semicarbazone*, m. p. 152°), and α-*phenylethyl Et ketone*, b. p. 225—228° (*semicarbazone*, m. p. 136°), but only the latter with H_2SO_4], from *α-phenyl*-β-*methylbutan*-β-*ol*, b. p. 115°/14 mm.; *α-phenyl*-β-*methyl*-Δ$^{\alpha}$-*pentene*, b. p. 212—215°/768 mm. [*oxide*, b. p. 131—132°/27 mm., isomerising by heat to *α-phenyl-α-methylvaleraldehyde*, b. p 235—240° (*semicarbazone*, m. p. 136—137°), and *α-phenylethyl Pr$^{\alpha}$ ketone*, b. p. 235—236° (*semicarbazone*, m. p. 129—130°), by heat and polymerising with H_2SO_4], from *α-phenyl*-β-*methylpentan*-β-*ol*; *αγ-diphenyl*-β-*methyl*-Δ$^{\alpha}$-*propylene*, b. p. 175—177°/20 mm. [*oxide*, b. p. 165—166°/8 mm., isomerising to *CH_2Ph α-phenylethyl ketone*, b. p. 205—206°/40 mm. (*semicarbazone*, m. p. 143—145°)], from *α-phenyl*-β-*benzylpropan*-β-*ol*, b. p. 197—198°/20 mm.; *α-phenyl*-β-*benzyl*-Δ$^{\alpha}$-*butylene*, b. p. 183—185°/14 mm. [*oxide*, b. p. 163—164°/6 mm., isomerising to αβ-*diphenyldiethyl ketone*, b. p. 190—192°/13 mm. (*semicarbazone*, m. p. 212—213°), by heat, and to a mixture of this and *CH_2Ph α-phenyl*-n-*propyl ketone*, b. p. 195—198°/25 mm. (*semicarbazone*, m. p. 144—145°), with H_2SO_4], from *α-phenyl*-β-*benzylbutan*-β-*ol*, b. p. 208—215°/12 mm.; *α-phenyl*-β-*benzyl*-Δ$^{\alpha}$-*pentene*, b. p. 315—317° [*oxide*, b. p. 195—197°/8 mm., isomerising to αβ-*diphenylethyl Pr$^{\alpha}$ ketone*, b. p. 210—212° (*semicarbazone*, m. p. 183°)], from *α-phenyl*-β-*benzylpentan*-β-*ol*, b. p. 203—204°/16 mm.; and *α-phenyl*-β-*benzyl*-γ-*methyl*-Δ$^{\alpha}$-*butylene*, b. p. 315—317° [*α-oxide*, b. p. 188—189°/14 mm., β-*oxide*, m. p. 88—90°, both isomerising with H_2SO_4 to αβ-*diphenylethyl Pr$^{\alpha}$ ketone*, b. p. 187—200°/27 mm. (*semicarbazone*, m. p. 122—123°)], from *α-phenyl-γ-methyl*-β-*benzylbutan*-β-*ol*, b. p. 200—201°/20 mm. α-Phenyl-β-methyl-αβ-propylene oxide, b. p. 87—90°/15 mm., does not isomerise on distillation at atm. pressure, but in presence of kieselguhr yields α-phenyl-α-methylpropaldehyde; in presence of $ZnCl_2$ or with H_2SO_4 at 0°, α-phenylethyl Me ketone is obtained. COPhPr$^{\beta}$ has b. p. 91·5—92·5°/10 mm. (semicarbazone, m. p. 167—168°); *Ph* iso*amyl ketone*, b. p. 246—247° (*semicarbazone*, m. p. 172—173°); *α-phenyl*-n-*propyl Me ketone*, b. p. 220—225° (*semicarbazone*, m. p. 189—200°); *α-phenyl*-n-*butyl Me ketone*, b. p. 240—242° (*semicarbazone*, m. p. 148—149°). α-Phenyl-α-methylbutaldehyde and α-phenyl-α-methylvaleraldehyde are obtained by dehydration of the corresponding *sec.-tert.*-glycols with 8% H_2SO_4. α-Phenyl-α-benzylbutaldehyde, b. p. 220—235°/35 mm. (*semicarbazone*, m. p. 175—176°), and *α-phenyl-α-benzylvaleraldehyde*, b. p. 195—200°/15 mm. (*semicarbazone*, m. p. 192°), are obtained by oxidation of the corresponding alcohols with CrO_3 in acetic acid. The following are obtained by reduction of the corresponding amides with Na and EtOH, the amides being obtained by hydrolysis of the nitriles with 85% H_2SO_4: β-*phenyl*-β-*methyl*-n-*amyl alcohol*, b. p. 159—160°/22 mm., from *α-phenyl-α-methylvaleronitrile*, b. p. 155—156°, and *amide*, b. p. 196—197°/21 mm.; and β-*phenyl*-β-*benzylpentan-α-ol*, b. p. 207—210°/15 mm., from *α-phenyl-α-benzylvaleronitrile*, m. p. 63°, and *amide*, m. p. 110°. *α-Phenyl-α-benzyl-propionitrile* (b. p. 194—195°) and -propionamide (m. p. 108°) are described.

R. BRIGHTMAN.

Affinity capacity and migratory power. XIII. Comparative migratory powers of acyclic radicals deduced from the dehydration of phenyldialkyl glycols. M. TIFFENEAU, (MME.) J. LÉVY, and P. JULLIEN (Bull. Soc. chim., 1931, [iv], 49, 1788—1795).—Dehydration by H_2SO_4, *d* 1·84, at 0°, of the glycols, OH·CHPh·CRR′·OH, where R=Me and R′=Et, Pr$^{\alpha}$, Pr$^{\beta}$, Bu$^{\alpha}$, Bu$^{\beta}$, or CH_2Ph affords the ketone CHPhR′·COMe when R′=Et, Pr$^{\beta}$, Bu$^{\alpha}$, or CH_2Ph, indicating that these radicals are superior in migratory power to Me; when R′=Pr$^{\alpha}$, the ketone, CHMePh·COR′, is also formed and exclusively when R′=Bu$^{\beta}$. When R=Et and R′=Me, Pr$^{\alpha}$, Pr$^{\beta}$, and Bu$^{\beta}$, migration of Et alone occurs; with R′=CH_2Ph migration of CH_2Ph preponderates and with R′=Bu$^{\alpha}$ the latter exclusively migrates. The order of migratory power given by these experiments is CH_2Ph>Bu$^{\alpha}$>Et>Pr$^{\beta}$>Me, Pr$^{\alpha}$>Bu$^{\beta}$, *i.e.*, inversely as their affinity capacities. The following are described: *α-phenyl*-β-*methylpentane*-αβ-*diol*, m. p. 59—60° (β); *α-phenyl*-β-*methylhexane*-αβ-*diol*, m. p. 49—50° (β), affording *α-phenyl*-n-*amyl Me ketone*, b. p. 250—251° (*semicarbazone*, m. p. 156—158°); *α-phenyl*-βδ-*dimethylpentane*-αβ-*diol*, m. p. 87—88° (β); *α-phenylmethyl Bu$^{\beta}$ ketone*, b. p. 237—240° (*semicarbazone*, m. p. 147·5—148°); *α-phenyl*iso*butyl Me ketone*, b. p. 115—118°/28 mm. (*semicarbazone*, m. p. 153—154°); αγ-diphenyl-β-methylpropane-αβ-diol, m. p. 96—97° (α); αβ-*diphenylethyl Me ketone*, b. p. 188—189°/20 mm. (*semicarbazones*, m. p. 144—145° and 168°); *α-phenyl*-β-*benzyl*-β-*ethylethylene glycol*, m. p. 115—116° (α); *α-phenyl*-β-*benzyl*-n-*butane*-αβ-*diol*, m. p. 126—127° (α); *α-phenyl*-β-*benzyl*-γ-*methyl*-n-*butane*-αβ-*diol*, m. p. 90° (α), giving αβ-*diphenylethyl Pr$^{\beta}$ ketone*, b. p. 195—200°/27 mm. (*semicarbazone*, m. p. 205—206°), and a *substance*, m. p. 37°; *α-phenyl*-n-*propyl Pr$^{\beta}$ ketone*, b. p. 253—254° (*semicarbazone*, m. p. 158—159°); *α-phenyl*-n-*amyl Et ketone*, b. p. 147—150°/16 mm. (*semicarbazone*, m. p. 104—105°); *α-phenyl*-n-*propyl Bu$^{\alpha}$ ketone*, b. p. 242° (*semicarbazone*, m. p. 141—142°); *α-phenyl*-n-*amyl Pr$^{\alpha}$ ketone*, b. p. 275—279° (*semicarbazone*, m. p. 100—101°).

R. BRIGHTMAN.

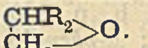
Affinity capacity and migratory power. XIV. Affinity capacity of anisyl and migratory power of Et compared with those of Me and Pr$^{\alpha}$ in molecular transpositions of anisyldialkyl glycols. P. WEILL (Bull. Soc. chim., 1931, [iv], 49, 1795—1806).—Dehydration of the glycols, OH·CHAr·CRR′·OH or isomerisation of the corresponding oxides, when Ar=anisyl, R=Et, R′=Me or Pr$^{\alpha}$, affords the ketone, CHArR·CO·R′ or CHArR′·CO·R, rupture of the oxide ring occurring on the side of the anisyl group. Accordingly, the affinity capacity of anisyl is superior to that of two acyclic groups. When R′=Me, the Et radical alone migrates, yielding CHArEt·COMe, indicating that Et has a greater migratory power than Me, but when R′=Pr$^{\alpha}$, the ketone CHArPr$^{\alpha}$·COEt is alone obtained, the alkyl group of stronger affinity capacity migrating.

α-Anisyl-β-*methylbutane*-αβ-*diol*, obtained in an α-form from *α-anisylpropan-α-ol*-β-*one*, b. p. 135—140°/25 mm. (from MgMeI and anisylglycollamide), and a β-form from α-anisylbutan-α-ol-β-one, on dehydration affords only γ-anisylpentan-β-one, also obtained by isomerisation of *α-anisyl*-β-*methyl*-αβ-*butylene oxide*, b. p. 135—140°/14 mm., from the α-anisyl-β-methyl-Δ$^{\alpha}$-butylene, b. p. 248°, obtained by dehydrating *α-anisyl*-β-*methyl*-n-*butyl alcohol*, b. p. 155—165°/35 mm. *α-Anisyl-*β*-methyl-*αβ*-butylene iodohydrin* with KOH yields 35% of *α-anisyl-α-methyl-*n*-butaldehyde*, b. p. 145°/12 mm. (*semicarbazone*, m. p. 144°; *oxime*, m. p. 87°, affording on dehydration 75% of *α-anisyl-α-methylbutyronitrile*, b. p. 135—136°/6 mm.), converted into *α-anisylethyl Et ketone*, b. p. 262—265°/4 mm. (*semicarbazone*, m. p. 116—117°; *oxime*, m. p. 69—70°), with H_2SO_4 at −10°. γ-Anisylpentan-γ-ol, b. p. 147—148°/20 mm. (yield 85% from Et anisate), in presence of sulphuric-pumice below 100° yields *γ-anisyl-*Δ^{β}*-pentene*, b. p. 235°. The *α-form* of *α-anisyl-*β*-ethylpentane-*αβ*-diol*, m. p. 91—92°, is obtained from $MgPr^{\alpha}Br$ and anisylbutan-α-ol-β-one; the β-*isomeride*, m. p. 79—80°, is similarly obtained from *α-anisylpentan-α-ol-*β*-one*, b. p. 178°/12—13 mm. On dehydration both yield *α-anisyl-*n*-butyl Et ketone*, b. p. 273° (*semicarbazone*, m. p. 129°), also obtained by isomerisation with H_2SO_4 of the *oxide*, b. p. 285°/760 mm., of *α-anisyl-*Δ^{γ}*-heptene*, b. p. 260°. The iodohydrin of the last with KOH yields α-anisyl-n-propyl Pr^{α} ketone. R. Brightman.

Affinity capacity and migratory power. XV. Migratory power of the phenyl radical. Dehalogenation of the iodohydrins of methylhydrobenzoin; semihydrobenzoin and semipinacolic transpositions. M. Tiffeneau and (Mme.) J. Lévy (Bull. Soc. chim., 1931, [iv], 49, 1806—1811).—The iodohydrin of methylhydrobenzoin, CPhMeI·CHPh·OH, with $AgNO_3$ affords αα-diphenylpropaldehyde, also obtained by dehydration of methylhydrobenzoin or isomerisation of *α-methylstilbene oxide*, m. p. 45—46°. Similarly, the iodohydrin, OH·CMePh·CHPhI, obtained from HOI and α-methylstilbene, affords αα-diphenylpropan-β-one, m. p. 61°, also formed by the dehydration of alkylhydrobenzoins but not hydrobenzoin. These reactions demonstrate the reality of the semipinacolic transposition and indicate that it applies in the dehydration of the alkylhydrobenzoins. The migration of Ph in the second case confirms the superior migratory power of Ph over Me. R. Brightman.

Affinity capacity and migratory power. XVI. Comparative migratory powers of different alkyl radicals and of these and aryl radicals. Influence of the anisyl radical on the dehydration of diarylalkyl glycols and on the isomerisation of the corresponding oxides. P. Weill (Bull. Soc. chim., 1931, [iv], 49, 1811—1823).—The semipinacolic dehydration of β-phenyl-α-anisylbutane-αβ-diol affords α-anisylbenzyl Et ketone and accordingly the sum of the affinity capacities of anisyl and H is greater than that of Ph and Et, and the migratory power of Ph is superior to that of Et. In the dianisyl glycols, OH·CHAr·CRAr·OH, where Ar=anisyl and R=Me and Et, semihydrobenzoin, semipinacolic, or vinylic transposition can occur according to the conditions of dehydration. The anisyl group diminishes the stability of a sec. OH group much less in presence of a second anisyl group near the tert. OH group. The substitution of anisyl for Ph thus affects the mode of dehydration by increasing the stability of the sec. CH·OH group and by modifying the transposition, which leads to elimination of the tert. OH group. The presence of Me is sufficient to determine vinylic transposition in presence of H_2SO_4. Rupture of the O ring in the three oxides always takes place on the side of the two aryl groups and the replacement of Ph by anisyl in oxides already containing an anisyl group does not affect the mechanism of isomerisation. Migration of H is exclusive only in oxides containing at least one anisyl group.

αβ-*Dianisylbutane-*αβ*-diol*, m. p. 111—112° (β-form; liquid α-form), when dehydrated with 20% or 50% H_2SO_4 or by heat, affords mainly *αα-dianisylbutaldehyde*, b. p. 190—191°/2 mm. (*semicarbazone*, m. p. 182°), and a little *dianisylmethyl Et ketone* (I), m. p. 51° (*semicarbazone*, m. p. 192—193°; *oxime*, m. p. 99°), also obtained from the aldehyde with H_2SO_4 at −5°. With H_2SO_4, *d* 1·84, (I) alone is formed. *Anisyl α-anisyl-*n*-propyl ketone*, b. p. 180—200°/17 mm. (*semicarbazone*, m. p. 150°), is obtained from *αα-dianisyl-*Δ^{α}*-butylene*, b. p. 225°/18 mm. (from *αα-dianisylbutyl alcohol*, m. p. 138°), by treating the iodohydrin with $AgNO_3$. αβ-*Dianisyl-*Δ^{α}*-propylene glycol*, b. p. 190°/3 mm. (β-isomeride), when dehydrated by heat or by 20% or 50% H_2SO_4, yields *αα-dianisylpropaldehyde*, b. p. 170—172°/2 mm. (*semicarbazone*, m. p. 184°; *oxime*, m. p. 125°), converted by H_2SO_4 into *αα-dianisylacetone*, m. p. 71° (*semicarbazone*, m. p. 110—157°; *oxime*, m. p. 125°), and by H_2SO_4, *d* 1·84, at −5°, into *anisyl α-anisylethyl ketone*, b. p. 222°/14 mm. (*semicarbazone*, m. p. 162—163°), also obtained from *αα-dianisyl-*Δ^{α}*-propylene*, m. p. 100—101°, by treating the iodohydrin with $AgNO_3$. *α-Phenyl-α-anisyl-*Δ^{α}*-butylene*, b. p. 220—222°/30 mm. (*oxide* isomerising to *α-anisylbenzyl Et ketone*), is obtained from *α-phenyl-α-anisylbutyl alcohol*, m. p. 59—60°. αα-Dianisylbutylene oxide affords αα-dianisylmethyl Et ketone, and αα-dianisylpropylene oxide gives αα-dianisylacetone. R. Brightman.



Affinity capacity and migratory power. XVII. Radicals, $Ph\cdot[CH_2]_n$, compared with hydrogen. Isomerisation of oxides, $\begin{matrix}CHR_2\\ CH_2\end{matrix}\!>\!O$. (Mme.) J. Lévy and J. Sfiras (Bull. Soc. chim., 1932, [iv], 49, 1823—1830).—γ-Phenyl-αβ-propylene oxide, b. p. 98—100°/17 mm., in presence of $ZnCl_2$ or when passed over Al_2O_3 at 260°, yields benzyl Me ketone; with aq. NH_3, 7% of *di-* (*hydrochloride*, m. p. 140°) and 48% of *tri-*(β*-hydroxy-γ-phenylpropyl*)*amine* (*hydrochloride*, m. p. 160—161°) and with $NHMe_2$ in C_6H_6, dimethyl-β-hydroxy-γ-phenylpropylamine, b. p. 140°/22 mm. (hydrochloride, m. p. 95°; *benzoate hydrochloride*, m. p. 155—156°), are formed. δ-Phenyl-αβ-butylene oxide, b. p. 106—109°/14 mm., similarly affords β-phenylethyl Me ketone, *di-* (*hydrochloride*, m. p. 137—139°), 1%, *tri-*(β*-hydroxy-δ-phenylbutyl*)*amine* (*hydrochloride*, m. p. 136°), 32%, and dimethyl-β-hydroxy-δ-phenyl-*n*-butylamine, b. p. 145°/14 mm. (*benzoate hydrochloride*, m. p. 155°); *ε-phenylpentene* αβ*-oxide*, b. p. 122°/16 mm., yields *γ-phenyl-*n*-propyl Me ketone*, b. p. 132—135°/17 mm. (*semicarbazone*, m. p. 127—128°; *oxime*, m. p. 52°), *tri-*(β*-hydroxy-ε-phenyl-*n*-amyl*)*amine* (*hydrochloride*, m. p. 148°) (yield, 23%), and dimethyl-β-hydroxy-ε-phenyl-*n*-amylamine (*benzoate hydrochloride*, m. p. 136°); *ε-phenylhexene* αβ*-oxide*, b. p. 136—139°/13 mm., yields *δ-phenyl-*n*-butyl Me ketone*, b. p. 150—153°/17 mm. (*semicarb-*

azone, m. p. 136—137°); *tri*-(β-*hydroxy*-ξ-*phenyl*-n-*hexyl*)*amine* (yield 15%) (*hydrochloride*, m. p. 78°), and *dimethyl*-β-*hydroxy*-ξ-*phenyl*-n-*hexylamine*, b. p. 171°/17 mm. (*hydrochloride*, m. p. 104°; *benzoate hydrochloride*, m. p. 126°).

The course of these isomerisations shows that the affinity capacities of the radicals $Ph\cdot[CH_2]_n$ are lower than that of H, whilst that of Ph is greater. The benzoates of the above NH_2-alcohols are local anæsthetics. R. Brightman.

Affinity capacity and migratory power. XVIII. Isomerisation of phenyl*cyclo*hexene and of 1-phenyl-4-methyl*cyclo*hexene oxide. Molecular transposition with change from a six- to a five-membered ring. (Mme.) J. Lévy and J. Sfiras (Bull. Soc. chim., 1931, [iv], 49, 1830—1838).—When phenyl*cyclo*hexene oxide, b. p. 136°/15 mm., is distilled at atm. pressure or heated with $ZnCl_2$ or sulphuric-pumice, 60% of 2-phenyl*cyclo*hexanone, m. p. 61° (*semicarbazone*, m. p. 196°; *oxime*, m. p. 169°), and 9% of 1-*phenyl*cyclo*pentane*-1-*aldehyde*, b. p. 134°/15 mm. (*semicarbazone*, m. p. 196·5°), is obtained. Similarly, 1-*phenyl*-4-*methyl*cyclo*hexene oxide*, b. p. 140—141°/15 mm., m. p. 36°, yields 55% of 2-*phenyl*-5-*methyl*cyclo*hexanone*, m. p. 62° (*semicarbazone*, m. p. 217°), and 2% of 1-*phenyl*-4-*methylpentane*-1-*aldehyde* (*semicarbazone*, m. p. 172°). Thus rupture of the oxide ring occurs on the side of the Ph group, indicating the stronger affinity capacity of Ph, but since the yields of *cyclo*pentane derivative are lower than those in the dehalogenation of *cyclo*hexene iodohydrins (10—20%), it is concluded that the presence of Ph decreases the migratory power of the CH_2 chain, a Me group in 4-position having a further adverse effect. A similar mechanism is suggested for the formation of the *cyclo*pentane ring by dehalogenation. With NH_3 at 150° for 10 hr. 1-phenyl*cyclo*hexene 1 : 2-oxide yields 25% of 2-*amino*-1-*phenyl*cyclo*hexan*-1-*ol*, m. p. 105° (*hydrochloride*, m. p. 140°), with traces of a *sec.*-amine, and with $NHMe_2$ in C_6H_6 at 160°, 2-*dimethylamino*-1-*phenyl*cyclo*hexan*-1-*ol*, b. p. 172—173°/18 mm. (*hydrochloride*, m. p. 174°; *benzoate hydrochloride*, m. p. 154°). 1-Phenyl-4-methyl*cyclo*hexene oxide similarly gives 25% of 2-*amino*-1-*phenyl*-4-*methyl*cyclo*hexan*-1-*ol*, b. p. 185°/17 mm. (*hydrochloride*, m. p. 135°), and 5% *di*-(2-*hydroxy*-2-*phenyl*-5-*methyl*cyclo*hexyl*)*amine*, b. p. 220—230°/15 mm. (*hydrochloride*, m. p. 156°), and 2-*dimethylamino*-1-*phenyl*-4-*methyl*cyclo*hexan*-1-*ol*, m. p. 103° (*hydrochloride*, m. p. 187°; *benzoate hydrochloride*, m. p. 187°). R. Brightman.

Affinity capacity and migratory power. XX. Benzyl radical. Dibenzyl glycol and the corresponding ethylene oxide. M. Tiffeneau, A. Orékhov, and (Mlle.) J. Lévy (Bull. Soc. chim., 1931, [iv], 49, 1840—1846).—γ-Phenyl-β-benzylpropane-β-diol, m. p. 100—101°, b. p. 359—360°, when distilled over kieselguhr yields traces of a *substance*, b. p. 305—310°; with H_2SO_4 at 0° resinous products only are obtained, and with 20% H_2SO_4 or anhyd. $H_2C_2O_4$, γ-*phenyl*-β-*benzyl*-αβ-*propylene oxide*, m. p. 75°, is formed, all attempts to isomerise which failed. In view of the stability of the oxide and its direct formation from the glycol, it is concluded that the affinity capacities of CH_2Ph and of H are very nearly the same. β-*Phenyl*-α-*benzylpropaldehyde* has b. p. 217—218°/20 mm. (*semicarbazone*, m. p. 122—123°; *oxime*, m. p. 70—71°); *benzyl* β-*phenylethyl ketone*, m. p. 42—43° (*semicarbazone*, m. p. 130—131°; α-*oxime*, m. p. 120—121°; β-*oxime*, m. p. 80—85°). R. Brightman.

Affinity capacity and migratory power. XXI. Deamination of phenylaminoalcohols. $OH\cdot CHPh\cdot CHR\cdot NH_2$. Intermediate formation of vinyl alcohols. Formation of acylbenzenes without transposition. M. Tiffeneau and (Mlle.) J. Lévy (Bull. Soc. chim., 1931, [iv], 49, 1847—1851).—Deamination of four phenylamino-alcohols, $OH\cdot CHPh\cdot CHR\cdot NH_2$, when R=Et, Pr^{α}, Pr^{β}, or Bu^{α}, with $NaNO_2$ in AcOH, yields the ketone $COPh\cdot CH_2R$, and not $CH_2Ph\cdot COR$. Accordingly, the glycols and ethylene oxides are not intermediate products, since these would yield $CH_2Ph\cdot COR$, and it is concluded that intermediate formation of the vinyl alcohol, $OH\cdot CPh{:}CHR$, is most probable. The following amino-alcohols are obtained by reduction of the oximes of the ketols $OH\cdot CHPh\cdot COR$ with Na and EtOH, Na–Hg in 95% EtOH, or H_2 and Ni in EtOH: β-*amino*-α-*phenyl*-n-*butyl*, b. p. 120—130°/23 mm. (*hydrochloride*, m. p. 225—226°; *chloroaurate*, m. p. 157°); β-*amino*-α-*phenyl*-n-*amyl* (*hydrochloride*, m. p. 170°); β-*amino*-α-*phenyl*-γ-*methyl*-n-*butyl* (*hydrochloride*, m. p. 159—160°), and β-*amino*-α-*phenyl*-n-*hexyl* (*hydrochloride*, m. p. 140—141°) *alcohol*. R. Brightman.

Orientation of α-chloroanthrones. E. de B. Barnett and C. L. Hewett (J.C.S., 1932, 506—509).—The view that only Cl atoms *o*- to a carbonyl group in the chloroanthraquinones can be replaced by CN on treatment with $Cu_2(CN)_2$ and $CH_2Ph\cdot CN$ receives strong support from the inactivity of 2-chloroanthraquinone. Reaction should occur with 1-chloro- and 1 : 8-dichloro-anthrone, but not with 4-chloro- or 4 : 5-dichloro-anthrone. Owing to the enolic properties of these compounds, resinification occurs and no nitrile is isolable. 1-Chloro-10 : 10-dibenzylanthrone cannot enolise and reacts with $Cu_2(CN)_2$ and $CH_2Ph\cdot CN$ to give 1-*cyano*-10 : 10-*dibenzylanthrone*, m. p. 276°, thus providing evidence that the orientation of 1-chloroanthrone is correct. 4-Chloroanthrone gives only resinous products with benzyl chloride and alkali. 1 : 8-Dichloro-10 : 10-di-*o*-chlorobenzylanthrone affords 1 : 8-*dicyano*-10 : 10-*di*-o-*chlorobenzylanthrone*, m. p. 264°, in contrast to 1 : 8-dichloro-10-benzylanthrone, which affords resinous products. Both 1 : 4- and 1 : 5-dichloro-10-benzylanthrone react with $Cu_2(CN)_2$ yielding 4-*chloro*-, m. p. 208°, and 5-*chloro*-1-*cyano*-10-*benzylanthrone*, m. p. 234°, respectively. Bromination of 1 : 8-dichloro-10-phenylanthrone affords 1 : 8-*dichloro*-10-*bromo*-10-*phenylanthrone*, m. p. about 224°, which by prolonged boiling with MeOH and $CaCO_3$ affords 1 : 8-*dichloro*-10-*methoxy*-10-*phenylanthrone*, m. p. 237°. Reaction of C_6H_6 with the above bromo-anthrone and $AlCl_3$ affords 1 : 8-*dichloro*-10 : 10-*diphenylanthrone*, m. p. above 310°, which when warmed with $NPhMe_2$ affords 1 : 8-*dichloro*-4′-*dimethylamino*-10 : 10-*diphenylanthrone*, m. p. 308°. J. L. D'Silva.

Reactions of benzoin and chlorobenzoin with primary aromatic amines. I. Preparation and structure of the anilides of benzoin. II. Velocity of reaction of chlorobenzoin. C. N. Cameron, A. C. Nixon, and S. Basterfield (Trans. Roy. Soc. Canada, 1931, [iii], 25, III, 145—156, 157—169; cf. A., 1930, 345).—I. Nuclear-substituted anilines react with benzoin and desyl chloride to give anilides, the capacity for reaction of the amines varying greatly with the substituent. Desyl chloride usually reacts more easily than benzoin. *o*-Substitution inhibits the reactivity of the NH_2 group. The following are prepared both from benzoin and desyl chloride and the appropriate amine in EtOH, and, in certain cases, without a solvent: *Ph* p-*ethoxy*-, m. p. 118°, p-*chloro*-, m. p. 162°, p-*carbethoxy*-, m. p. 183°, m-*bromo*-, m. p. 123°, and m-*chloro-anilinobenzyl ketone*, m. p. 129°. Benzoin is the source of *Ph* p-*nitro*-, m. p. 187°, and ω-p-*carboxymethyl-anilinobenzyl ketone*, m. p. 189°. Desyl chloride is the source of *Ph* p-*iodo*-, m. p. 157·5° (benzoin affords an amorphous product, m. p. above 285°), and p-*hydroxy-anilinobenzyl ketone*, m. p. 156°. A list of amines (mainly *o*-substituted) which do not react is included.

II. The reaction of desyl chloride with NH_2Ph at 25° is bimol. and gives fairly const. vals. for *K*. The concn. of the base does not greatly influence the val. of *K*, whilst the concn. of the Cl-compound does. Addition of NH_2Ph,HCl or the use of polar solvents accelerates the reaction, whilst non-polar solvents retard it. It is suggested that the retarded reaction is due to the absence of $H^{\cdot}$ or the separation of amine hydrochloride. The rate of reaction between desyl chloride and many substituted anilines in EtOH has been measured. The effect of the substituent on the reactivity of the NH_2 group is in the order $OEt > Me > H > p\text{-}Br > p\text{-}Cl > m\text{-}Cl > m\text{-}Br$. There is a qual. parallelism between the dissociation consts. of the bases and the above series. The effect of each of these groups on the velocity of reaction is correlated with the electrical characteristics of the group.

J. L. D'Silva.

Action of magnesium benzyl chloride on benzylidenephthalide. II. Preparation of *o*-phenylenedi(phenylglyoxal). R. Weiss and C. Alberti (Monatsh., 1932, 59, 220—227; cf. A., 1926, 401).—Short interaction of benzylidenephthalide and $CH_2Ph{\cdot}MgCl$ in cold Et_2O–PhMe gives dibenzylbenzylidenephthalan and dibenzylidenephthalan (I); more prolonged interaction or absence of cooling leads to 2-phenyl-3-benzylindone (II). (I) is oxidised by O_3 to $o\text{-}C_6H_4(CO)_2O$, whilst (II) gives an *ozonide* (?), m. p. 176—177°, decomposed by aq. NaOH to deoxybenzoin-*o*-carboxylic acid. (II) and $CH_2Ph{\cdot}MgCl$ afford 1-*hydroxy*-2-*phenyl*-1 : 3-*dibenzylindene*, m. p. 143—148° (*acetate*, m. p. 129—130°), whilst 2-phenyl-3-benzylidenehydrindone (*loc. cit.*) (ozonolysis product BzOH) yields an amorphous product. (I) and Br in $CHCl_3$ give, after treatment with H_2SO_3 to remove the excess of Br, o-*di*-(αα-*dibromophenylacetyl*)*benzene*, decomp. 104—105°, converted by EtOH at 100° into o-*phenylenedi*(*phenylglyoxal*), $o\text{-}C_6H_4(CO{\cdot}COPh)_2$, m. p. 137—139°, purified through its additive compound (m. p. 210°) with N_2H_4, which is decomposed into its components by dissolution in EtOH. H. Burton.

Condensation of *p*-tolyl methyl ether with *p*-benzoquinone. G. Huppmann (Suddeut. Apoth.-Ztg., 1931, 71, 302; Chem. Zentr., 1931, ii, 551).—In presence of $AlCl_3$, in CS_2, a reddish-brown product is formed. With AcOH and Zn the colourless liquid affords in presence of CO_2 the leuco-compound, di-*p*-methoxytolylquinol (?), $C_{22}H_{22}O_4$, m. p. about 138°.

A. A. Eldridge.

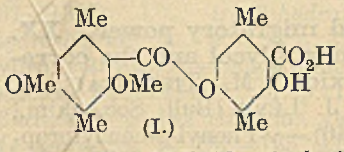
Preparation of anthraquinonesulphonic acids by the Friedel–Crafts reaction. E. Schwenk and H. Waldmann (Angew. Chem., 1932, 45, 17—21).—The sulphophthalic anhydrides interact with C_6H_6, its homologues, and substitution products in presence of $AlCl_3$ to give derivatives of *o*-benzoylbenzoic acid which are readily cyclised in the usual way to anthraquinonesulphonic acids. The *Ba* salt of 3-sulphophthalic anhydride is prepared by heating the *Ba* salt of the corresponding acid, $Ba[SO_3{\cdot}C_6H_4(CO_2H)_2]_2$, at 220°. The prep. of 2-benzoyl-3(or 6)-sulphobenzoic acid (*K H* salt), anthraquinone-1-sulphonic acid, 1 : 4-dichloro- and 1 : 4-dihydroxy-anthraquinone-5-sulphonic acids (from 3-sulphophthalic anhydride), and 2-benzoyl-4(or 5)-sulphobenzoic acid (*Na H* salt), 2-, and 3-chloro-, 1 : 4-dichloro-, and 1 : 4-dihydroxy-anthraquinone-6-sulphonic acids (from 4-sulphophthalic anhydride) is described. 1 : 4-Dihydroxy-anthraquinone-6-sulphonic acid is also obtained by condensation of 4-sulphophthalic anhydride with *p*-chlorophenol in H_2SO_4 in presence of H_3BO_3 at 200°. H. A. Piggott.

Coupling of hydroxyanthraquinones with salicin. A. Müller.—See this vol., 370.

Manufacture of aminoanthraquinonenitriles. I. G. Farbenind. A.-G.—See B., 1932, 222.

Constitution of alkannin. H. Raudnitz (Ber., 1932, 65, [*B*], 159—160).—Contrary to Dieterle and others (A., 1931, 1297), re-analysis of dihydroalkannin tetra-acetate (A., 1931, 1063) confirms the composition $C_{16}H_{14}O_4$ for the dye. 1-Methylquinizarin is not present in the products of the sublimation of alkannin under 0·03 mm. pressure. The prep. of 5 : 8-dihydroxy-1- or -2-methyl-1 : 2 : 3 : 4-tetrahydroanthraquinone along the lines followed by Dieterle is considered impossible. H. Wren.

Lichen substances. IX. Diffractaic acid, a barbatinic acid monomethyl ether. Y. Asahina and F. Fuzikawa (Ber., 1932, 65, [*B*], 175—178).—Extraction of the thallus of *Usnea diffracta*, Wain, with Et_2O and crystallisation of the solid extract from C_6H_6 yields *d*-usnic acid, m. p. 203°, $[\alpha]^{20}_{D}$ +492°, the mother-liquor from which affords *diffractaic acid*, m. p. 189—190° (*Na* salt), hydrolysed by KOH to CO_2, β-orcinol, and rhizonic acid Me ether, m. p. 105° (identical with that derived from Me β-orcinolcarboxylate and diazomethane and subsequent hydrolysis). Diffractaic acid is therefore a barbatinic acid Me ether (I) and probably identical with the dirhizonic acid of Hesse (A., 1906, i, 280). Treatment with diazomethane gives *Me diffractaate Me ether*, m. p. 106—107°, converted by moderate treatment



(I.)

with KOH–EtOH into rhizonic acid Me ether, m. p. 105°, traces of *iso*rhizonic acid, and Me *iso*rhizonate (hydrolysed to the acid by further action of KOH–EtOH). H. WREN.

Constitution of mangostin. I. S. YAMASHINO (Bull. Chem. Soc. Japan, 1932, 7, 1—8).—Mangostin (I), $C_{20}H_{22}O_5$ (cf. A., 1924, i, 1332), m. p. 176·5—177°, with Me_2SO_4 and KOH gives methylmangostin (II), m. p. 120·5—121° (*Ac* derivative, m. p. 191—191·5°), and a *substance*, m. p. 171—171·5°, converted by further methylation into (II). (II) with Br in C_6H_6 gives a *Br*$_3$-derivative, decomp. about 160°, unstable to H_2O and light. Alkali fusion of (I) yields AcOH, *iso*valeric and oxalic acid, phloroglucinol, an *acid*, m. p. 373°, a phenolic *substance*, m. p. 212°, and probably amyl alcohol. The phenol, when further fused with alkali, gives *iso*valeric acid, phloroglucinol, and probably amyl alcohol. (I) is thus not a lapachol derivative. R. S. CAHN.

Saponins. M. KOTAKE (Proc. Imp. Acad. Tokyo, 1932, 8, 12—15).—The sapogenin from *Panax repens*, m. p. 304° [*Ac* derivatives, m. p. 263°, 207—210°, and 306—312°; $(NO_2)_2$-derivatives, m. p. 240—242° and 211—213°; *Br*-derivative, m. p. 223—224°; yields with HI *substances*, $C_{23}H_{36}O_3$ (?), m. p. 337—338°, and $C_{29}H_{46}O_2$, m. p. 247—249°], is identical with that from *Aralia Chinensis*, L., and is $C_{29}H_{48}O_3$ or $C_{30}H_{52}O_3$ (lit. $C_{34}H_{52}O_5$ etc.). The sapogenin from *Kalopanax ricinifolius*, $C_{30}H_{48}O_4$, m. p. 330—332°, is identical with hederagenin. Dry distillation of a sapogenin yields CH_2O, H_2O, oils resembling terpenes, b. p. 95—96·5°, 104·5°, and 115—116·5°/16 mm. (mol. wt. about 190) (giving reduction products, b. p. 235—237°, 241—244°, and 255—258°/760 mm., respectively), and *substances*, $C_{21}H_{16}$, m. p. 246—248°, and $C_{25}H_{18}$, m. p. 306—308°. These substances are considered to be more closely related to the sapogenins than the products obtained by means of S and Se.
R. S. CAHN.

Toad poisons. VI. Degradation of bufotalin to a cholanic acid. H. WIELAND, G. HESSE, and H. MEYER (Annalen, 1932, 493, 272—280).—Acetylbufotalien (A., 1922, i, 784) and H_2 (Pd-black) in AcOH give acetylbufotalan and a small amount of an *acetoxycholanic acid* (I), $C_{26}H_{42}O_2$, m. p. 148°. Hydrolysis of (I) with 2*N*-MeOH–KOH gives the *hydroxycholanic acid*, m. p. 161° (slight previous sintering), also formed in small amount during the catalytic reduction of bufotalien, which at 300° gives H_2O and a *cholenic acid*, $C_{24}H_{38}O_2$, m. p. 169—170°. This is reduced catalytically (as above) to the *cholanic acid* (termed iso*bufocholanic acid*), $C_{24}H_{40}O_2$, m. p. 179°, $[\alpha]_D^{20}$ +50·5° in EtOH.

Acetylbufotalan and 2*N*-MeOH–KOH give bufotalanic acid, m. p. 153—154°, which when heated, or dissolved in cold EtOH, passes into bufotalan, m. p. 199°. Bufotalone is converted by conc. HCl into *bufotalienone*, $C_{24}H_{28}O_3$, m. p. 158°, whilst bufotalan is oxidised by CrO_3 in cold AcOH to *bufotalanone*, $C_{24}H_{36}O_3$, m. p. 196°. Acetylbufotalin is not oxidised by CrO_3, but is converted by conc. HCl into acetylbufotalien; it contains, therefore, a *tert.*-OH group and a >CH·OAc residue.

Toad poisons. IV. Bufagin and cinobufagin. H. JENSEN (Science, 1932, 75, 53—54).—Revised formulæ, viz., cinobufagin, $C_{25}H_{32}O_6$, and bufagin, $C_{24}H_{32}O_5$, are proposed. The reactions described indicate that the former contains a lactone, an OAc, a *sec.*- and a *tert.*-OH group, and the latter a lactone, a CHO, and a *tert.*-OH group. Catalytic reduction yields tetrahydro-cinobufagin and -bufagin, respectively. Both compounds resemble the plant cardiac aglucones in their chemical behaviour, the principles of the toad poisons being coupled with AcOH or HCO_2H instead of with carbohydrates.
L. S. THEOBALD.

Elemic acid from Manila elemi resin. III. Elemonic acid, its reduction product, and bromohydroelemonic acid. IV. Dihydroelemic acid and its derivatives. M. MLADENOVIĆ (Monatsh., 1932, 59, 7—15, 228—237).—III. Oxidation of elemolic acid with CrO_3 in AcOH gives elemonic acid (I), $C_{30}H_{46}O_3$, m. p. 274°, $[\alpha]_D^{20}$ −66·82° in $CHCl_3$ (not $C_{27}H_{40}O_3$; cf. A., 1924, i, 1312; 1931, 1067), and a smaller quantity of another acid (details to be published later). The derivatives of (I) also support the C_{30} formula. (I) is reduced by H_2 and Pd in AcOH at 100° to *tetrahydroelemonic acid*, $C_{30}H_{50}O_3$, m. p. 293°, $[\alpha]_D^{20}$ −54·69° in $CHCl_3$, and converted by HBr in cold $CHCl_3$ into *bromohydroelemonic acid*, $C_{30}H_{47}O_3Br$, m. p. 262°, $[\alpha]_D^{20}$ −10·8° in $CHCl_3$, which with MeOH–KOH regenerates (I).

IV. Catalytic reduction of elemic acid by the method previously described (A., 1931, 960) (in AcOH) gives dihydroelemic acid (II), m. p. 238° [*K* salt $(+3H_2O)$], and its *Ac* derivative (III), m. p. 248·5° (corr.), $[\alpha]_D^{20}$ −38·94° in EtOH, also prepared by acetylation of (II) with Ac_2O in pyridine and by catalytic reduction (Pd) of acetylelemic acid. (III) is hydrolysed by MeOH–KOH to (II). Analyses of the compounds support the C_{30} formula for elemic acid (cf. *loc. cit.*). The dihydroelemic acid of Ruzicka *et al.* (A., 1931, 1067) is probably impure (III). H. BURTON.

Saponin series. I. Glucoside of *Panax ginseng*, C. A. Mey. M. KOTAKE. **II. Saponins of *Kalopanax ricinifolius*.** M. KOTAKE and K. TAGUCHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 18, 1—4, 5—11).—I. The roots of *P. ginseng* contain a bitter glucoside (hydrolysed to a brown amorphous substance) and a bitter-sweet, non-hæmolytic saponin (possibly identical with ginsenin), which with H_2SO_4 in hot MeOH gives *parraxin*, $C_{38}H_{66}O_{12}$ or $C_{36}H_{68}O_{12}$, m. p. 246—248° (decomp.), hydrolysed by cold conc. HCl to CO_2, glucose, an amorphous substance, and *parraxigenin chloride*, $C_{30}H_{53}O_3Cl$, m. p. 209—211°, whence hot alcoholic KOH liberates *parraxigenin*, $C_{30}H_{52}O_3$, m. p. 256—258° (*Ac* derivative, m. p. 112—114°).

II. *K. ricinifolius* contains *kalosaponin* (I), amorphous, and *kalotoxin* (II), $C_{43}H_{70}O_{14}$, m. p. 260—261°. (I) with hot 10% NaOH gives iso*kalotoxin* (III), $C_{43}H_{70}O_{14}$, m. p. 258°. (II) or (III) with cold, conc. HCl, or (I), (II), or (III) with HCl in hot MeOH gives *kalosapogenin*, $C_{30}H_{48}O_4$ or $C_{31}H_{50}O_4$, m. p. 330° [*Ac* derivative, m. p. 167°; $(NO_2)_3$-derivative, m. p. 229—230° (transformed by Zn and HCl in AcOH into a *substance*, $C_{30}H_{42}O_5$, m. p. 320°)], which yields with hot

HCO_2H *formylanhydrokalosapogenin*, $C_{31}H_{46}O_4$, m. p. 161·5—162·5°, or a *substance*, $C_{33}H_{48}O_6$, m. p. 269—270·5°, and with HI and red P in hot AcOH a *substance*, $C_{34}H_{52}O_6$ or $C_{35}H_{54}O_6$, m. p. 258—260°, and a *substance*, $C_{30}H_{48}O_4$, m. p. 320°. The occurrence of the isomeric sapogenins is inexplicable.

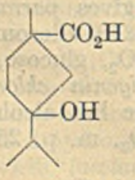
R. S. Cahn.

Oxidation of caoutchouc, gutta-percha, and balata with hydrogen peroxide. J. A. Mair and J. Todd (J.C.S., 1932, 386—399).—Oxidation of caoutchouc with H_2O_2 in $CHCl_3$–AcOH gave alcohol *C*I, viz., $C_{50}H_{76}(OH)_{16}$ (OH by Zerevitinov), presumably formed by direct addition of OH to the double linkings of the hydrocarbon. This with CrO_3 in AcOH gave aldehyde *C*I, viz., $C_{48}H_{86}O_{14}(CHO)_2$, which on oxidation with 30% HNO_3 gave acid *C*I, viz., $C_{48}H_{86}O_{14}(CO_2H)_2$; it is therefore presumed to contain two $CH_2{\cdot}OH$ groups. The action of Ac_2O and NaOAc on alcohol *C*I led to dehydration in addition to acetylation and gave acetate *C*I, $C_{50}H_{76}O_6(OAc)_4$, the alcohol *C*IA from which was in its turn oxidised to aldehyde *C*II and acid *C*II, $C_{48}H_{74}O_8(CO_2H)_2$. Further H_2O_2 oxidation of acetate *C*I gave acetate *C*II, $C_{50}H_{56}O_{16}(OH)_8(OAc)_4$, which was hydrolysed to the saturated alcohol *C*II, $C_{50}H_{56}O_{16}(OH)_{12}$. Guttapercha and balata gave a similar series of products, but of somewhat different composition owing to their greater initial ease of oxidation, *e.g.*, alcohol *G*I (gutta-percha), $C_{50}H_{68}O_4(OH)_{20}$, *B*I (balata), $C_{50}H_{72}O_4(OH)_{16}$; acid *G*I, $C_{48}H_{82}O_{22}(CO_2H)_2$, *B*I, $C_{48}H_{82}O_{18}(CO_2H)_2$; acetate *G*I $C_{50}H_{68}O_{10}(OAc)_8$, *B*I $C_{50}H_{72}O_8(OAc)_8$; acid *G*II, $C_{48}H_{70}O_{16}(CO_2H)_2$, *B*II $C_{48}H_{74}O_{14}(CO_2H)_2$; and acetate *G*II, $C_{50}H_{56}O_{16}(OH)_4(OAc)_8$, *B*II $C_{50}H_{56}O_{16}(OH)_4(OAc)_8$. The aldehydes were characterised (for analysis) as semicarbazones, and the acids as Pb or Ag salts. Corresponding products in the three series had very similar properties, and in each case the final saturated alcohols *C*II, *G*II, and *B*II had the same empirical composition. Attempts at determination of the mol. wt. of alcohol *C*I gave variable results.

H. A. Piggott.

Autoxidation of αβ-unsaturated ketones. IV. Autoxidation of carvenone and constitution of carvenolenic acid. W. Treibs (Ber., 1932, 65, [*B*], 163—168; cf. A., 1931, 1421).—Oxidation of carvenone by O_2 or H_2O_2 in alkaline EtOH closely resembles that of piperitone (*loc. cit.*), yielding *iso*butyric acid and the *hydroxy-acid* $C_{10}H_{18}O_3$ (cf. I),

(I.)



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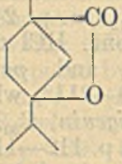

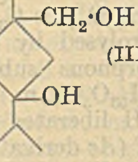

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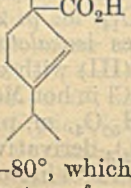
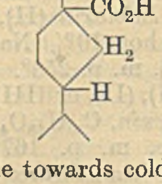




(V.)

m. p. 79—80°, which is stable towards cold $KMnO_4$, but readily transformed into the *lactone* (cf. II), m. p. 4—5°, rather difficultly hydrolysed by alkalis, but reduced by Na and MeOH to the glycol, $C_{10}H_{20}O_2$ (cf. III), b. p. 150°/14 mm., The hydroxy-acid or the lactone is transformed by boiling dil. H_2SO_4 into *carvenolenic acid* (cf. IV), b. p. 250—252° (*Me* ester). Oxidative degradation of Me carvenolenate affords little insight into its constitution, which is established by hydrogenation in presence of Pd and MeOH to *Me carvenolate* (*Me piperitolate* is described). Hydrolysis of the ester affords carvenolic acid, b. p. 255—257° (cf. V), the identity of which with fencholic acid is proved by conversion through the chloride into fencholamide, m. p. 96—97°. *Dihydroxycarvenololactone*, $C_{10}H_{16}O_3$, m. p. 138—139°, is isolated from that portion of the product of autoxidation which is not volatile with steam.

H. Wren.

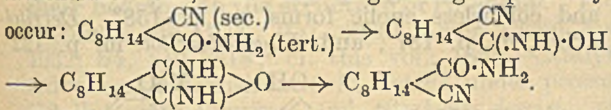
Racemisation phenomena with camphene and their reaction mechanism. I. P. Lipp and G. Stutzinger (Ber., 1932, 65, [*B*], 241—250).—Re-examination of the action of NH_2Ph on active bornyl chloride confirms the production of the compound designated “ bornylaniline ” by Ullmann and Schmid (A., 1911, i, 70). Attempts to establish its secondary nature lead to the isolation of the *nitronitroamine*, $C_{16}H_{21}O_4N_3$, m. p. 158°. The formation of “ bornylaniline ” by catalytic hydrogenation of camphoranil in presence of Pt-black and by addition of NH_2Ph in presence of NH_2Ph,HCl to camphene shows the compound to be iso*bornylaniline*. The following data are incidentally recorded: *iso*bornylaniline, b. p. 173—175°/14 mm., $d^{19·5}$ 1·021, $[\alpha]_D^{19·5}$ −89·07° (*hydrochloride*, decomp. 187°; *perchlorate*; *Bz* derivative, m. p. 142—143° (corr.); camphoranil, $d^{14·5}$ 0·99617, $[\alpha]_D^{20}$ +9·61°; *camphor*-p-*toluil*, b. p. 154—156°/1·3 mm., d^{20} 0·9808, $[\alpha]_D^{20}$ +25·89°; *fenchoneanil*, b. p. 154—156°/11 mm., $d^{12·85}$ 0·99583. The mechanism of the formation of camphene from pinene hydrochloride and NH_2Ph and the accompanying slow racemisation are explained as follows. Camphene production occurs initially through *iso*bornyl chloride and camphene hydrochloride. The “ primary camphene ” adds NH_2Ph under the influence of NH_2Ph,HCl formed in the first phase immediately in the 2-ω position. Thence the production of *iso*bornylaniline takes place directly or, under the influence of NH_2PhHCl, accompanied by a Nametkin transformation (cf. A., 1928, 182). The first change with short period of action leads to the active base, whereas the second, of longer duration, proceeds through mirror-image formation to the racemic variety. During the dry distillation of the reaction mixture, the *iso*bornylaniline is converted into NH_2Ph and a secondary camphene. Small amounts of camphene are present in the product before decomp. of the *iso*bornylaniline; these must be regarded as primary camphene and are found to be optically active if removed from the racemising action of NH_2Ph,HCl by suitable interruption of the change and modified method of isolation. The isolation of optically active camphene from bornyl chloride by other agents which remove HCl, *e.g.*, KOPh, is explained by the inability of camphene to add the phenoxide and to a definite acidity of the solution necessary for the santene displacement.

H. Wren.

Constitution of camphoric acid and its esters. Historical. J. BREDT (J. pr. Chem., 1932, [ii], **133**, 92—94).

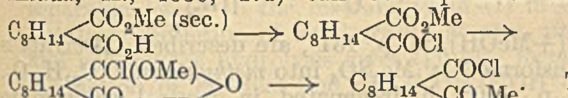
Stereoisomeric camphornitrilic acids and *cis*- and *cis–trans*-camphoric acid dinitriles and their reduction products : *cis*- and *cis–trans*-di(aminomethyl)camphoceanes. J. BREDT and M. DE SOUZA (J. pr. Chem., 1932, [ii], **133**, 84—87).—*cis*-Camphor-*sec*.-nitrilic acid amide (A., 1925, i, 254) and PCl_5 give *cis*-camphoric acid dinitrile (I), m. p. 160°, reduced by Na and EtOH to cis-*di(aminomethyl)camphoceane*, $C_8H_{14}(CH_2{\cdot}NH_2)_2$, b. p. 135—136°/14 mm., $[\alpha]_D^{22}$ −6·5° (*chloroplatinate*). *trans*-Camphoric acid amide and PCl_5 afford trans-*camphoric acid dinitrile*, m. p. 144—145°, similarly reduced to trans-*di(aminomethyl)camphoceane*, b. p. 135—136°/14 mm., $[\alpha]_D^{22}$ −20·8° (*chloroplatinate*). (I) and conc. H_2SO_4 at room temp. give the *amide*, m. p. 197—198°, of *cis*-camphor-*tert*.-nitrilic acid, convertible by successive treatment with H_2SO_4 and HNO_2 into *cis*-camphoric acid. H. BURTON.

Mechanism of the rearrangement of carboxy-derivatives of camphoric acid. I. Transformation of *cis*-camphor-*sec*.-nitrilic acid amide into *cis*-camphor-*tert*.-nitrilic acid amide. II. Transformation of *sec*.-(*ortho*-)methyl hydrogen camphorate into *tert*.-(*allo*-)methyl hydrogen camphorate. J. BREDT (J. pr. Chem., 1932, [ii], **133**, 87—91).—I. The amide of *cis*-camphor-*sec*.-nitrilic acid is converted by conc. H_2SO_4 at room temp. during 5—7 days into the amide of *cis*-camphor-*tert*.-nitrilic acid; the following changes probably occur:



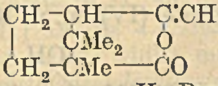
$$C_8H_{14}\Big<\begin{matrix}CN\ (sec.)\\ CO{\cdot}NH_2\ (tert.)\end{matrix} \longrightarrow C_8H_{14}\Big<\begin{matrix}CN\\ C(\colon NH){\cdot}OH\end{matrix} \longrightarrow C_8H_{14}\Big<\begin{matrix}C(NH)\\ C(NH)\end{matrix}\Big>O \longrightarrow C_8H_{14}\Big<\begin{matrix}CO{\cdot}NH_2\\ CN\end{matrix}.$$

II. The conversion of *ortho*-Me H camphorate into the chloride of *allo*-Me H camphorate (Qudrat-i-Khuda, A., 1930, 471) can be explained thus:



$$C_8H_{14}\Big<\begin{matrix}CO_2Me\ (sec.)\\ CO_2H\end{matrix} \longrightarrow C_8H_{14}\Big<\begin{matrix}CO_2Me\\ COCl\end{matrix} \longrightarrow C_8H_{14}\Big<\begin{matrix}CCl(OMe)\\ CO\text{———}\end{matrix}\Big>O \longrightarrow C_8H_{14}\Big<\begin{matrix}COCl\\ CO_2Me\end{matrix}.$$

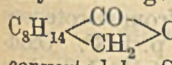
The structure assigned by Qudrat-i-Khuda (*loc. cit.*) to the unsaturated lactone from 5-acetyl-1 : 1 : 2-trimethyl*cyclo*pentane-2-carboxylic acid is not in accordance with Bredt's rule (cf. Windaus and Bohne, A., 1925, i, 552) and should be



$$\begin{array}{l}CH_2{-}CH\text{———}C\colon CH_2\\ |\quad\ \ CMe_2\quad\ O\\ CH_2{-}CMe\text{——}CO\end{array}.$$

H. BURTON.

β-Homocamphoric acid. Formation of β-camphor [epicamphor]. F. SALMON-LEGAGNEUR (Compt. rend., 1932, **194**, 467—469).—Interaction of β-homocamphor (A., 1931, 626) with $NaNH_2$ and amyl nitrite gives an *oximino*-derivative,



$$C_8H_{14}\Big<\begin{matrix}CO\\ CH_2\end{matrix}\Big>C\colon N{\cdot}OH,$$

m. p. 174—175°, which is converted by $SOCl_2$ (preferably in large excess) and subsequent treatment with H_2O into β-homocamphoro-β-nitrile, m. p. 154—156°; this with 85% H_2SO_4 gives β-*homocamphoramic acid*, m. p. 256°, hydrolysed by aq. (?) KOH to β-*homocamphoric acid*, m. p. 220—222°, $[\alpha]_D^{18}$ +27·3° in EtOH. Direct oxidation of β-homocamphor with HNO_3 gives a little β-homocamphoric acid and much dinitro-β-homocamphor, m. p. 80—82°; distillation of Pb β-homocamphorate gives β-camphor. H. A. PIGGOTT.

Resolution of racemates with the help of additive compounds. R. WEISS and A. ABELES (Monatsh., 1932, **59**, 238—240).—*d*-β-Naphthylcamphylamine (1 mol.) and 2 mols. of dl-2 : 4 : 6-*trinitro*-sec.-*butylaniline* (I), m. p. 78—80° (prepared from picryl chloride and $NH_2{\cdot}CHMeEt$ in EtOH), in EtOH give an additive (1 : 1) *compound*, m. p. 110—111°; part of the excess of (I) separates from the mother-liquors with m. p. 81—85°, $[\alpha]_D^{15}$ −2·6° in $CHCl_3$, after crystallisation from EtOH. H. BURTON.

Sclareol from the so-called "absolute" extract of *Salvia Sclarea*, L. M. JANOT (Ann. Chim., 1932, [x], **17**, 5—127).—A detailed account of investigations some of which have previously been published (A., 1931, 94, 737). The conclusion that sclareol, $C_{20}H_{36}O_2$ (Br_2-compound, $C_{20}H_{34}OBr_2$), is a diterpene di-*tert*.-alcohol related in type to *d*-pimaric acid is confirmed. Although it could not be separated from hydrocarbons formed by dehydration, sclareol yields an allophanate. Dehydration with naphthalene-2-sulphonic acid affords a mixture, difficult to separate, of isomeric sclarenes, $C_{20}H_{32}$ (dicyclic, $\models_3$), b. p. 125—128°/0·20 mm., and *cyclo*sclarenes (tricyclic, $\models_2$), b. p. 119—122°/0·10 mm., the proportion of the latter being increased when HCO_2H is employed. Dihydrosclareol, m. p. 114—115°, is similarly dehydrated to a mixture of dihydrosclarenes and dihydro*cyclo*sclarenes. Dehydrogenation of *cyclo*sclarene with Se gives a mixtures of hydrocarbons from which a dimethylphenanthrene, $C_{16}H_{16}$, is isolated as its *picrate*, m. p. 136°, some evidence of the presence of a trimethylphenanthrene also being obtained. Further evidence relating to the oxidation products of sclareol is recorded. Ozonolysis affords, in addition to CH_2O, a neutral *substance*, $C_{18}H_{30}O$, b. p. 138—142°/0·40 mm. (*dihydro*-derivative), in which the O is present as a $\geqslant C{\cdot}O{\cdot}C\leqslant$ group. Oxidation with $KMnO_4$ in $COMe_2$ gives a neutral *substance*, $C_{18}H_{30}O$, b. p. 142—146°/0·80 mm., m. p. 42° (reduced by PtO and AcOH to a *dihydro*-compound, m. p. 52°), and an aldehydic or ketonic *substance*, $C_{18}H_{34}O_2$, b. p. 142—152°/0·15 mm., characterised as its *oxime*, b. p. 180—185°/0·25 mm. The AcOH also formed originates in the $COMe_2$, since it is not obtained when pyridine is used as a solvent. CrO_3 in AcOH gives a lactonic *substance*, $C_{16}H_{26}O_2$, m. p. 123—124°. All the available data are readily explained on the basis of the structure previously suggested (*loc. cit.*, p. 737). Certain colour reactions of sclareol are investigated and thus the location of this compound almost exclusively in the flower, reproductive organs, and the seed is demonstrated. Sclareol possesses no physiological or toxic action on rabbits. J. W. BAKER.

2-Iodofuran and magnesium 2-furyl iodide. H. GILMAN, H. E. MALLORY, and G. F. WRIGHT (J. Amer. Chem. Soc., 1932, **54**, 733—736).—Na furoate and I in aq. KI at 130—140° (bath) give 20% of 2-*iodofuran*, b. p. 43—45°/15 mm. (more stable in Et_2O), convertible into Mg 2-furyl iodide (95% yield). C. J. WEST (*b*).

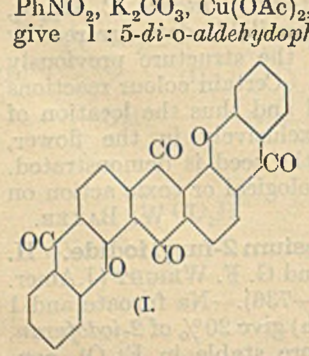
Alcohols obtained by the interaction of primary tetrahydro-α-furylamine and nitrous acid. N. V. Williams (Bull. Acad. Sci. U.S.S.R., 1931, 1117—1122).—This reaction yields (1) primary tetrahydro-2-furfuryl alcohol, b. p. 86·5—87°/25 mm. (cf. Wienhaus, A., 1920, i, 863), and (2) 2-hydroxytetrahydrofuran, b. p. 93—95°/25 mm., which gives δ-hydroxyvaleraldehyde-*p*-bromophenylhydrazone, m. p. 70—71°, with *p*-bromophenylhydrazine (cf. Helferich, A., 1919, i, 386). T. H. Pope.

Amino-acids. I. Synthesis of furylalanine. V. Deulofeu (Z. physiol. Chem., 1932, **204**, 214—218).—Furylalanine was synthesised (*a*) by Flatow's method (A., 1910, ii, 321), but using conc. aq. $Ba(OH)_2$ for hydrolysis of the benzoylfurylalanine (m. p. 149°; lit. 162°) in place of NaOH, (*b*) by hydantoin condensation. Furfuraldehyde and hydantoin in presence of NaOAc give *furfurylidenehydantoin*, m. p. 230°, which on reduction with Na–Hg yields *furfurylhydantoin*, m. p. 154°. Hydrolysis of the latter with aq. $Ba(OH)_2$ affords furylalanine. 2-Thiohydantoin similarly gives *furfurylidene-2-thiohydantoin*, m. p. 250—251° (decomp.), from which $CH_2Cl{\cdot}CO_2H$ does not eliminate S, and *furfuryl-2-thiohydantoin*, m. p. 143—144°. J. H. Birkinshaw.

Comparison of the stability of some anthocyanidins and anthocyanins towards dilute ferric chloride solutions. R. Robinson and A. León (Anal. Fís. Quím., 1932, **30**, 31—36).—Solutions of these compounds containing a 3-OH group are rapidly decolorised by dil. $FeCl_3$ solution, whilst those containing 3-OMe or 3-glucosidoxy-groups or not substituted in the 3-position are stable. Since pelargonin, cyanin, and malvin are stable, they are 3 : 5-diglucosides, the 5-position being already assigned to one glucose residue. The prep. of cyanenin chloride (5-glucoside) by partial hydrolysis of cyanin chloride is described. R. K. Callow.

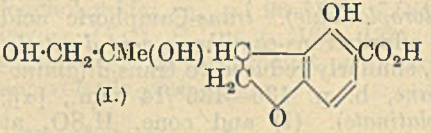
Preparation of dibromofluorescein. M. A. Phillips (J.C.S., 1932, 724—725).—Fluorescein with 2 mols. Br in 80% AcOH at 80° gives an 85—88% yield of (the hydrobromide of) dibromofluorescein, m. p. 285°. H. A. Piggott.

Anthraquinone-2 : 1 : 6 : 5-dixanthone. O. Dischendorfer and E. Fransević (Monatsh., 1932, **59**, 105—112).—1 : 5-Dichloroanthraquinone and *o*-$OH{\cdot}C_6H_4{\cdot}CHO$ condense in presence of $PhNO_2$, K_2CO_3, $Cu(OAc)_2$, and " Naturkupfer C " to give 1 : 5-*di*-o-*aldehydophenylanthraquinone*, m. p. 324° (decomp.) (slight previous sintering) [*dioxime*, m. p. 256° (decomp.) (slight previous sintering); *diphenylhydrazone*, m. p. 136° (decomp.)], oxidised by CrO_3 and conc. H_2SO_4 in AcOH to 1 : 5-*di*-o-*carboxyphenylanthraquinone*, m. p. 281° (decomp.) (sinters at 278°) [*Me₂* ester, m. p. 175° (sinters at 170°)]. Treatment of the acid with PCl_5 in $PhNO_2$ gives *anthraquinone*-2 : 1 : 6 : 5-*dixanthone* (I), darkens from 380°, not melted at 400°, which imparts a violet shade (changing to yellow in air) to cotton from an alkaline vat. H. Burton.

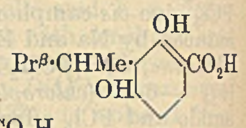


(I.

Rotenone, the active constituent of the *Derris* root. VIII. Tubadiolic acid, tetrahydrotubaic acid, derritol, and rotenol. Constitution of rotenone. S. Takei, S. Miyajima, and M. Ōno (Ber., 1932, **65**, [*B*], 279—289; cf. A., 1931, 847).—Oxidation of tubaic acid by $KMnO_4$ gives *tubadiolic acid* (I), m. p. 201° (*Me* ester, m. p. 163°), obtained also from derritol and rotenonic acid. Hydrogenation of tubaic acid in alkaline solution in presence of Pd–$BaSO_4$ gives iso*dihydrotubaic acid*, m. p. 166°, further hydrogenated in AcOEt to *tetrahydrotubaic acid* (II), m. p. 193°, which is oxidised to an *acid*, $C_6H_{12}O_2$ (p-*iodophenacyl* ester, m. p. 85°). The 2-*Me*, m. p. 112°, 4-*Me*, m. p. 156°, and 2 : 4-*Me₂*, m. p. 109—110°, *ethers* of tetrahydrotubaic acid are described.

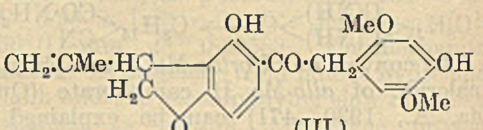


(I.)

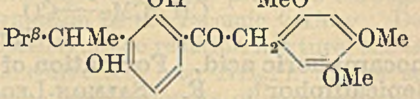


(II.)

An improved method for the reduction of rotenone to derritol and rotenol is described. Derritol (III), for which the authors return to the formula $C_{21}H_{22}O_6$, shows keto–enolic desmotropy owing to the presence of the $\cdot CO{\cdot}CH_2\cdot$ group and exists in yellow ketonic and colourless enolic forms, m. p. 158°. *Derritoloxime*, m. p. 187°, and *dihydroderritol*, m. p. 122°, or (+MeOH), m. p. 131°, are described. Derritol is transformed by Me_2SO_4 into *methylderritol*, $C_{21}H_{21}O_6$, m. p. 120°, hydrogenated in neutral solution to *methyldihydroderritol*, m. p. 109° (*oxime*, m. p. 171°; *acetylmethyldihydroderritoloxime*, m. p. 98°), whereas in alkaline solution it affords *methyldihydro*iso*derritol*, m. p. 145°, further reduced in AcOEt to *methyltetrahydroderritol* (IV), m. p. 160° [probably identical with the " methylderritolic acid " of LaForge and Smith (A., 1930, 781)]. The *oxime*, m. p. 189°, *Me ether*, m. p. 98°, and *diacetylmethyltetrahydroderritoloxime*, m. p. 82°, are described. iso*Derritol*, from *iso*rotenone by Zn dust and KOH–EtOH, has m. p. 148°. Oxidation of methylderritol in $COMe_2$ by NaOH–H_2O_2 gives 2 : 4 : 5-*trimethoxyphenylacetic acid*, m. p. 87°, obtained also from methyldihydroderritol or methyltetrahydroderritol. Treatment of the acid with $KMnO_4$ affords 2 : 4 : 5-*trimethoxybenzoic acid*, m. p. 143°, obtained also directly from methylderritol, and oxidised by dil.



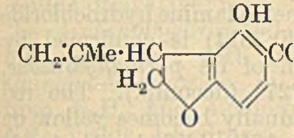
(III.)



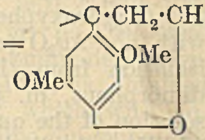
(IV.)

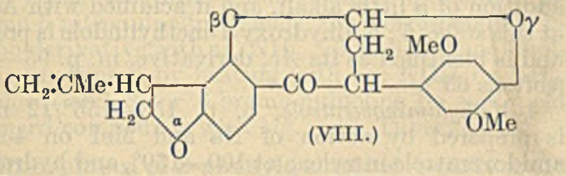
HNO_3 to 1-*nitro*-2 : 4 : 5-*trimethoxybenzene*, m. p. 129°, identical with the product of the action of conc. HNO_3 on 1 : 3 : 4-trimethoxybenzene.

Rotenol (V), m. p. 119°, and *rotenoloxime*, m. p. 184°, yield a reddish-brown coloration with $FeCl_3$, whereas *acetylrotenoloxime*, m. p. 85—86°, does not, so that rotenol contains a CO group and an OH in the tubaic acid portion of the mol. Oxidation of rotenol with H_2O_2 affords a little tubaic acid and an acid, $C_{12}H_{14}O_5$ ($XH{\cdot}CO_2H$), m. p. 90° or 131—132° after thorough desiccation, which appears identical with the netoric acid of Smith and LaForge. It contains 1 CO_2H and 2 OMe groups and a non-substitutable O. It is oxidised to a *ketone*, $C_{11}H_{12}O_4$ (XO), m. p. 121° (p-*nitrophenylhydrazone*, m. p. 223°).


(V.)

X =

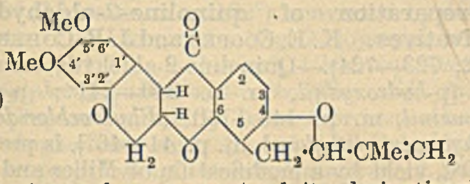



(VIII.)

The modified constitution (VIII) is ascribed to rotenone in explanation of its action towards reducing agents. H. WREN.

Rotenone. XIX. Alkali-soluble hydrogenation products of rotenone and its derivatives and their bearing on the structure of rotenone. F. B. LAFORGE and H. L. HALLER (J. Amer. Chem. Soc., 1932, **54**, 810—818; cf. this vol., 165).—Catalytic reduction of derrisic acid in AcOEt under pressure (50 lb.) gives dihydro- and *tetrahydro-derrisic acid* (I), m. p. 204—206° (the *Et* ester, m. p. 180°, gives a coloration with $FeCl_3$ and is sol. in cold dil. alkali), separable owing to the insolubility of (I) in $CHCl_3$. Catalytic reduction of Et derrisate at atm. pressure and subsequent hydrolysis gives (I), also formed by the action of Zn dust and aq. EtOH–KOH on dehydrodihydrorotenonic acid (II). (I) and Me_2SO_4 in 5% KOH afford the *Me* ester, m. p. 111—112° (6-*Ac* derivative, m. p. 111°), of 4-*methyltetrahydroderrisic acid* (III), m. p. 164°, which gives a colour with $FeCl_3$ and is oxidised by alkaline H_2O_2 to derric acid. Acetylation of (I) or (II) affords 4-*acetyldehydrodihydrorotenonic acid*, m. p. 202°, whilst methylation (Me_2SO_4) of (II) gives 4-*methyldehydrodihydrorotenonic acid*, m. p. 169°, converted by Zn dust and 15% KOH in EtOH into (III). *iso*Derrisic acid and amyl nitrite in AcOH–HCl give a 1 : 2-*diketone*, $C_{23}H_{22}O_9$, m. p. 195°, which also gives a coloration with $FeCl_3$.

(*A*.)



The reactions of rotenone (and its derivatives) are explicable by the structure (*A*). (I) and (II) are phenols which can be methylated in the 4-position; (I) is a dihydric phenol and its ester can be acetylated in position 6. Rotenol is a mono- and derritol a di-hydric phenol. All rotenone derivatives containing a OH group in position 6 are alkali-insol., but they give colorations with $FeCl_3$. The lactone group is not present in rotenone or its derivatives; the alkali-sol. hydrogenation products previously designated acids are phenols. C. J. WEST (*b*).

Behaviour of the pyridine group on electrolytic oxidation. I. Pyridine. M. YOKOYAMA and K. YAMAMOTO (Bull. Chem. Soc. Japan, 1932, 7, 28—34).—Electrolysis with a Pb anode of C_5H_5N dissolved in dil. H_2SO_4 yields HCO_2H, CO, CO_2, NH_3, HNO_3, and NH_2Me with some $NHMe_2$ and/or NMe_3. The amines arise through condensation with NH_3 of the CH_2O first formed. C. W. DAVIES.

5-Amino-α-picoline and its derivatives. R. GRAF (J. pr. Chem., 1932, [ii], **133**, 19—35).—The preps. of aldehydecollidine and 6-methylnicotinic acid are modified. The latter [*Me* ester, m. p. 32°; *Et* ester, b. p. about 130°/15 mm., 222—224° (slight decomp.)/760 mm. (by Emich's method); *amide*, m. p. 194°] with $Cu(OAc)_2$ gives the salt, $C_{14}H_{12}O_4N_2Cu,Cu(OAc)_2$ (cf. A., 1924, i, 873). The *hydrazide*, m. p. 133—135° [*benzylidene*, o-*chlorobenzylidene*, and *vanillylidene* derivatives, m. p. 184—185°, 183—184°, and 245—246° (decomp.), respectively], with HNO_2 in cold *N*-HCl yields the *azide* (I), m. p. 44—45°, and secondary *hydrazide*, m. p. 247—250°. (I) with NH_2Ph in dry Et_2O gives the *anilide*, m. p. 134—137°, with 5-amino-α-picoline the condensation *product*, $C_{13}H_{13}ON_3$, m. p. 275—277° (decomp.), with EtOH the *urethane*, m. p. 132—133°, and with boiling H_2O the s-*carbamide* derivative, m. p. 285—288° (decomp.). 5-*Amino-α-picoline*, m. p. 95—96° [*dihydrochloride*, m. p. 215—218° (decomp.); *Ac* and *Bz* derivatives, m. p. 122—123° and 110—111°, respectively], was obtained by boiling (I) with dil. AcOH (1 : 1), by decomp. of the urethane with hot 40% KOH, and by Hofmann degradation of the amide. It led to 5-chloro-α-picoline [oxidised by $KMnO_4$ to 5-chloro-α-picolinic acid, $+H_2O$, m. p. 169—170° (acid *chloride*, m. p. 94°; *Me* and *Ph* esters, m. p. 85—87° and 92°, respectively; *amide*, m. p. 200—201°)], 5-*bromo-α-picoline*, m. p. 32°, 5-*bromo-α-picolinic acid*, m. p. 175°, 4-*iodo-α-picoline*, m. p. 48—49° (*hydriodide*, m. p. 235—238°), 5-*iodo-α-picolinic acid*, m. p. 188—190°, and 5-*hydroxy-α-picolinic acid*, m. p. 165—167°. The structure of comenamic acid (A., 1883, 792) is thus proved.

R. S. CAHN.

4 : 6-Dichloro- and 4 : 5 : 6-trichloro-α-picolinic acid. R. GRAF (J. pr. Chem., 1932, [ii], **133**, 36—50).—α-Picolinic acid hydrochloride heated with $SOCl_2$ (1·75 parts; 10 days) gives ?-chloro-, 4 : 6-dichloro- (I), and 4 : 5 : 6-trichloro- (II) -α-picolinic acid, (I) and (II) being separated by distillation of the acid chlorides and subsequent crystallisation of the Me esters. s-*Di*-(4 : 6-*dichloropicolinoyl*)*hydrazine* melts above 300°. The *hydrazide*, m. p. 154° (*benzylidene* derivative, m. p. 165°), of (II) with boiling aq. AcOH (1 : 2) yields 4 : 6-dichloro-2-aminopyridine, m. p. 105° (*Ac* derivative, m. p. 218—219°), which with boiling HI gives 4-*chloro*-6-*iodo*-2-*aminopyridine*, m. p. 137°, with HNO_2 in conc. HCl gives 2 : 4 : 6-trichloropyridine, and with HNO_2 in dil. acid gives 4 : 6-*dichloro-2-hydroxypyridine*, m. p. 151°. The *azide*, m. p. 74°, of (I) with boiling, abs. EtOH yields the *Et* ester of (I), m. p. 75°. (I) and boiling 80% H_2SO_4 afford 4-chloro-2-hydroxy-α-picolinic acid. The *Me* ester, m. p. 125°, of (II) (m. p. 123° after sintering at 108°), HI, and red P at 150° give 5-chloro-α-picolinic acid, thus proving the structure of (II), but when boiled, give 5-*chloro*-4-*iodo*-α-*picolinic acid*, m. p. 159° (decomp.), transformed by boiling $SOCl_2$ into the 4 : 5-dichloro-acid. The *amide* of (II) has m. p. 169°, the *Ph* ester m. p. 138°, and the *acid chloride* m. p. 70°. The Me ester of (II) with boiling 80% H_2SO_4 yields 4 : 5-dichloro-6-hydroxy-α-picolinic acid. 3-Amino-α-picolinic acid affords 3-*chloro*-α-*picolinic acid* (*amide*, m. p. 140°; *Me* ester, an oil), which decomposes at the m. p. (121°) into CO_2 and 3-chloropyridine. R. S. CAHN.

Anhydride of *s*-pyridinetetracarboxylic acid and its condensation products. G. MACHEK (Monatsh., 1932, **59**, 175—183).—*s*-Pyridinetetracarboxylic acid (I) (+$2H_2O$), best purified by decomp. of the Ag salt with a 10% excess of dil. HCl, is obtained anhyd. when heated from 80° to 100° during 20—30 min. The anhyd. acid is converted by short heating with Ac_2O into pyridine-3 : 5-dicarboxylic acid and 25% of the *dianhydride* (II), decomp. 277—278° (darkens at about 220°), of (I). (II), C_6H_6, and $AlCl_3$ at 94—95° give a *mixture*, decomp. 135° (softens at 105°), of dibenzoylpyridinedicarboxylic acids, which could not be cyclised, convertible by $SOCl_2$ into a *mixture*, decomp. 115° (softens at about 90°), of chlorides, which with C_6H_6 and $AlCl_3$ affords 2 : 3 : 5 : 6-*tetrabenzoylpyridine*, decomp. 165—170° (darkens at about 140°). H. BURTON.

Binuclear isomerism of diphenyl type. I. (MISS) A. J. CHALMERS, F. LIONS, and A. O. ROBSON (J. Proc. Roy. Soc. New South Wales, 1930, **64**, 320—336).—The methosulphate of 2-(o-*carboxyphenyl*)-3-*carboxypyridine*, m. p. 238—239° (decomp.), could not be resolved through the *dibrucine*, +$7H_2O$, m. p. 235° (decomp.), [α] −26·8°, or the *distrychnine* salt, [α] −23·4° and −25·1°. F. R. SHAW.

Nitroindoles. H. BAUER and E. STRAUSS (Ber., 1932, **65**, [*B*], 308—315).—The following *nitrophenylhydrazones* are prepared in good yield by the addition of the aldehyde or ketone to a very dil. solution of the requisite nitrophenylhydrazine in HCl or AcOH: *propaldehyde*-o-, m. p. 72°; -m-, m. p. 83°; -p-, m. p. 125°; *Me Et ketone* o-, m. p. 73°; m-, m. p. 99·5°; p-, m. p. 124°; *Et acetoacetate* p-*nitrophenylhydrazone*, m. p. 118°, converted by conc. H_2SO_4 into a *nitropyrazolone*, $C_{10}H_9O_3N_3$, m. p. 218°; *Et lævulate* p-*nitrophenylhydrazone*, m. p. 156°. Treatment of the propaldehydephenylhydrazones with boiling HCl (*d* 1·19) affords 3 : 3′-*dimethyl*-2 : 2′-*propylidene*-7 : 7′-*dinitrodi-indole*, m. p. 205°, -6 : 6′(4 : 4′)-*dinitrodi-indole*, m. p. 258°, and -5 : 5′-*dinitrodi-indole*, m. p. 268°. Similarly derived from COMeEt are 7-*nitro*-, m. p. 164°, 6(4)-*nitro*-, m. p. 126°, and 5-*nitro*-, m. p. 186°, -2 : 3-*dimethylindole*. 5-*Amino*-, m. p. 178°, and 5-*acetamido*-, m. p. 173° (decomp.), -2 : 3-*dimethylindole* are described. Bromination in AcOH gives *bromo*-7-*nitro*-, m. p. 172° (decomp.), and *bromo*-5-*nitro*-, not molten below 300° after becoming discoloured at 176°, -2 : 3-*dimethylindole*. Treatment of 2 : 3-dimethylindole with conc. H_2SO_4 and KNO_3 at 0° affords the 5-NO_2-compound. It is therefore probable that in the nitration of proteins the NO_2 group enters the tryptophan preponderatingly in the 5 position. H. WREN.

Oxidation of β-3 : 4-dihydroxyphenylethylmethylamine with silver oxide. Isolation of 5 : 6-dihydroxy-1-methylindole and synthesis of 5 : 6-dimethoxy-1-methylindole. H. BURTON (J.C.S., 1932, 546—549).—The formation of 1-methyl-2 : 3-dihydroindole-5 : 6-quinone by oxidation of β-3 : 4-dihydroxyphenylethylmethylamine hydrochloride with aq. Ag_2O (cf. A., 1930, 814) is confirmed by isolation from the solution of its *phenylhydrazone*, dimorphous, m. p. 226—227° (decomp.). The red solution of the quinone gradually becomes yellow on addition of a little alkali, and if acidified with AcOH at this stage, 5 : 6-dihydroxy-1-methylindole is present and is identified as its Ac_2 derivative, m. p. 95—100° (softens 65°).

4-*Methylaminoveratrole*, b. p. 153—155°/12 mm., is prepared by action of Na and MeI on 4-acetamidoveratrole in xylene at 100—150°, and hydrolysis of the product with conc. KOH in EtOH. It reacts with glyoxal sodium hydrogen sulphite in aq. EtOH to form *Na* 5 : 6-*dimethoxy*-1-*methylindolyl* 2-*sulphite* (+$1H_2O$), m. p. 187° (decomp.), hydrolysed by aq. HCl to 5 : 6-*dimethoxy*-1-*methyloxindole*(?), m p. 120—121°, and reduced by vac. distillation with Zn dust to 5 : 6-dimethoxy-1-methylindole, m. p. 138—139°, identical with that prepared by Dulière and Raper's method (*loc. cit.*). H. A. PIGGOTT.

Action of sulphurous acid and its salts on quinoline derivatives. II. N. N. VOROSCHCOV and J. M. KOGAN (Ber., 1932, **65**, [*B*], 142—145; cf. A., 1930, 1445).—8-Hydroxyquinoline is converted almost quantitatively by $(NH_4)_2SO_3$ and 20% NH_3 at 150° into 8-aminoquinoline, m. p. 65—65·5°. 6-Amino-, m. p. 115°, is obtained similarly from 6-hydroxy-quinoline. 8-*Aminoquinoline*-5-*sulphonic acid* (*Na* salt; *hydrochloride*) is described.

H. WREN.

Quinoline derivatives. L. MONTI and G. VERONA (Gazzetta, 1932, **62**, 14—18).—*p*-Methoxyacetoacetanilide, m. p. 116—117° (A., 1931 831), with hot conc. H_2SO_4 gives 2-*hydroxy*-6-*methoxy*-4-*methylquinoline*, m. p. 268° (*picrate*, m. p. 196—198°). p-*Acetylacetoacetanilide*, m. p. 108—110°, from *p*-aminoacetophenone and Et acetoacetate, does not undergo ring-closure in presence of H_2SO_4 or Ac_2O, but is hydrolysed. E. E. J. MARLER.

Preparation of quinoline-2-aldehyde and derivatives. K. E. COOPER and J. B. COHEN (J.C.S., 1932, 723—724).—Quinoline-2-aldehyde, m. p. 67—69° [p-*hydroxyanil*, m. p. 240—241°; p-*dimethylaminoanil*, m. p. 148—150° (*dihydrochloride*); p-*dimethylaminomethylanil*, m. p. 44—46°], is prepared in >50% yield by a modification of Miller and Spady's method (cf. A., 1886, 265). It condenses with 6-acetamidoquinaldine methochloride in EtOH in

presence of piperidine to form 6-*acetamido*-2-(2′-*quinolylstyryl*)*quinoline methochloride*, m. p. 278° (decomp.), hydrolysis of which with HCl at its b. p. gives the free *NH_2*-compound, m. p. 262° (decomp.).
H. A. Piggott.

Quinoline derivatives. W. Brydówna (Rocz. Chem., 1932, **12**, 89—99).—*Cinchonic acid azide*, m. p. 69—70°, yields on boiling with EtOH 4-*quinolylurethane*, m. p. 206—207°, which on hydrolysis gives 4-aminoquinoline. *Cinchonic acid benzylidenehydrazone*, m. p. 220—221°, is prepared by the action of PhCHO on the corresponding hydrazone. 4-*Iodoquinoline methiodide*, m. p. 234—237° (decomp.), obtained by the action of MeI on 4-chloroquinoline, reacts with NH_2Ph to yield the corresponding 4-*anilino*-derivative, m. p. 220—222°, with $NHPh{\cdot}NH_2$ the 4-*phenylhydrazino*-derivative, m. p. 204—205° (decomp.), and with NH_3 the 4-amino-derivative. *Quinolyl*-4-*hydrazine*, m. p. 140—142°, is obtained from N_2H_4 and 4-chloroquinoline, which with aq. NH_3 yields 4-hydroxy- and 4-amino-quinoline. 6-Bromo-5-nitroquinoline yields the corresponding 6-amino-derivative with aq. NH_3. 3- or 6-Bromoquinoline is unaffected by heating with aq. KOH or NH_3. 4-Chloro- and 3- or 6-bromo-quinoline do not yield Grignard compounds with Mg. R. Truszkowski.

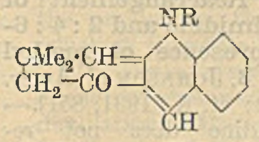
Dimorphism of 2-phenylquinoline-4-carboxylic acid. L. Kofler and W. Dernbach (Arch. Pharm., 1932, **270**, 153—155).—By micro-sublimation 2-phenylquinoline-4-carboxylic acid is prepared in an unstable, triclinic (m. p. 196—197°) and a stable, rhombic (m. p. 211—213°) form, the former tending to pass into the latter above 160°. R. S. Cahn.

Quinoline derivatives. XXXIV. Derivatives of 2-phenylquinoline-4′-carboxylic acid and 4′-amino-2-phenylquinoline. H. John [with H. Ottawa] (J. pr. Chem., 1932, [ii], **133**, 13—18; cf. A., 1931, 1429).—2-Phenylquinoline-4-carboxylic acid and $SOCl_2$ give the *acid chloride*, whence the following derivatives were prepared: *Et* (m. p. 87°), β-*chloroethyl* (m. p. 98°), *Pr^α* (m. p. 72°), and *Pr^β* (m. p. 75°) esters; *amide*,* m. p. 234°; *diethylamide*,* m. p. 112°; β-*hydroxyethylamide*, m. p. 182°; *carbamide* derivative,* m. p. 233°; *hydrazide*, m. p. above 300° (*benzylidene* derivative, m. p. above 300°). The amide and NaOBr at 80—90° give 4′-amino-2-phenylquinoline.* The hydrochloride, sulphate, nitrate, mercurichloride, and picrate of the substances marked * are described.
R. S. Cahn.

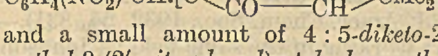
Quinoline derivatives. XXXV. 2-(4-Hydroxy-5-methyl-2-*iso*propylphenyl)quinolines. H. John and E. Andraschko (J. pr. Chem., 1932, [ii], **133**, 114—119).—Isatin and 4-hydroxy-5-methyl-2-*iso*propylacetophenone (I) in 33% KOH give 2-(4-*hydroxy*-5-*methyl*-2-iso*propylphenyl*)*quinoline*-4-*carboxylic acid*, m. p. 279° (*Me* ester, m. p. 192°), converted by distillation into 2-(4-*hydroxy*-5-*methyl*-2-iso*propylphenyl*)-*quinoline*, m. p. 125°. 6-*Bromo*-2-(4-*hydroxy*-5-*methyl*-2-iso*propylphenyl*)*quinoline*-4-*carboxylic acid*, m. p. 295°, is prepared similarly from 5-bromoisatin. *o*-Aminoacetophenone and (I) give 2-(4-*hydroxy*-5-*methyl*-2-iso*propylphenyl*)-4-*methylquinoline*, m. p. 81°. Various salts of these compounds are described.
H. Burton.

Carbylamines. XVIII. Reaction of phenylcarbylamine with nitrosobenzene. T. Bonciani and M. Passerini (Gazzetta, 1931, **61**, 959—963).—Phenylcarbylamine when heated with PhNO gives diphenylcarbamide and a compound $C_{21}H_{15}N_3$ (I), m. p. 212—213°, probably 3 : 4-*quinolinequinonedianil*, giving on hydrolysis NH_2Ph, a *compound* $C_{15}H_{10}ON_2$, m. p. 215—217°, probably a 3 : 4-quinolinequinonemonoanil, and a compound $C_9H_5O_2N$, m. p. 182—185°, probably 3 : 4-*quinolinequinone*, which changes spontaneously to a *compound*, m. p. above 285°. E. E. J. Marler.

Reactivity of 5 : 5-dimethyldihydroresorcinol. II. Behaviour towards *o*-nitro- and *o*-amino-benzaldehyde. B. H. Iyer and G. C. Chakravarti (J Indian Inst. Sci., 1932, **14**, A, 157—171; cf. this vol. 279).—Unlike other substituted benzaldehydes, 1 mol of *o*-aminobenzaldehyde (I) (modified prep.) condenses under all conditions tried with only 1 mol. of dimethyldihydroresorcinol (II), yielding 4-*keto*-2 : 2-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroacridine* (III), m. p. 117° (*picrate*, m. p. 197—198° after sintering at 184°; *chloroplatinate*; *methiodide*, m. p. 224—225°), yielding quinoline-2 : 3-dicarboxylic acid on oxidation by HNO_3 and with $NH_2{\cdot}NHPh$ the phenylhydrazones of (I) and (II). (II) and the Ac derivative of (I) in hot EtOH give 2′-*acetamido*-2 : 6-*diketo*-4 : 4-*dimethyl*-1 : 2 : 3 : 4 : 5 : 6-*hexahydrobenzhydrol*, $+H_2O$, m. p. 153—154° (slowly giving at 105—110° o-*acetamidobenzylidenedimethyldihydroresorcinol*, m. p. 197—199°), but in presence of $ZnCl_2$ form the *substance* (IV*a*; R=Ac), $+H_2O$, m. p. 203—204° (also obtained from the two previous products), which with KOH in hot EtOH affords the *substance* (IV*b*; R=H), m. p. 245—250° (decomp.), isomerised to (III) by acids; (III) is formed directly from (IV*a*) if aq.-alcoholic KOH is used. 5-Nitro-2-acetamidobenzaldehyde, (II), and KOH in EtOH yield 6-*nitro*-4-*keto*-2 : 2-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroacridine*, m. p. 82—83°, whilst in presence of $ZnCl_2$ the 6-*NO_2*-derivative, m. p. 171°, of (IV*a*) is formed. *o*-Nitrobenzaldehyde, (II), and KOH in aq. EtOH give o-*nitrobenzylidenedimethyldihydroresorcinol*,



(IV.)

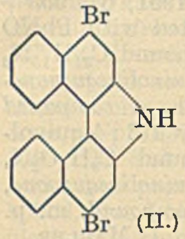


$$C_6H_4(NO_2){\cdot}CH{:}[C\!<\!\begin{smallmatrix}C(OH){\cdot}CH_2\\ CO\text{——}CH\end{smallmatrix}\!>\!CMe_2]_2,$$

m. p. 195°, and a small amount of 4 : 5-*diketo*-2 : 2 : 7 : 7-*tetramethyl*-9-(2′-*nitrophenyl*)*octahydroxanthen*, m. p. 253—254° [produced quantitatively from the previous compound by H_2SO_4, and reduced, best by Zn dust, AcOH, and HCl, to a mixture containing (III) and a phototropic *substance*, m. p. 246—249°]. R. S. Cahn.

ββ-Dinaphthacarbazole. A. Corbellini and L. Marconi (Gazzetta, 1932, **62**, 39—50).—ββ-Dinaphthacarbazole (I) (*K* derivative; *Bz* derivative, m. p. 269—272°), obtained during the prep. of 2 : 2′-diamino-1 : 1′-dinaphthyl by reduction of ββ-azonaphthol (A., 1929, 1172) with $NaNO_2$ in AcOH, gives N-*nitroso*-ββ-*dinaphthacarbazole*, m. p. 142—145°, which on reduction with Zn and AcOH regenerates (I), and a small amount of 2-*nitro*-ββ-*dinaphthacarbazole*, m. p. 267—268°, which is also obtained by treating

(I) with 1 mol. of HNO_3 (*d* 1·4) in AcOH, and is reduced by $SnCl_2$ to 2-*amino*-ββ-*dinaphthacarbazole* [*hydrochloride*; *Ac* derivative, m. p. 311° (corr.)]. Bromination of (I) in AcOH gives only 2 : 11-*dibromo*-ββ-*dinaphthacarbazole* (II), m. p. 197°. Nitration of (I) with 2 mols. of HNO_3 (*d* 1·4) gives 2 : 11-*dinitro*-ββ-*dinaphthacarbazole*, m. p. 324°, reduced by $SnCl_2$ to 2 : 11-*diamino*-ββ-*dinaphthacarbazole* (*Ac_2* derivative, m. p. above 360°). (I) and (II) are oxidised by chromic acid to phthalic anhydride. E. E. J. MARLER.



(II.)

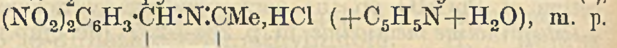
Polymorphism of *iso*propylallylbarbituric acid. R. FISCHER (Arch. Pharm., 1932, **270**, 149—152).—By sublimation or crystallisation from aq. EtOH *iso*propylallylbarbituric acid is obtained in a stable (m. p. 138·5—140·5°) and an unstable (m. p. 133·5—134·5°) form. The latter passes into the former rapidly at 136—137° and slowly at room temp. A third form, m. p. 140·5°, possibly exists. R. S. CAHN.

Spontaneous oxidation of dialuric acid. III. Oxidation of amino-acids by dialuric acid. E. S. HILL (J. Biol. Chem., 1932, **95**, 197—201).—Alloxan, formed by the autoxidation of dialuric acid, reacts with NH_2-acids (glycine, alanine, glutamic acid, and phenylalanine) giving dialuric acid, CO_2, NH_3, and the next lower aldehyde. F. R. SHAW.

Pyrimidines. CXXIII. Rearrangement of 4-chloro-2 : 6-dimethoxypyrimidine and 2 : 4 : 6-trimethoxypyrimidine in presence of methyl iodide. H. J. FISHER and T. B. JOHNSON (J. Amer. Chem. Soc., 1932, **54**, 727—732; cf. A., 1931, 851).—4-Chloro-2 : 6-dimethoxypyrimidine does not rearrange in presence of cold MeI, but at 100°, 4-*chloro*-1 : 3-*dimethyluracil*, m. p. 111°, is formed. 2 : 4 : 6-Trimethoxypyrimidine rearranges even in cold MeI to give 2-*keto*-4 : 6-*dimethoxy*-3-*methylpyrimidine*, m. p. 95·5—97°, and 4-*methoxy*-1 : 3-*dimethyluracil*, m. p. 164—166°. The mechanism of these changes is discussed. 2-*Amino*-4 : 6-*dimethoxypyrimidine*, m. p. 95°, results from the 4 : 6-dichloro-2-amino-derivative and NaOMe. C. J. WEST (*b*).

Pyrimidine azo-derivatives. M. T. BOGERT and D. DAVIDSON (J. Amer. Chem. Soc., 1932, **54**, 831).—The authors are working in the same field as Johnson, Baudisch, and Hoffmann (this vol., 66). C. J. WEST (*b*).

Derivatives of piperazine. M. GODCHOT and M. MOUSSERON (Compt. rend., 1932, **194**, 616—617).—2-Chloro*cyclo*hexanone reacts with piperazine hydrate at 140° to give N-2-*keto*cyclo*hexyl*-, m. p. 4° [separated as its *dithiocarbamate*, m. p. 165° (decomp.)], and NN′-*bis*-(2-*keto*cyclo*hexyl*)-, m. p. 113—114°, -*piperazine*, reduced by Na and EtOH, respectively, to the corresponding 2-*hydroxy*-, m. p. 67—68° [*picrate*, m. p. 220° (decomp.); *dithiocarbamate*, m. p. 205° (decomp.)], and *bis*-2-*hydroxy*-, m. p. 205—206° (*picrate*, m. p. 215°), derivatives; reduction with Pt and H_2 in AcOH gives the respective stereoisomeric *forms*, m. p. 105—106° (*picrate*, m. p. 150°; *dithiocarbamate*, m. p. 155°), and m. p. 160—161° (*picrate*, m. p. 180°), of these *sec*.-alcohols. J. W. BAKER.

Course of the reaction in a new type of rearrangement of ketoximes. III. P. W. NEBER and A. BURGARD (Annalen, 1932, **493**, 281—294).—The mechanism of the rearrangement previously described (A., 1926, 1247; 1929, 188) is studied. 2 : 4-Dinitrobenzyl Me ketoxime (*Bz* derivative, m. p. 140°), which could not be made to undergo the Beckmann rearrangement, is converted by *p*-$C_6H_4Me{\cdot}SO_2Cl$ or $PhSO_2Cl$ in pyridine at 0° into the *hydrochloride* (I),  $\underbrace{(NO_2)_2C_6H_3{\cdot}CH{\cdot}N{:}}CMe,HCl$ $(+C_5H_5N+H_2O)$, m. p. 161° [corresponding *sulphate* $(+C_5H_5N)$, m. p. 141·5° (decomp.), and *picrate* $(+C_5H_5N)$, m. p. 142·5° (decomp.)]. The free *base* (II), m. p. 79°, from (I) and aq. Na_2CO_3, gives 2 : 4-$(NO_2)_2C_6H_3{\cdot}CO_2H$ when oxidised with $KMnO_4$ in moist $COMe_2$, is converted by conc. HCl into a *substance*, $C_9H_5O_4N_2Cl$, m. p. 136° (decomp.), by 2*N*-NaOH in EtOH into a *compound*, m. p. 205° (decomp.), by Ac_2O at 0° into α-*acetamido*-β-*keto*-α-2 : 4-*dinitrophenylpropane*, m. p. 164·5° (*oxime*, m. p. 168°), and by successive treatment with 36% H_2SO_4 at room temp. and aq. NaOAc at 0° into 3 : 6-*di*-(2 : 4-*dinitrophenyl*)-2 : 5-*dimethyl*-3 : 6-*dihydro*-1 : 4-*diazine* (III) m. p. 213° (decomp.). (II) and *p*-$C_6H_4Me{\cdot}SO_3H$ in hot EtOH give the p-*toluenesulphonate*, m. p. 158°, of α-*amino*-ββ-*diethoxy*-α-2 : 4-*dinitrophenylpropane*, m. p. 90°. This acetal is hydrolysed by conc. HCl to α-*amino*-β-*keto*-α-2 : 4-*dinitrophenylpropane hydrochloride*, m. p. 168° (decomp.), converted by aq. NaOAc into (III). These results show that, contrary to the previous assumption (*loc. cit.*), the reaction does not begin by a Beckmann rearrangement, but through the formation of the *p*-toluenesulphonate of the cyclic ketimine [as (II)].

Bromination of 2 : 4-dinitrobenzyl Me ketone in AcOH gives two *Br*-derivatives, m. p. 98° and 117·5°, both of which are oxidised to 2 : 4-$(NO_2)_2C_6H_3{\cdot}CO_2H$; the latter is brominated further to αγ-*dibromo*-β-*keto*-α-2 : 4-*dinitrophenylpropane*, m. p. 108°. 2 : 4-*Dinitrobenzyl iodide*, m. p. 78°, is prepared from the chloride and KI in EtOH. H. BURTON.

New reaction of certain diazosulphonates derived from β-naphthol-1-sulphonic acid. IX. Preparation of phthalazine, phthalazone, and phthalimidine derivatives from 5-nitro-*o*-toluidine. F. M. ROWE and F. J. SIDDLE (J.C.S., 1932, 473—483; cf. A., 1931, 835).—Na 1-(4′-nitro-2′-methylbenzeneazo)-2-keto-1 : 2-dihydronaphthalene-1-sulphonate is slowly converted by cold NaOH into *Na H* 3-(4′-*nitro*-2′*methylphenyl*)-1 : 3-*dihydrophthalazine*-1-*sulphonate*-4-*acetate*, which with dil. HCl (conc. acid liberates the sulphonic acid which is difficult to hydrolyse further) affords 1-*hydroxy*-3-(4′-*nitro*-2′-*methylphenyl*)-1 : 3-*dihydrophthalazine*-4-*acetic acid* (I), m. p. 238° (*Me*, m. p. 186°, *Et*, m. p. 165°, esters; *Ac* derivative, m. p. 228°; *anilide*, m. p. 211—212°). Reduction of (I) with $Na_2S_2O_4$ or boiling acid $SnCl_2$ affords 1-*hydroxy*-3-(4′-*amino*-2′-*methylphenyl*)*tetrahydrophthalazine*-4-*acetic acid* (II), m. p. 217° (*Ac* derivative, m. p. 265°), which with boiling H_2SO_4 or long boiling with conc. HCl yields 4′-*amino*-3-*phenyl*-2′-*methylphthalaz*-1-*one*, m. p. 255°

($+\frac{1}{2}H_2O$, m. p. 130°; *Ac* derivative, m. p. 300—302°). This phthalazone is reduced to 1-*keto*-3-(4′-*amino*-2′-*methylphenyl*)*tetrahydrophthalazine*, m. p. 203—205° (*Ac* derivative, m. p. 212—214°), by $Na_2S_2O_4$ and by Zn and HCl to 4′-*amino*-N-*phenyl*-2′-*methylphthalimidine*, m. p. 176—177° (*Ac* derivative, m. p. 185°), from which 4′-*hydroxy*-N-*phenyl*-2′-*methylphthalimidine*, m. p. 227°, is prepared. Boiling mineral acids or $PhNO_2$ partly reconvert the phthalazine into the phthalazone. (I) with boiling aq. H_2SO_4 gives 4′-*nitro*-3-*phenyl*-2′-*methylphthalaz*-1-*one*, m. p. 279° (*sulphate*, m. p. 244—246°; *hydrochloride*, m. p. 195—199°, both resolidifying and melting at 279°; *picrate*, m. p. 208—210°), which, with Me_2SO_4 and crystallisation from MeOH affords a compound, m. p. 149—150° (from EtOH, the compound has m. p. 93°), both decomposed on drying. When gradually heated to 140°, either is converted into 4-*keto*-1-*methoxy*-3-(4′-*nitro*-2′-*methylphenyl*)-3 : 4-*dihydrophthalazine*, m. p. 184—185°, which, with HBr, affords 1 : 4-*diketo*-3-(4′-*nitro*-2′-*methylphenyl*)-*tetrahydrophthalazine*, m. p. 267°. 4′-Nitro-3-phenyl-2′-methylphthalaz-1-one gives with $COMe_2$, 1-*hydroxy*-4-*acetonyl*-3-(4′-*nitro*-2′-*methylphenyl*)-3 : 4-*dihydrophthalazine*, m. p. 186—187°, which, unlike berberine-acetone, is unaltered by boiling its EtOH solution with $CHCl_3$ (cf. A., 1890, 1011). No other nitro-3-phenylphthalaz-1-one shows a reaction with $COMe_2$. Reduction of the phthalaz-1-one with Na_2S and Zn and HCl affords 4′-amino-3-phenyl-2′-methylphthalaz-1-one and 4′-amino-*N*-phenyl-2′-methylphthalimidine. (I) reacts with conc. H_2SO_4 and $Na_2Cr_2O_7$ to give 4′-*nitro*-3-*phenyl*-2′ : 4-*dimethylphthalaz*-1-*one* (III), m. p. 209—210° (*picrate*, m. p. 229—230°), which with Me_2SO_4 affords 4′-*nitro*-1-*methoxy*-3-*phenyl*-2′-*methyl*-4-*methylene*-3 : 4-*dihydrophthalazine*, m. p. 118°. (II) and $Na_2Cr_2O_7$ afford 4′-*amino*-3-*phenyl*-2′ : 4-*dimethylphthalaz*-1-*one*, m. p. 287—288° (*Ac* derivative, m. p. 304—305°), also obtained by hydrolysing (II) with Na_2CO_3, NaOH, or best with EtOH–KOH or by reducing (III) with Na_2S. On reduction with $Na_2S_2O_4$, the phenyldimethylphthalazone gives 1-*keto*-3-(4′-*aminophenyl*)-2′ : 4-*dimethyltetrahydrophthalazine*, m. p. 204—205°; reduction with Zn and HCl affords 4′-*amino*-N-*phenyl*-2′ : 3-*dimethylphthalimidine*, m. p. 183° (*Ac* derivative, m. p. 231°). Phthalaldehydic acid and 5-nitro-*o*-tolylhydrazine in boiling EtOH give the *lactone* of o-*carboxybenzaldehyde*-5-*nitro*-o-*tolylhydrazone*, m. p. 225—226°, which with warm conc. H_2SO_4 or amyl-alcoholic HCl affords 4′-*nitro*-3-*phenyl*-2′-*methylphthalaz*-4-*one*, m. p. 187—188°. Unlike the isomeric phthalaz-1-one, it does not react with mineral acids, picric acid, or Me_2SO_4. J. L. D'Silva.

Anthraquinolylguanidines. M. Battegay and H. Silbermann (Compt. rend., 1932, 194, 380—382).—1-Aminoanthraquinone, cyanamide dihydrochloride, and an indifferent diluent ($PhNO_2$ or *m*-cresol) give with dry HCl at 70—150° a guanidine (cf. A., 1913, i, 1394) which suffers ring closure to give C-*amino*-1 : 9-*pyrimidineanthrone*, m. p. 290—295° [*hydrochloride* $+3H_2O$, m. p. 275—280° (decomp.); *benzoate*, m. p. 205—209° after softening at 135°]. Oxidation of the hydrochloride with HNO_3 affords pyrimidoneanthrone. 2-*Anthraquinonylguanidine*, m. p. 244—246° (decomp.), is prepared as above [*hydrochloride* $+H_2O$, m. p. 285—290° (decomp.); *dibenzoate*, m. p. 274°]. J. L. D'Silva.

Colorimetric determination of allantoin. K. Ro (J. Biochem. Japan, 1932, 14, 391—403).—The method of Fosse and Bossuyt (A., 1929, 196) is investigated and modified. F. O. Howitt.

Mercaptotetrazoles. R. Stollé [with A. Strittmatter] (J. pr. Chem., 1932, [ii], **133**, 60—64).—The *Hg* salt of 5-thiol-1-methyltetrazole decomposes at about 240° after previous sintering. The following 5-thiol-1-alkyl(or aryl)-tetrazoles were prepared by boiling the appropriate thiocyanate and NaN_3 in EtOH: *allyl*-, m. p. 69°; Ph-, m. p. 152° [*K* (decomp. about 240°), *Na* (m. p. 96°, decomp. about 145°), NH_4 (decomp. about 176°), and *Pb* (decomp. about 224°) salts]; m-*xylyl*-, decomp. 141°; β-*naphthyl*-, m. p. 164° (decomp.). The NH_4 salt of the *o*-tolyl derivative has m. p. 157°. R. S. Cahn.

Chemistry of the thiazole group. R. F. Hunter (Proc. Muslim Assoc. Adv. Sci., 1931, **1**, 1—47).—A review.

Alkaloids of *Anabasis aphylla*. II. Constitution of anabasine. III. Bases of high b. p. A. Orékhov and G. Menschikov (Ber., 1932, 65, [*B*], 232—234, 234—241; cf. A., 1931, 498).—II. 2 : 3′-Dipyridyl, b. p. 294—295° (monopicrate, m. p. 153—154°; dipicrate, m. p. 165—168°), prepared from phenanthroline (improved method) is identical with the product of the dehydrogenation of anabasine, which is therefore 2-piperidyl-3-pyridine.

III. The mixture of bases of high b. p. (*loc. cit.*) cannot be separated into its components by fractional distillation. Dissolution in 2*N*-HCl followed by fractional pptn. with 2*N*-NaOH yields *aphyllidine*, $C_{15}H_{22}ON_2$, m. p. 100—103°, $[\alpha]_D^{20}$ +27·5° in MeOH (*picrolonate*, m. p. 235—236°; *methiodide*, m. p. 217—220), *aphylline*, $C_{15}H_{24}ON_2$, m. p. 52—53° becoming transparent at 57°, $[\alpha]_D^{20}$ +10·3° in MeOH [*hydrochloride*, $[\alpha]_D^{20}$ +13·6° in H_2O; *picrolonate*, m. p. 230—231° (decomp.); *methiodide*, m. p. 212—213° (decomp.)], and *base* V, $C_{16}H_{26}O_2N_2$ or $C_{16}H_{24}O_2N_2$, m. p. 137° (decomp.). Aphylline and aphyllidine, like matrine and lupanine, are monacid bases. They are indifferent towards benzoylating agents and do not evolve CH_4 with MgMeI. They are not affected by KOH–EtOH. Attempts to hydrogenate aphyllidine to aphylline were unsuccessful. Aphylline methiodide is readily converted through the NH_4 base or by boiling KOH–MeOH into *de*-N-*methylaphylline*, $C_{16}H_{26}ON_2$, m. p. 113—115° (yield 82%), the *methiodide* of which, m. p. 223—226° [or $+0·5H_2O$, m. p. (indef.) 159—164°], is transformed by Ag_2O and subsequent distillation into *de*-N-*dimethylaphylline*, $C_{17}H_{28}ON_2$, b. p. about 230°/6 mm. The *methiodide*, m. p. 167—172°, of the last-named compound is converted into NMe_3 and *hemiaphyllylene*, $C_{15}H_{20}ON$, b. p. 217—220°/7 mm., which has only very feebly basic properties. Since the Hofmann degradation must be thrice applied to cause evolution of NMe_3, the basic N atom of aphylline, like that of lupinine and sparteine, must be in dicyclic union. Aphyllidine methiodide is very readily transformed into *de*-N-*methylaphyllidine*, $C_{16}H_{24}ON_2$, m. p. 121—122°, converted through the *methiodide*, m. p. 115° and m. p. 225° after re-solidification, into *de*-N-*dimethylaphyllidine*, $C_{17}H_{26}ON_2$, b. p. 230—245°/6 mm. The non-cryst. *methiodide* of the last-named compound passes into NMe_3 and a strongly basic liquid, b. p. 235—255°/11 mm. Normal evolution of NMe_3 appears to occur in part only, but it seems justifiable to assume that the basic N atom of aphyllidine is in dicyclic union. H. WREN.

Alkaloid extracted from the root of *Stemona tuberosa*, Loureiro (a drug from Annam). E. LOBSTEIN and J. GRUMBACH (Compt. rend., 1932, 194, 386—389).—*Stemonine*, $C_{22}H_{33}O_4N$, m. p. 160°, $[\alpha]_D$ +76·5°, extracted from the root by the Stas–Otto method, is slightly basic, contains a pyrrole nucleus, but exhibits no phenolic, aldehydic, or ketonic reactions, neither does it contain OMe or OEt groups. Its physiological effects are described. J. L. D'SILVA.

New alkaloid from *Holarrhena antidysenterica* seeds. R. D. HAWORTH (J.C.S., 1932, 631—634).—*Norconessine*, $C_{23}H_{38}N_2$, b. p. 238—240°/0·7 mm. [*dihydrogen dioxalate*, m. p. 225—227° (decomp.); *dihydrochloride*, m. p. 340° (decomp.)], is isolated, and separated from conessine by virtue of the greater solubility of its H oxalate in H_2O. It is oxidised by aq. HIO_3 to *dihydroxynorconessine*, basic, m. p. 264—266°, the decomp. of which by heating above its m. p. gives vapours that give the pyrrole reaction. *Norconessine dimethiodide*, m. p. 310—312° (decomp.), when treated with Ag_2O in aq. solution gives NMe_3 and apo*norconessine*, $C_{22}H_{33}N$, b. p. 190—192°/0·2 mm. [*picrate*, m. p. 244—245°; *methiodide*, m. p. 274—276° (not further degraded by aq. Ag_2O)], the *methochloride* of which (from methiodide and AgCl) is reduced by Na–Hg and H_2O to *dihydro*apo*norconessine*, b. p. 190°/0·3 mm. [*picrate*, m. p. 260° (decomp.)]. H. A. PIGGOTT.

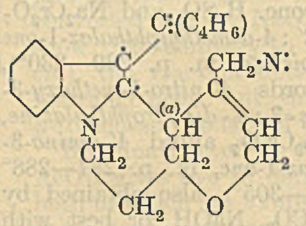
Alkaloids of the bark of *Holarrhena antidysenterica* (Kurchi bark). II. S. GHOSH and I. B. BOSE (Arch. Pharm., 1932, 270, 100—108; cf. A., 1928, 1265).—Kurchine, $C_{23}H_{38}N_2$ [*H oxalate*, +0·25H_2O, m. p. 221°; *dihydrochloride*, +H_2O, decomp. 220°; *dihydrobromide*; *dihydriodide*, m. p. 275° (decomp.); *sulphate*, decomp. 270°; *chloroplatinate*, decomp. from 240°; *chloroaurate*, m. p. 160—166° after sintering at 120°], has m. p. 75° after sintering at 73°, $[\alpha]_D^{22}$ −7·57° in $CHCl_3$, +6·4° in EtOH. Kurchichine, $C_{20}H_{36}ON_2$ [*dihydrochloride*, m. p. above 260°; *dihydrobromide*, m. p. 260° (decomp.); (?*di*)-*hydriodide*, m. p. 259—260°; *sulphate*, +2H_2O, and *oxalate*, m. p. above 270°; *chloroplatinate*, decomp. from 210°; *chloroaurate*, decomp. from 195°], has m. p. 175° and $[\alpha]_D^{22}$ −11·44° in $CHCl_3$, −8·45° in EtOH. Colour and pptn. reactions of the bases are recorded. R. S. CAHN.

Synthesis of quinine. K. KINDLER (Chem.-Ztg., 1932, 56, 165).—A review (cf. A., 1931, 1433; this vol., 289). R. K. CALLOW.

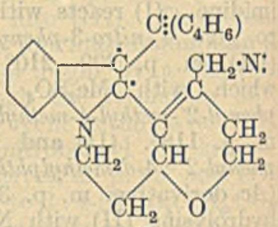
New reactions of quinine salts, and a new volumetric method of determining the alkaloid. M. J. PAPAVASSILIOU (J. Pharm. Chim., 1932, [viii], 15, 167—177).—$PdCl_2$ gives an amorphous ppt. with quinine, which becomes cryst. if the pptn. is carried out in the presence of Cl_2 water. If CrO_3 is also present, quinine gives a yellow, amorphous ppt., and strychnine a cryst. ppt. Quinine reduces $K_2Cr_2O_7$ or $KMnO_4$ in presence of H_2SO_4, and may be determined by adding excess of $KMnO_4$ to a hot H_2SO_4 solution, then excess of $H_2C_2O_4$, and titrating the excess with $KMnO_4$. A. J. MEE.

Quantitative separation of pilocarpine from quinine by means of gallotannin. M. NIERENSTEIN (Analyst, 1932, 57, 94—95; cf. B., 1929, 615).—Quinine gallotannate adsorbs from 15 to 18% of alkaloidal pilocarpine, although the quinine is completely pptd. T. McLACHLAN.

Strychnine and brucine. XV. *neo*Strychnidine and derivatives. O. ACHMATOWICZ (the late) W. H. PERKIN, jun., and R. ROBINSON (J.C.S., 1932, 486—500).—"Methyl-ψ-strychnidine" (A., 1927, 888) is formed from "methyl-ψ-strychnidine methiodide," which is identical with methyl*neo*strychnidinium iodide, by loss of MeI, and is also obtained by heating the similarly prepared benzyl- and ethyl-*neo*strychnidinium chlorides; it is an isomeride of strychnidine, and the name *neo*strychnidine (I) is proposed (cf. also A., 1927, 1208). It differs from strychnidine merely in the position of a double linking and the following formulæ are suggested [a C atom of the C_4H_6 group may possibly be interpolated at (*a*)]:



Strychnidine.



(I.)

Benzylstrychnidinium hydroxide, m. p. 306—307° (+1H_2O), prepared by action of aq. Ag_2O on the chloride (prep. improved) gives (I) on thermal decomp. Strychnidine benzylochloride (A) when distilled with 10% KOH in MeOH until the temp. reaches 140° gives (I) and *methoxybenzyldihydro*neo*strychnidine* (II), b. p. 268—271°/1 mm. This on electrolytic reduction (cf. A., 1924, i, 1337) gives *methoxybenzyltetrahydrostrychnidine*, m. p. 106—107°; it does not react with MeI, but in its presence in $COMe_2$ gives a mixture of isomeric *oxy*-derivatives, $C_{29}H_{34}O_3N_2$ (A), m. p. 249°, (B), m. p. 269°, neither of which could be acetylated or converted into an oxime or a semicarbazone. Decomp. of (II) with 20% H_2SO_4 at its b. p. gives (I) and (after addition of NaI) *benzyl*neo*strychnidinium iodide*, m. p. 238—240° (decomp.) (+1*MeOH*, m. p. 186—188°) [*chloride* (AgCl), m. p. 230—232° (decomp.)]; if derived from insufficiently purified (II) the iodide on decomp. gives also *oxy*neo*strychnidine*, $C_{21}H_{24}O_2N_2$, m. p. 239—240°. Similarly, from *strychnidine ethiodide*, m. p. 335° (*chloride*, m. p. 300—302°), *methoxyethyldihydro*neo*strychnidine* (III), m. p. 102—103° (*methiodide*, m. p. 258—260°), *methoxyethyltetrahydrostrychnidine*, m. p. 175—176°, *ethyl*neo*strychnidinium* *iodide*, m. p. 285—286° (decomp.), and *chloride*, m. p. 285—286° (decomp.) [reconverted into (III) by 20% KOH–MeOH], and (I) are prepared. The use of $NaOBu^{a}$ in BuOH in place of KOH–MeOH with the benzyl-, ethyl-, and methyl-strychnidinium salts gives the corresponding butoxyalkyldihydro*neo*strychnidines [and (I)], which were not isolated cryst., but were converted into (I) and derivatives as above. CH_2PhCl and MeI convert (I) into its quaternary salts, but only the more sparingly sol. forms were obtained.

Reduction of (I) electrolytically at 100° or with H_2 and Pd–charcoal gives dihydrostrychnidine (A), m. p. 215—216°. Oxidation of methoxymethyldihydro*neo*strychnidine (IV) with $KMnO_4$ in $COMe_2$ gives a *substance*, $C_{23}H_{30}O_3N_2,COMe_2$, m. p. 167—168°, converted by MeI at 100° into *oxy-* (IV) [(B) form of A., 1927, 888 (?)], $C_{23}H_{30}O_3N_2$, m. p. 305—306°, which does not react with Ac_2O, NH_2OH, or $(CO{\cdot}NH_2)_2NH$, and is demethylated by 20% H_2SO_4 at its b. p. to the oxymethyl*neo*strychnidinium salt (*iodide*, m. p. 238—240°; *chloride*, glassy, on thermal decomp. gives a gum). The iodide, m. p. 238—240°, is also obtained by a similar demethylation of oxymethoxydihydro*neo*strychnidine (A) (*loc. cit.*). A second *substance*, $C_{22}H_{28}O_4N_2$, m. p. 186—188°, is produced in small amount by the oxidation.

Tetrahydrostrychnine methosulphate, m. p. 266—268° (decomp.), *methiodide*, m. p. 312—314° (decomp.), *methochloride*, m. p. 270—272°, and *benzylochloride*, m. p. 202—204°, are described. The methosulphate and methochloride are converted by MeOH–KOH at 100° into a mixture in which (IV), methoxymethylhexahydrostrychnine, and (probably) (I) and tetrahydro*neo*strychnine were detected by electrolytic reduction; the crude mixture with boiling 20% H_2SO_4 gives methyl*neo*strychnidinium iodide, and tetrahydro*neo*strychnine (?) and its metho-salt [*methiodide*, m. p. 242—243°; *methochloride*, m. p. 265—267°, converted into (I) by thermal decomp.]. *Tetrahydroneostrychnine benzyloiodide*, m. p. 205—207° [*chloride*, amorphous, ready decomp. to (I)], is similarly prepared. The action of KOH–MeOH at 110° on $CH_2Ph{\cdot}NMe_3Cl$ or $CH_2Ph{\cdot}NPhMe_2Cl$ gives $CH_2Ph{\cdot}OMe$; $NaOBu^{a}$ in $Bu^{a}OH$ similarly gives $MeOBu^{a}$ and $NPhMe_2$ with $NPhMe_3I$. H. A. PIGGOTT.

Strychnos alkaloids. LXIII. Bromination of tetrahydrostrychnine and its oxidation to strychnine-*p*-carboxylic acid. H. LEUCHS and H. BEYER (Ber., 1932, **65**, [*B*], 201—207).—Bromination of the alkaloid $C_{21}H_{26}O_2N_2$ in H_2O yields *dibromotetrahydrostrychnine*, $C_{21}H_{24}O_2N_2Br_2$, m. p. 264—266° (slight decomp.), $[\alpha]_D^{17}$ −174·9°/*d* in $CHCl_3$ [*hydrobromide*; *methiodide*, m. p. (vac.) 285° (decomp.); O-*Ac* derivative $C_{23}H_{26}O_3N_2Br_2$, m. p. 260—261°, $[\alpha]_D^{17}$ −163·2°/*d* in $CHCl_3$ and its *methiodide*, m. p. 280° (decomp.); the *O*-Ac compound is identical with that formulated $C_{21}H_{24}O_2N_2Br_2$]. Hexahydrostrychnine, similarly brominated, yields *dibromohexahydrostrychnine*, $C_{21}H_{26}O_2N_2Br_2$, m. p. about 210° or (+MeOH) m. p. 135—138° (decomp.), $[\alpha]_D^{12}$ −92·2°/*d* in $CHCl_3$, also obtained by hydrogenation of the tetrahydro-base in presence of AcOH and PtO_2. The *methiodide*, m. p. 262° (decomp.), and *Ac* derivative, $C_{23}H_{28}O_3N_2Br_2$, m. p. 184—186° (obtained also by hydrogenating the acetylated base, $C_{23}H_{26}O_3N_2Br_2$), are described. The *compound* $C_{23}H_{28}O_3N_2Br_2,MeI$ has m. p. 258—259° (decomp.). Tetrahydrostrychnine is converted by HCl or HBr in AcOH into the O-*Ac* derivative, m. p. 166—168°, $[\alpha]_D^{16}$ −78·6°/*d* in 0·1*N*-HCl. *Diacetyltetrahydrostrychnine methiodide*, m. p. 165—168° (decomp.) from $COMe_2$ or decomp. 90—95° from MeOH, and *acetyltetrahydrostrychnine methiodide*, m. p. 310° (decomp.) after becoming discoloured at 290°, are described. Revision of the oxidation of tetrahydrostrychnine with CrO_3 shows that the amino-acid, $C_{21}H_{22}O_4N_2$, is *strychnine*-p-*carboxylic acid*, $C_{22}H_{22}O_4N_2$; this conclusion is confirmed by analyses of the sulphate, hydrochloride, hydrobromide, Et ester hydrochloride, and Et ester methiodide. Dihydrostrychnine-*p*-carboxylic acid, $C_{22}H_{24}O_4N_2$, its *perchlorate* and *hydrochloride*, $[\alpha]_D^{15}$ +32·9°/*d*, are described. H. WREN.

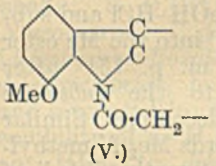
Strychnos alkaloids. LXIV. Oxidations with permanganate in the brucine series and reduction of the acids formed by degradation. H. LEUCHS and F. KRÖHNKE (Ber., 1932, **65**, [*B*], 218—226).—Brucinonic acid is converted by MeOH–HCl and subsequently by MeI in MeOH at 100° into the Me ester and the *Me₂* ester, $C_{26}H_{32}O_9N_2$, m. p. 151° after softening at 147°, hydrolysed to the *substance* $C_{24}H_{28}O_9N_2$, m. p. 207—211° (decomp.). Similar esterification of brucinolic acid affords Me_2 *N*-methylbrucinolate hydrate, the so-called "methiodide" of which is decomposed by 2*N*-$KHCO_3$ and $CHCl_3$ to a non-cryst. resin which yields the hydriodide, $C_{26}H_{31}O_9N_2,HI$, m. p. 140—144°. The so-called "methiodide" of the Me_2 ester of *N*-methylbrucinonic acid oxime hydrate (A., 1923, i, 941) is transformed by *N*-$KHCO_3$ and $CHCl_3$ into the *ester* $C_{26}H_{33}O_9N_3$, m. p. 80° after softening at 75° and m. p. 110° (decomp.) or 110—119° (decomp.) (from H_2O or AcOEt) after re-solidification. The *hydrochloride*, *hydrobromide*, *hydriodide*, m. p. 184° after softening, and *perchlorate* are described. The *oxime hydrate* of N-*methylbrucinonic acid* (also *pentahydrate*) and the *oxime* of *Me brucinonate hydroperchlorate* have been prepared.

Catalytic reduction (PtO_2) of brucinonic acid in 50% AcOH gives brucinolic acid in 75% yield. Electrolytic reduction in presence of 50% H_2SO_4 affords *dihydrobrucidinonic acid*, decomp. about 300°, $[\alpha]_D^{25}$ +64·9°/*d* in 0·1*N*-NaOH [*Ac* derivative, m. p. 275° (decomp.)], and *brucidinolic acid*, $C_{23}H_{28}O_7N_2$, decomp. above 270°, $[\alpha]_D^{23}$ +42·2°/*d* in 0·1*N*-NaOH; the last-named acid is also produced by electrolytic reduction of brucinolic acid, which is not reduced catalytically by H_2. Dihydrobrucinonic acid gives *dihydrobrucidinonic acid*, $C_{23}H_{28}O_7N_2$, $[\alpha]_D^{24}$ +69·4°/*d* in *N*-NaOH, when electrolytically reduced.

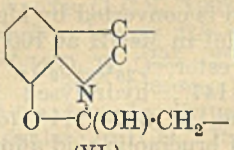
[With H. SCHULTE-OVERBERG.] 2-Ketonucidine-3-acetic acid is oxidised by $KMnO_4$ to the *substance* $C_{19}H_{24}O_7N_2$, m. p. 248—250° (decomp.), $[\alpha]_D^{12}$ +46·1°/*d*. Carboxy*apo*nucine is catalytically hydrogenated to two stereoisomeric acids $C_{16}H_{22}O_4N_2$, one of which, m. p. 292—294°, $[\alpha]_D^{20}$ −6·3°/*d*, yields a *perchlorate*, $[\alpha]_D^{20}$ −11·8°/*d*, whereas the other gives a *perchlorate*, $[\alpha]_D^{15}$ −21·6°/*d*. H. WREN.

Methylation of vomicinic acid. Derivatives of vomicine. H. WIELAND and F. CALVET (Anal. Fís.

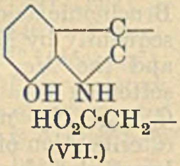
Quim., 1932, **30**, 59—70).—The course of methylation of vomicinic acid by MeI in MeOH–KOH is more complex than that of strychnine, and differs from the previous description (A., 1929, 708). Initially, the NH-group is attacked, giving *N*-methylvomicinic acid (I), $C_{23}H_{28}O_5N_2$ (+5H_2O), m. p. 255° (decomp.), $[\alpha]_D^{20}$ +20·7°, and its *Me* ester (II), m. p. 262—266° (decomp.), $[\alpha]_D^{20}$ +38·6° in EtOH (also prepared from the acid and CH_2N_2). Then ON-*dimethylvomicinic acid* (III) (formerly described as the betaine), m. p. 242—244° (loses 2H_2O at 170°), $[\alpha]_D^{20}$ +48° [*hydriodide*, m. p. 185—200° (loss of H_2O)], and its *Me* ester (IV), m. p. 214—216°, $[\alpha]_D^{20}$ +61·7° in EtOH, are formed. *Methylvomicine* (V), m. p. 286—290°, $[\alpha]_D^{20}$ +16·4° in EtOH, was once isolated; it gives vomicine with HCl. (III) and CH_2N_2 yield (IV); (IV) is hydrolysed to (III). (IV) gives a *methiodide*, m. p. 210° (decomp.), yielding with Ag_2O a *betaine* (+4H_2O), m. p. 195—198°, $[\alpha]_D^{20}$ +14·2° in EtOH [*methiodide*, m. p. 245—250° (decomp.)]. The structures (VI) and (VII) are suggested for vomicine and vomicinic acid.



(V.)



(VI.)



(VII.)

Hydrogenation of (IV) yields the *dihydro*-compound, m. p. 183—185°. Methylation of bisdehydrovomicinic acid gives an *ester* (*hydrochloride*, $C_{48}H_{56}O_{10}N_4$,2HCl, m. p. above 320°), hydrolysed to an *acid*, $C_{46}H_{52}O_{10}N_4$, decomp. 290°.

Benzylidenevomicine, m. p. 280° (decomp.), is formed by condensing vomicine with PhCHO in EtOH. " Benzoylvomicine hydrochloride " (A., 1929, 708) is an additive compound of vomicine and BzCl. An analogous additive *compound*, m. p. 185°, is formed by dihydrovomicine. *Vomicinic acid nitrosoamine* has m. p. 190° (decomp.). R. K. Callow.

Deoxycodeine. III. Constitution of the so-called α-dihydrodeoxycodeine. Bisdihydrodeoxycodeine. E. Mosettig, F. L. Cohen, and L. F. Small. **IV. Tetrahydrodeoxycodeine.** L. F. Small and F. L. Cohen (J. Amer. Chem. Soc., 1932, **54**, 793—801, 802—809; cf. A., 1931, 1077).—III. The contradiction presented in the supposed existence of the isomeric non-phenolic bases dihydrodeoxycodeine-*D* (I) and α-dihydrodeoxycodeine is removed with the discovery that the latter is bimol.; it is renamed *bisdihydrodeoxycodeine* (II). α-Chlorocodide is reduced catalytically (Pd–$BaSO_4$) to mainly (I), according to the amount of catalyst used; with Pd–$CaCO_3$ or PtO_2, (II) results. Bromo- and iodocodides behave like α-chlorocodide, whilst β-chlorocodide gives (I) and tetrahydrodeoxycodeine irrespective of the catalyst. (II), obtained as a glassy solid, has $[\alpha]_D^{26}$ −113·3° in EtOH, and gives a *methiodide*, m. p. 246—250° (decomp.), $[\alpha]_D^{23}$ −8·6° in EtOH, and an amorphous *dimethiodide*, m. p. 230—250° (gradual decomp.), $[\alpha]_D^{28}$ −71·5° in $CH_2Ph{\cdot}OH$. (II) could not be reduced electrolytically in H_2SO_4. Partial reduction of α-chlorocodide gives a glassy solid, not distillable at 200°/1 mm., whilst β-chlorocodide affords a little tetrahydrodeoxycodeine and much unchanged material.

IV. Tetrahydrodeoxycodeine (III), always obtained from ordinary solvents as the *hemihydrate* (IV), m. p. 141—147°, $[\alpha]_D^{20}$ −32·4° in 95% EtOH, $[\alpha]_D^{19}$ −66·0° in C_6H_6, is obtained anhyd. with m. p. 123—124°, $[\alpha]_D^{18}$ −72·3 in C_6H_6, by vac. sublimation of (IV), changing after several months into a second anhyd. form, m. p. 157—158°, $[\alpha]_D^{21}$ −70·2° in C_6H_6, $[\alpha]_D^{24}$ −33·6° in 95% EtOH. (III) and MeI in MeOH–NaOMe give the *methiodide*, m. p. 256—257°, $[\alpha]_D^{21}$ −3·54° in EtOH, of *tetrahydrodeoxycodeine Me ether*, an oil [*methochloride*, m. p. 255—256° (decomp.), $[\alpha]_D^{22}$ −9·5° in H_2O, prepared from the methiodide and AgCl, and converted by distillation at 0·4 mm. into the ether; *hydriodide*, m. p. 217—218° (sinters at 97—100°), $[\alpha]_D^{21}$ −21·8° in EtOH]. The methiodide of (III) is decomposed by boiling 50% KOH to *de*-N-*methyltetrahydrodeoxycodeine* (V), m. p. 152—154°, $[\alpha]_D^{24}$ +66·2° in MeOH, reduced catalytically to a *dihydro*-derivative (VI), m. p. 148—150°, $[\alpha]_D^{26}$ −14·5° in 95% EtOH (*hydrochloride*, m. p. 251—252°, $[\alpha]_D^{26}$ −82·1° in 95% EtOH). Dihydrodeoxycodeine-*A* methiodide and 20 or 50% KOH give, according to the length of treatment, unchanged methiodide, the methohydroxide, or crude (V); hydrogenation of the tarry reaction mixture affords (VI). The identity of (III) with dehydroxytetrahydrocodeine and with dihydrothebacodine is discussed. C. J. West (*b*).

Nomenclature of alkaloids similar to berberine. W. Awe (Arch. Pharm., 1932, **270**, 156—162).—It is proposed that tetrahydroprotoberberine be called " berbine " and that the names of related alkaloids be derived from this. R. S. Cahn.

Trypanocidal action and chemical constitution. XII. Arylthioarsenites derived from κ-thiolundecoic acid. A. Cohen (J.C.S., 1932, 593—598; cf. this vol., 70, 180).—*κ-Disulphidoundecoic acid* (I), m. p. 92°, is prepared by interaction of Na_2S_2 and κ-bromoundecoic acid in presence of $NaHCO_3$, and on reduction with Zn and HCl in aq. AcOH gives *κ-thiolundecoic acid* (II), m. p. 47° [*Hg mercaptide*, m. p. 185—187° (decomp.)], which is readily oxidised to *κ-sulphoundecoic acid*, m. p. 63—65° [*Na_2* salt (+1H_2O)], by HNO_3 (*d* 1·4 or 1·2). *κ-Xanthatoundecoic acid* (III), m. p. 49°, is prepared as described by Bauer and Stockhausen (A., 1931, 824) and is converted into (II) by NH_3 in aq. EtOH, which then gives (I) with H_2O_2 as described by these authors; considerable differences occur, however, in their description of the m. p. and properties of (I), (II), and (III). *Di-(κ-carboxydecyl)-benzamide-*, m. p. 270° (decomp.: previous sintering), and *-acetamide-*p*-thioarsenite*, m. p. 117—118°, are prepared by interaction of κ-thiolundecoic acid with benzamide- and acetamide-*p*-arsenoxides in aq. $NaHCO_3$. Both are toxic to *T. equiperdum*. H. A. Piggott.

***p*-Xylylarsinic acid.** A. Cohen and H. King (J.C.S., 1932, 501—503).—*p*-Xylylarsinic acid, prepared both according to Michaelis (A., 1902, i, 411) or by the Bart–Schmidt reaction (this vol, 180), has m. p. 192°, and gives with HNO_3 (*d* 1·5) at −5°, or, better, with HNO_3–H_2SO_4 at −10°, the 6-*NO_2*-

derivative, m. p. 242° (decomp.). This is reduced by $Fe(OH)_2$ to an *azoxy*-compound and 6-*amino*-p-*xylyl*-2-*arsinic acid*, m. p. about 255° (decomp.) (*Ac* derivative, dimorphic, decomp. 238—258°, and above 300°), the orientation of which follows from its conversion by H_2O at 135° into *p*-xylidine. Neither the NH_2- nor the NHAc-derivative has trypanocidal activity.
H. A. Piggott.

Isomeric nitro- and amino-naphthylarsinic acids. C. R. Saunders and C. S. Hamilton (J. Amer. Chem. Soc., 1932, 54, 636—641).—Improved methods of separation of the isomeric NO_2-derivatives formed by nitrating α- and β-$C_{10}H_7{\cdot}NH_2$ are given. 2-, m. p. 202° (decomp.), and 4-, not melted at 250°, -*nitro*-1-*naphthylarsinic acids*, prepared by the usual method, are reduced to 2-, decomp. about 216°, and 4-*amino*-1-*naphthylarsinic acids*, m. p. 210° [*Ac*, m. p. 271° (decomp.); N-*carbethoxy*-, m. p. 250°, and N-β-*hydroxyethyl*, m. p. 250°, derivatives]. 1-*Nitro*-, m. p. 192° (decomp.), 8-*nitro*-, m. p. above 265°, 1-*amino*-, m. p. 177° (decomp.) [*Ac*, m. p. 240—245° (decomp.), and N-*carbethoxy*-, m. p. 191° (decomp.), derivatives], and 8-*amino*-2-*naphthylarsinic acids* are also prepared. 4-*Benzeneazo*-1-*naphthylarsinic acid* is obtained in 8% yield from 4-benzeneazo-α-naphthylamine.
C. J. West (*b*).

[Path to optically active germanium compounds.] E. Krause (Ber., 1932, 65, [*B*], 374; cf. A., 1931, 1435; this vol., 181).—A reply to Schwarz (this vol., 291).
H. Wren.

Isolation of mercury from its organic derivatives. G. A. Razubaiev and M. M. Koton (J. Gen. Chem. Russ., 1931, 1, 864—874).—The production of metallic Hg by heating different types of compounds with H_2 under pressure in the presence of various solvents has been examined. No Hg is formed in 24 hr. from HgCl and HgPhCl in C_6H_6 below 325° or from p-$C_6H_4Me{\cdot}HgCl$ below 300° in EtOH. $HgCl_2$ gives 75% of Hg at 200° and the Ph and p-C_6H_4Me compounds up to 95%, and some aldehyde is also formed. In control experiments without H_2 no Hg was liberated, whilst a somewhat greater decomp. of $HgCl_2$ was observed in aq. solution; it is concluded that the reaction is favoured by ionisation.

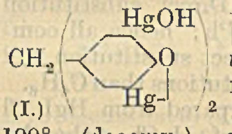
$Hg(CH_2Ph)_2$ decomposes equally readily in C_6H_6 or EtOH, although EtOH is more effective at lower temp.; the presence of H_2 has no effect and the reaction is thus a simple pyrogenic decomp. into Hg and dibenzyl. The decomp. of $HgPh_2$ is, however, greatly assisted by H_2, and the products are Hg and C_6H_6, not diphenyl, so that H_2 actually takes part in the reaction; this is interpreted as a dissociation of the compound into Hg and the Ph radical which is then reduced to C_6H_6. Support for this view is found in the observation that in EtOH solution the presence of H_2 is no longer essential, the reduction of the free radical taking place at the expense of the solvent with the production of aldehyde; similarly, in $Pr^{\alpha}OH$ and $Pr^{\beta}OH$, EtCHO and $COMe_2$ are produced and other oxidisable compounds have the same effect. A quant. study of the decomp. of $HgPh_2$ shows that the reaction is not a simple one. It is independent of the concn.; the addition of free Hg has no effect, but aldehyde greatly accelerates the reaction, whilst C_6H_6 and methyl*cyclo*hexane have the reverse effect.
G. A. R. Kon.

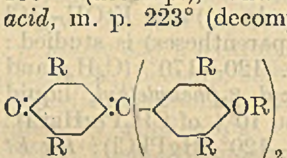
Decomposition of unsymmetrical mercuri-organic compounds: method of establishing the relative degree of electronegativity of organic radicals. II. M. S. Kharasch and A. L. Flenner (J. Amer. Chem. Soc., 1932, 54, 674—692; cf. A., 1925, i, 1107).—The effects of lengthening the C chain on the electronegativity of an aliphatic radical and of the introduction of various *o*-, *m*-, and *p*-substituents on the electronegativity of the Ph radical are studied. The validity of the method used (A., 1927, 165) for determining the relative electronegativity of org. radicals is discussed. A table of the order of electronegativity of numerous org. radicals is given and used to study (*a*) the existence of free radicals, (*b*) the relative electronegativity of aliphatic radicals, and (*c*) substitution in the C_6H_6 ring. Increase in the C chain causes a decrease in the electronegativity of straight-chain aliphatic radicals; alternation is not observed. *iso*-Radicals are less electronegative than the *n*-, but more so than *tert.*-groups. The introduction of Ph on C_{β} of the Et radical causes a marked decrease in electronegativity. Direct substitution reduces the electronegativity of Ph; hence all compounds formed from C_6H_6 by direct substitution will be less reactive towards new substitutions than C_6H_6.

The following HgR′R″ are prepared from HgR′Cl and MgR″Br and the action of $HgCl_2$ (whereby Hg R′Cl and HgR″Cl are produced) and EtOH–HCl (reaction products given in parentheses) is studied: *Hg Ph* β-*phenylethyl*, m. p. 120—170° (C_6H_6 and $CH_2Ph{\cdot}CH_2{\cdot}HgCl$); *Hg benzyl* β-*phenylethyl*, liquid (90% of $CH_2Ph{\cdot}CH_2{\cdot}HgCl$ and 10% of $CH_2Ph{\cdot}HgCl$); *Hg Ph thiophenyl*, m. p. 80—120° (HgPhCl); *Hg Et heptyl*, liquid ($C_7H_{15}HgCl$); *Hg Bu heptyl*, liquid (70% of $C_7H_{15}HgCl$ and 30% of HgBuCl); $HgBu^{\alpha}Bu^{\beta}$, liquid (mainly $HgBu^{\alpha}Cl$ and a little $HgBu^{\beta}Cl$); *Hg Et cyanide*, m. p. 180° (decomp.) (HgEtCl); *Hg* o-*anisyl cyanide*, m. p. 175° (decomp.) (o-$OMe{\cdot}C_6H_4{\cdot}HgCl$); $HgPr^{\alpha}Pr^{\beta}$, liquid (85% of $HgPr^{\beta}Cl$ and 15% of $HgPr^{\alpha}Cl$); *Hg Ph* p-*chlorophenyl*, prepared from p-$C_6H_4Cl{\cdot}MgCl$, m. p. 190—210° (decomp.) (80% of p-$C_6H_4Cl{\cdot}HgCl$ and 20% of HgPhCl), prepared from MgPhCl, m. p. 190—210° (70% of p-$C_6H_4Cl{\cdot}HgCl$); *Hg Ph* o-*chlorophenyl*, m. p. 90° (decomp.) (90—95% of o-$C_6H_4Cl{\cdot}HgCl$ and 5—10% of HgPhCl); *Hg Ph* m-*chlorophenyl*, m. p. 68° (decomp.) (m-$C_6H_4Cl{\cdot}HgCl$); *Hg* o-*chlorophenyl* m-*chlorophenyl*, m. p. 165—200° (decomp.) (70% of o-$C_6H_4Cl{\cdot}HgCl$); *Hg Ph* o-*tolyl*, m. p. 65° (decomp.) (HgPhCl); *Hg* o-*tolyl* p-*tolyl*, prepared from *o*- and p-$Me{\cdot}C_6H_4{\cdot}MgCl$, m. p. 195—200° and 200—210°, respectively (80% of *p*- and 20% of o-$Me{\cdot}C_6H_4{\cdot}HgCl$); *Hg* o-*tolyl* p-*chlorophenyl*, m. p. 210—230° (95% of p-$C_6H_4Cl{\cdot}HgCl$); *Hg Ph* p-*tolyl*, m. p. 120—155° (decomp.) (90% of HgPhCl and 10% of p-$Me{\cdot}C_6H_4{\cdot}HgCl$); *Hg Ph* m-*tolyl*, m. p. 65—70° (decomp.) (80% of HgPhCl and 20% of m-$Me{\cdot}C_6H_4{\cdot}HgCl$); *Hg* m-*tolyl* p-*tolyl*, m. p. 180—205° (decomp.) (90% of *m*- and 10% of p-$Me{\cdot}C_6H_4{\cdot}HgCl$); *Hg* o-*chlorophenyl* m-*chlorophenyl*, m. p. 95—100° (decomp.) (80% of *m*- and 20% of o-$C_6H_4Cl{\cdot}HgCl$); *Hg* m-*tolyl* p-*chlorophenyl*, m. p.

165—220° (decomp.) (90% p-$C_6H_4Cl\cdot HgCl$ and 10% m-$Me\cdot C_6H_4\cdot HgCl$); *Hg* o-*tolyl* o-*anisyl*, liquid (o-$Me\cdot C_6H_4\cdot HgCl$); *Hg* m-*chlorophenyl Me*, liquid (HgMeCl); *Hg* o-*anisyl* p-*anisyl*, m. p. 102° (decomp.) (o-$OMe\cdot C_6H_4\cdot HgCl$); *Hg* p-*anisyl* α-*naphthyl*, m. p. 130—150° (decomp.) (α-$C_{10}H_7\cdot HgCl$); *Hg* o-*anisyl* α-*naphthyl*, m. p. 200—202° (decomp.) (α-$C_{10}H_7\cdot HgCl$).
C. J. West (*b*).

Mercury derivatives of certain phenols and polycyclic phenolic acids. M. Dominikiewicz (Rocz. Chem., 1932, **12**, 79—88).—2 : 2′-*Dioxyacetylmercuri*-3 : 3′ : 5 : 5′-*tetra-acetylmercuridiphenyl* and 2 : 2′-*dihydroxy*-? : ?′-*diacetylmercuridiphenyl* are formed from 2 : 2′-diphenol and $Hg(OAc)_2$ in AcOH solution; in aq. solution the product is 2 : 2′-*dihydroxy*-3 : 3′ : 5 : 5′-*tetra-acetylmercuridiphenyl*. 4 : 4′-Diphenol yields 4 : 4′-*dihydroxy*-3 : 3′-*diacetylmercuri*- and -3 : 3′ : 5 : 5′-*tetra-acetylmercuridiphenyl*. The following further substances have been prepared and described : 4 : 4′-*dihydroxy*-3 : 3′ : 5 : 5′-*tetrahydroxymercuridiphenylmethane anhydride* (I), *dihydroxyacetylmercurihexa-acetylmercuriaurin* (II, R = Hg·OAc), *hexa-acetylmercuriaurin*, 4 : 4′-*dihydroxy*-3 : 3′-*diacetylmercuridiphenylmethane*-5 : 5′-*dicarboxylic acid*, *triacetylmercuriaurintricarboxylic acid* (III), 3- and 1-*acetylmercuri*-1- and -4-*hydroxy*-β-*naphthoic acids* (*anhydrides*), the *triacetylmercuri*-derivatives of naphthochrome-blue, 3-*iodo*-1-*hydroxy*-β-*naphthoic acid*, m. p. 190° (decomp.), and 1-*iodo*-4-*hydroxy*-β-*naphthoic acid*, m. p. 223° (decomp.).


(I.)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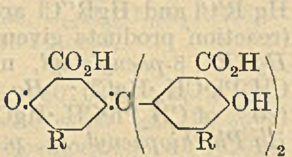
(III.)

R. Truszkowski.

Rearrangement reactions of magnesium benzyl chloride. H. Gilman and J. E. Kirby (J. Amer. Chem. Soc., 1932, **54**, 345—355).—$CH_2Ph\cdot MgCl$ (I) undergoes rearrangement reactions with various compounds. The rearrangement may be exclusively *ortho* or *para*, or of both types (in varying proportions depending on the reactants and experimental conditions). Some reagents (*e.g.*, CO_2) behave normally. The rearrangements of (I) and related compounds containing the group $\cdot\dot{C}:\dot{C}\cdot C\cdot MgX$, can be correlated with the allylic or three-carbon system rearrangements. (I) and Br give 63% of CH_2PhBr; PhCN affords 53·4% of $Ph\cdot CO\cdot CH_2Ph$; phenacyl chloride furnishes a product yielding only BzOH on oxidation; diphenylcarbamyl chloride furnishes (after hydrolysis) $CH_2Ph\cdot CO_2H$ but no toluic acids; AcCl gives o-$Me\cdot C_6H_4Ac$ and related products; ethylene oxide affords an oil, b. p. 113—115°/10 mm., oxidised to BzOH and terephthalic acid; the product from $CH_2Cl\cdot OEt$ indicates that approx. 53% of the reaction is normal, whilst 16% of *ortho* and 31% of *para* rearrangement occurs; with $ClCO_2Et$ approx. 20% of *ortho* rearrangement occurs; HCO_2Et gives both types of rearrangement (*para* comparatively small); CH_2PhCl gives 64·8% of $(CH_2\cdot Ph)_2$. Mg *cyclo*hexylmethyl bromide and CH_2O afford 46% of β-*cyclo*hexylethyl alcohol. C. J. West (*b*).

Sulphur addition with the aid of thiophosphoryl chloride and the catalysis of triaryl thiophosphate formation. H. B. Gottlieb (J. Amer. Chem. Soc., 1932, **54**, 748—750).—$P(OPh)_3$, b. p. 209—210°/1 mm., m. p. 17—22°, and $PSCl_3$ give 65% of Ph_3 thiophosphate, b. p. 230—240°/1 mm., m. p. 48°; tri-o-tolyl thiophosphate, b. p. 260—265°/1 mm., m. p. 45°, is similarly prepared. $PCl(OPh)_2$, b. p. 165—174°/1 mm., and $PSCl_3$ give Ph_2 chlorothiophosphate, b. p. 180—183°/1 mm., m. p. 64°, whilst $PPhCl_2$ affords *phosphenyl thiochloride*, $PPhSCl_2$, b. p. 150°/26 mm. Small quantities of PCl_3 catalyse the formation of triaryl thiophosphates from phenols and $PSCl_3$. C. J. West (*b*).

Non-identity of "pure" and "isoelectric" gelatins. R. J. Williams, L. Friedman, and D. M. Woods (Science, 1932, **75**, 199).—Migration to the anode occurs when electrodialysed, non-ionogenic, "pure" gelatin is electrolysed, indicating that "pure" and isoelectric gelatins are different.
L. S. Theobald.

Colours produced by the interaction of alloxan with amino-acids and proteins. F. Lieben and E. Edel (Biochem. Z., 1932, **244**, 403—412).—Arranged according to the intensity of the transient pink colour which they give by interaction with alloxan, the following NH_2-acids form the descending series: cysteine and histidine (equal), glycine, glutamic acid, tryptophan, phenylalanine, arginine, asparagine, tyrosine, leucine, serine, valine, lysine. Proline gives no colour and cystine a colour peculiar to itself. The presence of a free NH_2-group (but not of a free CO_2H group) is a necessary condition for the production of the colour. Some aromatic NH_2-derivatives give no colour. The depths of the colours given by NH_4HS and varying amounts of alloxan attain maxima and a table showing the amount of alloxan corresponding with each max. can be used in determining the latter substance. The NH_4HS–alloxan colour is deepened by addition of $(NH_4)_2CO_3$. With proteins and animal organs the alloxan colour reaction runs parallel with the nitroprusside reaction and seems to depend on the presence of free SH groups (in addition to free NH_2-groups).
W. McCartney.

Simplified micro-combustion method for determination of carbon and hydrogen. C. Kuroda and M. Wada (Bull. Inst. Phys. Chem. Res. Tokyo, 1932, **11**, 143—159).—A method requiring about 0·01 g. of the material for analysis is outlined.
R. Cuthill.

Semi-micro-determination of carbon, hydrogen, and nitrogen. H. Berger (J. pr. Chem., 1932, [ii], **133**, 1—12).—Details of apparatus etc. are given, which improve but do not perfect the determination of C, H, and N with 25—35 mg. of substance.
R. S. Cahn.

Determination of chlorine in organic substances by a wet method. B. Sjollema and J. W. Dienske (Biochem. Z., 1932, **245**, 76—79).—The Cl of org. substances is determined by oxidation with alkaline $KMnO_4$ and titration of the Cl′ by Volhard's method. P. W. CLUTTERBUCK.

Distillation apparatus for the Parnas and Wagner micro-Kjeldahl method. F. A. HOPPE-SEYLER (Mikrochem., 1932, **10**, 446—449).—The apparatus, described in detail, is of simplified construction and reduces condensation of H_2O to a min.; it also reduces the time required for distillation. H. F. GILLBE.

Methods for determining formaldehyde. J. BÜCHI (Pharm. Acta Helv., 1931, **6**, 1—54; Chem. Zentr., 1931, ii, 1172).—The H_2O_2, Na_2SO_3, Hg, and I methods give concordant results, but the NH_4Cl method gives vals. approx. 0·1% low. MeCHO and $COMe_2$ falsify all results, especially those of the I methods; EtOH influences only these. Directions for determining CH_2O in pure solutions with Na_2SO_3, thymolphthalein, and *N*-HCl are given. L. S. THEOBALD.

Determination and separation of saligenin, salicylic acid, and salicylaldehyde. R. BERG, W. GRIMMER, and A. MÜLLER (Chem.-Ztg., 1931, **55**, 975).—The Et_2O solution of the three compounds is extracted with 0·05*N*-$NaHCO_3$, which removes salicylic acid and some aldehyde. The solution is titrated with 0·05*N*-H_2SO_4 until colourless, an excess is added, and the solution boiled to expel CO_2, cooled, and titrated with 0·05*N*-NaOH until yellow; the difference corresponds with salicylic acid. The Et_2O is removed from the ethereal layer and the aldehyde converted into salicylaldoxime. The solution is extracted with Et_2O, the extract shaken with *N*-NaOH, and the alkaline solution neutralised with AcOH and treated with 3% $CuSO_4$ solution to remove the aldoxime. After filtration the saligenin is extracted from the filtrate with Et_2O and weighed after removing the solvent. A. R. POWELL.

Iodometric determination of caffeine. G. WALLRABE (Apoth.-Ztg., 1931, 341—343; Chem. Zentr., 1931, ii, 1170—1171).—The caffeine compound is acidified with dil. H_2SO_4 and a given vol. of 0·1*N*-I solution added. The pptd. $C_8H_{10}O_2N_4,HI,I_4$ is collected and the filtrate titrated with $Na_2S_2O_3$; 1 c.c. of 0·1*N*-I solution = 4·85 mg. of caffeine. L. S. THEOBALD.

2 : 4-Dinitrophenylhydrazine in determination of carbonyl compounds. O. FERNÁNDEZ, L. SOCÍAS, and C. TORRES (Anal. Fís. Quím., 1932, **30**, 37—49).—Under definite conditions in aq.-alcoholic H_2SO_4 solution, the 2 : 4-dinitrophenylhydrazones of camphor, menthone, pulegone, citral, and furfuraldehyde are pptd. in 98—99% yield, and accurate quant. determinations are claimed by this method. R. K. CALLOW.

Detection of quinotoxine in presence of quinine. M. BACHSTEZ. **Detection of strychnine.** A. W. NUNN.—See this vol., 301.

Modification of Van Slyke nitrogen distribution method. J. W. CAVETT.—See this vol., 438.

Biochemistry.

Calorimetry of blood and blood constituents from healthy and diseased men and animals. A. GIGON, M. NOVERRAZ, and E. HOFFMANN (Biochem. Z., 1932, **245**, 440—451).—The calorific val. of blood (man, cow, bull, calf, horse, pig, rabbit) and of its constituents (corpuscles, serum, plasma) varies with age, species, and state of health. In some cases the serum has a higher calorific val. than has the plasma, in others the reverse is true. Disease in man has often great effects on the val.; pernicious anæmia and Schüller–Christian disease lead to particularly pronounced variations. There are sometimes unexpectedly pronounced variations in the amount of C and N in dried blood. W. McCARTNEY.

Chamber for measuring oxygen consumption of animals. A. E. KOEHLER (J. Biol. Chem., 1932, **95**, 67—72).—A simple type of chamber for animals such as dogs is described. F. O. HOWITT.

Measurements of oxygen consumption of small animals. J. E. DAVIS and H. B. VAN DYKE (J. Biol. Chem., 1932, **95**, 73—78).—The apparatus of Koehler (cf. preceding abstract) is modified for use with animals such as mice and rats. F. O. HOWITT.

Determination of carbon dioxide tension in small amounts of blood. J. K. W. FERGUSON (J. Biol. Chem., 1932, **95**, 301—310).—A micro-method of determining the CO_2 tension in blood by measuring the reduction in the vol., after addition of 3% aq. NaOH, of a bubble of air equilibrated with the blood in a capillary tube, is described. The experimental error is <2 mm. Hg. The effect of glycolysis may be overcome by a preliminary washing of the capillary tube with aq. NaF. A. LAWSON.

Dog blood. D. B. DILL, H. T. EDWARDS, M. FLORKIN, and R. W. CAMPBELL (J. Biol. Chem., 1932, **95**, 143—152).—The physico-chemical properties of oxygenated dog's blood were determined and compared with those of human blood. The buffer val. of the serum is less than (approx. 16%), and that of the whole blood equal to, those of the corresponding fluids of man. No appreciable differences exist in the distribution of Cl′ and HCO_3' between cells and plasma, in the O_2 dissociation curve or in the CO_2 tension of the arterial blood. Dog's blood has a Cl′ content 4—8% greater than that of human blood and the ratio $Na^{\cdot}/K^{\cdot}$ of the corpuscles is very high. F. O. HOWITT.

Animal species and dissociation curve of blood. H. KÔNO (Japan. J. Med. Sci., III, Biophys., 1931, 2, 35—45).—Individual and species differences are due mainly to quant. differences in the alkali reserve of the blood. CHEMICAL ABSTRACTS.

Influence of salts on the dissociation curve of hæmoglobin. H. KÔNO (Japan. J. Med. Sci., III, Biophys., 1931, 2, 1—24).—The effect is attributed to the physical action of the ions; there is no difference between ions in depressing the dissociation curve.

The action is slight compared with that of acid and alkali. Chemical Abstracts.

Copper as a supplement to iron in hæmoglobin formation in the pig. C. A. Elvehjem and E. B. Hart (J. Biol. Chem., 1932, **95**, 363—370).—When pure Fe is added to the whole-milk diet of anæmic pigs, a small increase in the hæmoglobin content of the blood takes place, but complete recovery is obtained only after addition of Cu. A. Lawson.

Spectrum and catalytic effects of iminazole-hæmin. W. Langenbeck (Naturwiss., 1932, **20**, 124).—When an aq. NH_3 or Na_2HPO_4 solution of hæmin is brought in contact with iminazole or 4(5)-methyliminazole (I) the colour changes from brown to reddish-brown. The absorption spectrum of an aq. NH_3 solution containing 0·1% of (I) and 0·005% of hæmin consists of three bands very similar to the spectrum obtained from an alkaline solution of methæmoglobin.

The catalytic and peroxidase effects of hæmin are influenced by the presence of methyliminazole and the p_H optimum is 7. The catalytic effect of hæmin with different bases and the p_H optima are discussed. W. R. Angus.

Micro-determination of blood-peroxidase. H. Masamune and K. Kodama (J. Biochem. Japan, 1932, **14**, 475—479).—The method of Willstätter and Stoll (A., 1918, i, 555) is modified for use with 0·01 c.c. of blood. F. O. Howitt.

Catalase of leucocytes. K. G. Stern (Z. physiol. Chem., 1932, **204**, 259—282).—The catalase content of leucocytes of different origin was compared. The enzyme solutions were obtained from plasmolysates and extracts from dried preps. The activity is of the same order as that of similarly treated erythrocytes. For the polymorphonuclear exudate leucocytes of the rabbit, the optimum p_H is 7, the temp. coeff. Q_{10} is 1·3 for 0—18°. At 37° the activity is depressed, at 52° inactivation is complete. The enzyme is specifically inhibited by $Fe^{\cdot\cdot}$, HCN, and CO, but not by 2 : 2′-dipyridyl, tripyridylferrous sulphate, and H_2. Inhibition by CO_2 and O_2 is due to change of p_H. The catalysed reaction is usually unimol.; the catalase of leucocytes agrees in general with that of liver and erythrocytes. J. H. Birkinshaw.

Blood-chlorine during asphyxiation. II. T. Saso (J. Biochem. Japan, 1932, **14**, 419—438).—Oral administration of H_3PO_4, AcOH, and other acids to rabbits induces hyperchloræmia. The plasma-Cl increases and then falls to normal or subnormal levels, according to whether lethal or sub-lethal doses are administered. Such phenomena are characteristic of asphyxiation, the relation of which to acidosis is discussed (cf. A., 1931, 375).

F. O. Howitt.

Blood analysis. Determination of chlorine, sodium, potassium, lecithin, cholesterol, cholesteryl ester, and neutral fat in blood-serum. L. Wacker (Biochem. Z., 1932, **245**, 149—158).—Modifications of known methods are described.

P. W. Clutterbuck.

Determination of small amounts of bromide in blood and urine. K. O. Møller (Biochem. Z., 1932, **245**, 282—289).—By means of a method based on that of Toxopéus (A., 1930, 639) the bromide content of biological fluids (blood, urine) can be determined in 1 c.c. W. McCartney.

Spectrographic examination of human body-fluids. L. Karczag and M. Hanák (Biochem. Z., 1932, **245**, 166—173).—The selective absorption curve of normal human blood-serum is a combination of the individual curves of the albumin and globulin fractions. Differences in age, blood group, or type of illness had no influence on the selective absorption of blood-sera. Treatment with CH_2O, heat-inactivation, and irradiation with *X*-rays influence the selective absorption of sera from different sources in the same way. The absorption curve of cerebrospinal fluid is the interference curve of the individual selectively absorptive components (proteins, uric acid, etc.). Treatment of the fluid with CH_2O caused a change in absorption. The ultra-filtrate of the serum gave in no case a pure uric acid curve, and of cerebrospinal fluid showed a flatter curve than did the fluid itself. P. W. Clutterbuck.

Urobilinogen in blood-serum. L. F. Loeb (Biochem. Z., 1932, **244**, 426—430).—Urobilinogen is probably not produced in the kidneys. By a modification of Niemann's method (A., 1925, i, 1206) it can be determined in urine and in blood-serum in concns. of $\nless$ 3 mg. per 100 c.c. In various diseases the urobilinogen content of the urine increases, sometimes considerably, and in icterus catarrhalis and cirrhosis of the liver there is also a great increase in the amount in the blood-serum. W. McCartney.

Refractometric investigation of serum-protein. VIII. Determination of the protein fractions in horse-serum. D. von Deseö (Biochem. Z., 1932, **244**, 382—389; cf. A., 1931, 1319).—Provided that 50% aq. $(NH_4)_2SO_4$ is used for the pptn., the refractometric method of determination yields results in good agreement with those obtained by the gravimetric method after twelve-fold dilution.

W. McCartney.

Fractional precipitation of serum-globulin at different hydrogen-ion activities. H. K. Reiner and L. Reiner (J. Biol. Chem., 1932, **95**, 345—361).—Globulin is pptd. from normal and anti-pneumococcus horse serum at p_H 5·0—7·0. Repeated pptn. at p_H 5·1 and 6·8, respectively, gives from both sera two fractions, the p_H pptn. curves, N content, and acid- and base-binding capacities of which are different. The N val. for the ppt. from a mixture of the two fractions compared with that of the single fractions pptd. under the same conditions supports the view that combination takes place in the mixed solutions either by interionic forces or by virtue of the tendency which amphions have of association near their isoelectric points. A. Lawson.

Critical temperature of serum. Ionic equilibrium of serum as a function of its temperature. V. P. L. du Noüy (Ann. Inst. Pasteur, 1932, **48**, 187—207).—When horse serum is heated at 58° for 10 min. and then diluted with distilled H_2O, the globulin which is pptd. separates in a dispersed form which tends to remain in suspension, whereas if the serum is unheated or heated for 10 min. at $<57°$, the pptd. globulin tends to fall rapidly out of suspension. The crit. temp. is remarkably sharply defined within the limits of about 1° and is lower for longer periods of heating, being 58° for 5 min. and 53° for 2 hr. A similar phenomenon is observed with the sera of other animals, the crit. temp. varying according to the animal from 55° to 59° for a period of heating of 10 min. The relation of this phenomenon to the state of the globulin and the modification induced in the latter by heat is discussed. W. O. Kermack.

Calcium and calcæmia in man. C. O. Guillaumin (Bull. Soc. Chim. biol., 1932, **14**, 85—196).—A lecture.

Phosphorus partition of the blood of animals and chemical diagnosis of aphosphorosis. A. I. Malan (J. S. African Chem. Inst., 1932, **15**, 4—9).—In aphosphorosis the inorg. P of the blood of cattle and sheep is lower than in normal healthy animals, and indications of the disease can be obtained in the early stages when clinical symptoms are insufficient to render a diagnosis possible. Addition of bone meal or Na_2HPO_4 to the basic diet raises the blood-inorg. P to normal levels and improves the condition of the animals. P. G. Marshall.

Bound sugar of blood. A. M. de Vries (Biochem. Z., 1932, **245**, 473—479).—The amount of bound sugar (hydrolysable substance) in the blood of rabbits exhibits considerable individual variations, but is only slightly affected by the taking of samples of the blood or by injection of physiological NaCl solutions. Injection of liver extracts, of insulin, or of the materials separated from crude insulin during purification has no effect on the amount of bound sugar in the blood. W. McCartney.

Behaviour of the so-called bound sugar (hydrolysable reducing substance) in human blood-plasma. A. M. de Vries (Biochem. Z., 1932, **245**, 480—487; cf. preceding abstract).—Neither in healthy nor in diseased persons can any relation between the amounts of free and bound sugar of the blood-plasma be found. The blood in cancer and tuberculosis more often contains a high proportion of bound sugar than does that of healthy persons or persons suffering from other diseases.
W. McCartney.

Distribution of sugar between blood-cells and plasma. M. Jacoby and H. Friedel (Biochem. Z., 1932, **244**, 357—365; A., 1931, 858).—Of the sugar content of the blood the cells usually contain considerably less than 30% and this amount is rarely exceeded. When the content is high the proportion in the cells is less than normal, since their capability to take up sugar is limited. The concn. of sugar in the cells is lower at acid reaction than at neutral because the cell vol. is greater in the former case than in the latter. The increase in vol. results from absorption of H_2O. W. McCartney.

Modifications of glucose and water in the blood resulting from administration of glucose and water. A. Galamini and E. Serianni (Atti R. Accad. Lincei, 1931, [vi], **14**, 378—381).—Administration (to man) of glucose (60 g.) in H_2O (200 c.c.) in a no. of doses increases the blood-sugar more than when the glucose is given in one dose. With further increase in the no. of doses, the blood-sugar increases less or may even decrease without preliminary increase. In general, the H_2O content of the blood diminishes slightly as the sugar increases and *vice versa.* T. H. Pope.

Blood-sugar in man following rectal administration of glucose. E. L. Scott and J. F. B. Zweighaft (Arch. Int. Med., 1932, **49**, 221—226).—Rectal administration of glucose to fasting subjects produced no rise in the blood-sugar curve from the fasting level. The slight fall observed may be due to increased pancreatic activity following the absorption of a small quantity of glucose. H. Davson.

Glycolysis. A. P. Barer (J. Clin. Invest., 1931, **10**, 507—520).—Glycolysis is not correlated with age or sex. The optimal temp. is 37°; citrates and oxalates retard, whilst fluorides arrest, it. Glycolysis is not dependent on the initial glucose concn. of the blood, and it is not affected by insulin *in vitro.*
Chemical Abstracts.

Determination of glutathione. M. Delaville and L. Kowarski (Compt. rend. Soc. Biol., 1931, **106**, 1220—1224; Chem. Zentr., 1931, ii, 2362).—The direct iodometric titration of glutathione in hepatic and arterial blood yields much smaller vals. than does the indirect method of oxidising the SH-compounds with excess of I, in which the time allowed for oxidation has an effect. A method for determining total glutathione is advanced. In the blood of horses this content varies with the individual, the mean val. being approx. 50 mg. per 100 c.c.
L. S. Theobald.

Antiprothrombin and globulins. A. Fischer (Biochem. Z., 1932, **244**, 464—485; cf. A., 1931, 1441; this vol., 73).—There is an abs. correspondence between the antiprothrombin action and the globulin content of blood-serum. With serum-albumin antiprothrombin forms complexes which, physico-chemically, closely resemble natural globulins. It is concluded that the latter are produced by the action of heparin alone, which very rapidly converts serum-albumin into globulin, on a sp. protein of blood.
W. McCartney.

Nature of Bordet's "colloide de bœuf" and of "conglutinin." I. Györffy (Biochem. Z., 1932, **244**, 435—439).—The flocculated material obtained by Bordet and Streng and supposed to consist of erythrocytes actually consists of protein (derived from residual fibrinogen) which is pptd. by some complementary substance from the guinea-pig's blood. Consequently it is superfluous to assume the existence of a special " colloide de bœuf " (or conglutinin).
W. McCartney.

Kinetics of hæmolysis in amboceptor–complement systems. E. Ponder (Proc. Roy. Soc., 1932, B, **110**, 18—45).—Hæmolysis in a system containing amboceptor, sheep's red blood-cells, and guinea-pig complement when components are added in this order proceeds according to the equation previously found (A., 1930, 1306) for hæmolysis by a simple agent such as saponin, provided that complement be regarded as the essential hæmolytic component. Only a part, however, of the complement is fixed on or near the cells and is active. This fraction increases with increase of amboceptor and is zero when no amboceptor is present. Exactly the same degree of hæmolysis may be obtained with high concns. of complement and a small quantity of amboceptor as with small concns. of complement and large quantities of amboceptor provided these quantities are such that the amount of complement taken up by the cells is the same in both cases. The fraction of amboceptor taken up by the cells is approx. const. and equal to 75% of the amount of that added over a considerable range of concns. W. O. Kermack.

Hæmolytic action of compounds of the filicic acid group. A. Jodlbauer (Arch. exp. Path. Pharm., 1932, 164, 457—463).—Aq. extracts of an intimate mixture of MgO and Extractum filicis have a hæmolytic action on red blood-corpuscles, max. at p_H 8·2. Previous heating of the solution at 90° for 1½ hr. markedly increases the hæmolytic action at 20°, but longer heating gradually destroys it. The solutions are sensitive to light particularly in presence of sensitisers such as eosin. The anthelminthic and hæmolytic actions of various extracts run parallel.

W. O. Kermack.

Antigenic property of serum-lipin. O. Ishikawa (Sei-i-kwai Med. J., 1931, 49, No. 8, 130—146).—Lipin isolated from the sera of man, horse, cattle, dog, pig, goat, fowl, and duck and giving no biuret, xanthoproteic, or ninhydrin tests, when injected into the rabbit, produced antibodies only when an accelerating substance (cattle-serum lipin) was present. There was no definite specificity among the serum-lipins of these animals. The antibody of the serum-lipin does not combine with the serum or the lipin-free serum-proteins, nor does the antibody of a serum or of its lipin-free serum-protein combine with the serum-lipin. The antibody of the serum-lipin seems to be sp.

Chemical Abstracts.

Masking of haptenes by lipins. H. Rudy (Biochem. Z., 1932, 245, 431—439).—Native serum does not mask the antigenic property of brain-extract in complement-fixation, although the isolated serum-lipins display this effect. H. W. Dudley.

Antigenic properties of yeast invertase. K. Matsuoka (Japan. J. Exp. Med., 1930, 8, 615—626).—Anti-invertase serum, decreasing the optical rotation produced by the action of invertase on sucrose, can be prepared by the injection of yeast autolysate. Heating destroys the antigenic property of invertase, but addition of serum to the heated autolysate reactivates it. Invertase is not completely destroyed by incubation with anti-invertase serum. No antibodies were produced by injection of sucrose, but a weak anti-invertase serum was prepared by injecting sucrose together with normal serum.

Chemical Abstracts.

Cold hæmotoxin in heated serum. II. Cold, non-complementary hæmolysis by the heated normal serum. III. Chemical nature and the influence of inhibitors. K. Toshima (J. Biochem. Japan, 1931, 13, 441—464).—II. The activity of the cold, non-complementary hæmolytic factor in heated normal serum varies in the order: rabbit>chicken, pig>man, goose, etc. The greatest effect is exhibited with sera heated at 90° and occurs below 5° (usually at 0°); cold hæmolysis occurs in serum free from amboceptor, and in isotonic solutions of KCl, KNO_3, and KBr, but not of sulphates or in an isotonic sucrose solution. The factor is present in the albumin fraction and is weakened by exposure of heated (but not unheated) serum to light. Treatment with Et_2O or $CHCl_3$ diminishes the effect: 0·1N-HCl or -NaOH is inactive.

III. The factor is not salted out by $(NH_4)_2SO_4$ or extracted with EtOH, $COMe_2$, Et_2O, or $CHCl_3$. It is non-dialysable, but is not related to glycogen. Cold hæmolysis is markedly inhibited by fresh, unheated sera, by serum-albumin or cholesterol (but not by lecithin), by egg-yolk but not egg-white, by peptone, caseinogen, and trypsin, but not by ovalbumin or pepsin. Chemical Abstracts.

Relationship between heated immunised serum viscosity and its antibody. T. Takayama (Sei-i-kwai Med. J., 1930, 49, No. 12, 1—70).—The viscosity of the serum was parallel with the degree of destruction of the antibodies. The main viscosity changes are due to those of the globulin fractions. Normal serum-albumin and -globulin undergo approx. the same changes in viscosity when heated.

Chemical Abstracts.

Normal immune bodies of the new-born. T. Takayama (Sei-i-kwai Med. J., 1930, 49, No. 7, 86—103).—The serum of the new-born contains hæmolytic amboceptor and complement, but the hæmolytic power is much weaker than that of the mother. The order of ease of hæmolysis is: rabbit, pig, horse, cattle, guinea-pig, goat. That of the mother is: pig, goat, rabbit, guinea-pig, horse, cattle. The new-born has normal agglutinin, but less than the mother. The serum of the new-born agglutinates corpuscles in the order: rabbit, pig, horse, cattle, guinea-pig, goat; that of the mother: rabbit, pig, horse, guinea-pig, goat, cattle. The agglutinin of the new-born resists heating at 62·5—65° for 30 min. and is destroyed at 65—67·5°: that of the mother resists heating at 65—67·5° and is destroyed at 67·5—70°.

Chemical Abstracts.

Occurrence of an anticoagulant in the extract of the testes and eggs of the lamprey (*Petrom. planeri*). C. Jucci (Boll. Soc. Ital. Biol. sperim., 1930, 5, 4 pp.; Chem. Zentr., 1931, ii, 1715).—The extract retards or inhibits the coagulation of the blood of a selachian (*Scyllium*); experiments with human blood gave an indefinite result.

A. A. Eldridge.

Physiological-chemical analysis of the depressor action of organ extracts. K. Felix and A. von Putzer-Reybegg (Arch. exp. Path. Pharm., 1932, 164, 402—416).—In extracts of organs (placenta, kidney, stomach, and mesentery) having a depressor action, the following substances have been isolated by a modification of the method of Kossel and Kutscher: choline, acetylcholine, histamine, adenylic acid, and adenosine. Another substance of unknown composition and very high activity has also been isolated (not pure), which is of relatively low mol.

wt., is not inactivated by treatment with boiling mineral acid, is more unstable to alkalis, readily sol. in EtOH, MeOH, and H_2O, but not in Et_2O. It appears in the guanidine fraction.

W. O. Kermack.

Depressor action of certain organ extracts. F. Lange (Arch. exp. Path. Pharm., 1932, **164**, 417—440).—From all vascular organs of warm- and cold-blooded animals a substance may be extracted which has a very strong depressor action and is different from any of the known vaso-dilator compounds.

W. O. Kermack.

Contents of glycogen and galactogen (animal sinistrin) in *Helix pomatia*. F. May (Z. Biol., 1932, **92**, 319—324; cf. A., 1931, 642).—Polysaccharides were isolated from the body of the snail by hydrolysis with KOH followed by repeated pptn. with EtOH. The product has $[\alpha]_D$ +158·3° and yields 17·9% of galactose on acid hydrolysis. The sp. rotation when considered as that of a mixture of glycogen and galactogen indicates a content of 17·45% of the latter, thus confirming that galactogen is a polymeride of galactose. F. O. Howitt.

Galactogen content of eggs of *Helix pomatia*. F. May (Z. Biol., 1932, **92**, 325—330).—The eggs on hydrolysis with KOH and treatment with EtOH (cf. preceding abstract) yield a polysaccharide, $[\alpha]_D$ −22·73°, free from glycogen and consisting of pure galactogen, which forms about 38% of the org. matter of the egg. F. O. Howitt.

Glycogen content of human kidney. K. Lang (Arch. exp. Path. Pharm., 1932, **164**, 449—456).—In various diseases of man the glycogen content of the kidney varied from 12 to 142 mg. per 100 g. with a mean val. of 20—30 mg. In diabetes the figure is sometimes but not always relatively high. The result of the histological test for glycogen does not always correspond with the quantity present as determined chemically. W. O. Kermack.

Cephalin from human brain. III. Fatty acids of oxidised cephalin. M. Bülow and I. H. Page (Z. physiol. Chem., 1932, **205**, 25—37; cf. A., 1931, 380).—The fall in the I, C, H, N, and P vals. of cephalin on keeping is not due to liberation of fatty acids by hydrolysis, or to an oxidative elimination of acids of low mol. wt., since only about 1% of the total acids are H_2O-sol., of which ¼ is volatile in steam. On the other hand, considerable amounts of OH-acids are present (about 5% of the total acids); these can be acetylated (Ac val. 0·5—1·5%). The fraction insol. in light petroleum amounts to 3—4%. The liquid acids show a small N content not removable by washing. J. H. Birkinshaw.

Importance of lipins for permeability. M. Mansheim (Biochem. Z., 1932, **244**, 268—277).—The findings of Nierenstein (Pflüger's Archiv, 1920, **179**, 233) and of Krebs and Nachmansohn (A., 1927, 895) concerning the parallelism between the ability of basic dyes to colour vital tissue, to dissolve in lipins, and to be adsorbed by kaolin are confirmed. All factors (*e.g.*, alkaline reaction and addition of oleic or nucleic acid for basic dyes, acid reaction for acid dyes) which lead to deposition of dyes inhibit their diffusion into gelatin gels. The diffusion is not influenced by the presence of neutral fat. It follows that the diffusion of both basic and acid dyes in gelatin proceeds most easily through the pores, *i.e.*, in H_2O, and that solubility in lipins is significant for deposition; the same holds for the diffusion of easily diffusible dyes in living animal and vegetable cells. In gelatin membranes the diffusion through the pores cannot be prevented by the presence of narcotics, nor is the diffusion of dyes, salts, glucose, or sucrose affected by the presence of solutions of homologous alcohols or esters of appropriate concn.

W. McCartney.

Plasma-protein of striated muscle. K. Yanagi (J. Biochem. Japan, 1931, **14**, 305—323).—Myosin, myogen, and myogen-fibrin were isolated from muscle-plasma by fractional heat-coagulation (A., 1896, ii, 48). Myosin in aq. solution at room temp. is slowly converted into myogen, which in turn changes to sol. myogen-fibrin, these changes being dependent on the salt concn. and $[H^{\cdot}]$ of the solution. Hence the three fractions represent phases of a single protein and are probably produced during the treatment for separation. F. O. Howitt.

Method for studying the scale structure of medullated and pigmented animal fibres. J. I. Hardy (J. Text. Inst., 1932, **23**, 1—5T).—Impressions of the scale structure are obtained by mounting the fibres on a microscope slide and embedding them in a solution of celluloid in $COMe_2$, and the casts so obtained are examined microscopically.

B. P. Ridge.

Method for revealing the scale structure of wool and hair. J. Manby (J. Text. Inst., 1932, **23**, 4—13T).—The hairs are arranged on a microscope slide and mounted without a coverglass so that the medium used covers approx. the lower half of the fibre only. For wool fibres and hairs with pronounced scales 5% xylene balsam is a suitable mountant, but when the scales are very fine the following are preferred: 1% celluloid in amyl acetate, 25% glycerol in H_2O, or 3% glycerol jelly. B. P. Ridge.

Relation between the colloid content of the thyroid and its bromine and iodine content. F. Tanino (Klin. Woch., 1931, **10**, 1406; Chem. Zentr., 1931, ii, 1872).—The total I is slightly lower in thyroids rich in colloids than in those of low colloid content, but the degree of dependence is small. In glands low in colloids Br : I=8; the higher Br content of glands high in colloids increases the ratio to 16. For the glands of individuals treated with I the quotient is about 1. A. A. Eldridge.

Alleged iodide elimination from di-iodotyrosine in tryptic digestion. G. Barkan and G. Kingisepp (Z. physiol. Chem., 1932, **204**, 219—232).—Electrometric titration shows that iodide is very slowly eliminated at slightly alkaline reaction from di-iodotyrosine. The process is slightly accelerated by active trypsin, but to a much smaller extent than Ostwald's experiments indicate (A., 1909, i, 860). $AgNO_3$ appears to produce a ppt. other than iodide (possibly an adsorption effect or formation of an insol. complex of di-iodotyrosine).

J. H. Birkinshaw.

Fluorescent substances in hens' egg-shells. H. Bierry and B. Gouzon (Compt. rend., 1932, **194**, 653—655).—The fluorescence spectrum, produced by ultra-violet light, of the porphyrin extracted from the brown egg-shell of a hen shows a red band between 618 and 650 mμ, and on further exposure a wide green band. The corresponding spectrum for the white egg-shell shows a narrower red band at 622—645 mμ, and a less intense green band on further exposure. The latter spectrum resembles that of hæmatoporphyrin. A. Lawson.

Calcium content of rats. H. Aida (Biochem. Z., 1932, **244**, 303—307).—No increase in the Ca content of rats results from the subcutaneous administration of small amounts (0·025% of the Ca content of the diet) of $CaCl_2$, $CaBr_2$, and CaI_2, whether the animals rest or exercise vigorously. W. McCartney.

Application of optical spectroscopy to the determination of heavy elements in tissue. W. Mankin (Chem. Eng. Min. Rev., 1932, **24**, 142—144).—Zn, Al, Li, Mn, and Cu have been detected in the arc spectrum of cancer material, and Li, Zn, Ba, Al, Pb, As, and Cu in that of egg contents. The technique of the method is described. N. H. Hartshorne.

Solvent action of gastric juice on calcium phosphate. A. M. Montefredine (Arch. Farm. sperim., 1932, **53**, 192—200).—The solvent action of gastric juice on $Ca_3(PO_4)_2$ is greater than that calc. from its acidity. Repptn. occurs in the filtrate. The formation of an unstable Ca–protein complex is assumed. R. K. Callow.

Vitamin-*A*, -*B* (*B*$_1$) and -*G* (*B*$_2$), contents of milk throughout the year. F. L. MacLeod, J. B. Brodie, and E. R. MacLoon (J. Dairy Sci., 1932, **15**, 14—22).—Seasonal changes were small. A. G. Pollard.

Vitamin-*A* content of the milk of Holstein, Ayrshire, Jersey, and Guernsey cows. H. P. Davis and I. L. Hathaway (Nebraska Agric. Exp. Sta. Res. Bull., 1931, No. 54, 14 pp.).—No significant differences were observed. A. G. Pollard.

Lactose and chloride concentrations of milk produced during irregular intervals between milkings. C. L. Roadhouse and J. L. Henderson (J. Dairy Sci., 1932, **15**, 1—5).—Milking at irregular intervals did not affect the lactose and Cl′ concn. A. G. Pollard.

Existence of several sugars in the serum of human milk. M. Polonovski and A. Lespagnol (Compt. rend. Soc. Biol., 1930, **104**, 555—557; Chem. Zentr., 1931, ii, 1712).—The mother-liquors from the MeOH crystallisation of gynolactose afford a very slightly dextrorotatory sugar; it is hygroscopic, of reducing power similar to that of lactose, fairly stable towards AcOH, and on hydrolysis with strong acids affords galactose as one of the products. A. A. Eldridge.

Isolation of [a new] sugar from human milk. M. Polonovski and A. Lespagnol (Compt. rend. Soc. Biol., 1930, **104**, 557—558; Chem. Zentr., 1931, ii, 1712—1713).—The fresh milk is treated with 8 vols. of EtOH and kept for several hr.; it is evaporated to half its original vol. under reduced pressure, extracted with Et_2O and light petroleum, and evaporated to dryness. The residue is extracted with boiling MeOH until it contains pure lactose; on evaporation the extract deposits first lactose, then chiefly gynolactose, which is recrystallised from MeOH and EtOH. The MeOH solution, free from gynolactose, is treated with abs. EtOH, when a slightly dextrorotatory sugar is pptd. It is purified by further treatment with MeOH and abs. EtOH. A. A. Eldridge.

Glucosuria and maltosuria. E. Herzfeld (Biochem. Z., 1932, **245**, 71—75).—Sugar-free urines gave negative Nylander and osazone tests. Frequently, especially in cases previously showing glycosuria, the Nylander test was negative, but the osazone test positive, both glucose and conjugated glycuronic acid being present. In some cases the Nylander test was faintly positive, but the sugar val. by polarimeter and osazone tests was negative, the presence of conjugated glycuronic acid being then readily detectable. In more than 50 of 800 urines (chiefly from diabetes) the simultaneous presence of maltose as well as of glucose was shown by the osazone test. P. W. Clutterbuck.

Carbohydrate content of normal urine and its relationship to nutrition. B. Lustig and L. Landau (Biochem. Z., 1932, **245**, 174—181).—The carbohydrate content of the normal 24-hr. urine is 1·38—2·53 g. and the amount of dextrins 34—183 mg. Administration of glucose, sucrose, dextrin, or potato starch did not affect the amount of total or EtOH-precipitable carbohydrate of the subsequent 4-hr. urine and the protein–sugar content was also unchanged. After administration of flesh, only a small increase of total and a considerable increase of EtOH-precipitable carbohydrates were obtained. By administration of liver, considerable increase in total and EtOH-precipitable carbohydrate was obtained. After 24 hr. fasting, the total carbohydrate excretion is halved, but the EtOH-precipitable fraction is unchanged. P. W. Clutterbuck.

Determination of oxyproteic acid in urine. S. Horiguchi (J. Biochem. Japan, 1931, **14**, 257—263).—Urine (250 c.c.) is freed from inorg. SO_4'', PO_4''', etc. by addition of $Ba(OH)_2$, conc., and treated with 20 vols. of abs. EtOH. The EtOH-insol. Ba salts are dissolved in H_2O, and Ba is removed by excess of H_2SO_4. Free SO_4'' is determined in the filtrate by the benzidine method and total S by oxidation with $Cu(NO_3)_2$ followed by a second SO_4'' determination. The difference gives oxyproteic acid-S, the human excretion of which averages 150 mg. per day. F. O. Howitt.

Excretion of neutral sulphur and oxyproteic acid in urine. S. Horiguchi (J. Biochem. Japan, 1931, **14**, 265—278).—The amounts of neutral- and oxyproteic acid-S in urine which normally show only a small variation are increased in hyperthyroidism, by ingestion of large amounts of protein, and by strenuous exercise. F. O. Howitt.

Allantoin content of urines of pregnancy and the new-born and of amniotic fluid. K. Ro (J. Biochem. Japan, 1932, **14**, 413—417).—In no instance could allantoin be detected. F. O. Howitt.

Determination of uric acid in urine. J. Renaudin (J. Pharm. Chim., 1932, [viii], 15, 109—112).—The method is a modification of that of Ronchèse. A. Lawson.

Determination of uric acid in human urine. A. A. Christman and S. Ravwitch (J. Biol Chem., 1932, 95, 115—126).—The method of Benedict and Franke (A., 1922, ii, 669) frequently leads to erroneous results depending on the vol. of urine used. One source of such errors is the presence of NH_2-acids, the effect of which is minimised by replacement of the 5% NaCN solution by one of 5% NaCN, 10% Na_2CO_3, and 15% urea. A preliminary pptn. of the uric acid by the ammoniacal Ag–Mg reagent (A., 1915, ii, 602) prior to its colorimetric determination is recommended when greater accuracy is desired. F. O. Howitt.

Antigenic properties and group specificity of human urine. Y. Tokunoyama (Tohoku J. Exp. Med., 1931, 17, 293—305).—The EtOH-sol. fraction of human urine is antigenic for rabbits if mixed with a foreign protein (pig serum) before injection. It contains Forsmann antigen, a species-sp. and a group-sp. lipoid antigen. Chemical Abstracts.

Chicken urine. E. J. Coulson and J. S. Hughes (Poultry Sci., 1930, 10, 53—58).—The N distribution is tabulated. Chemical Abstracts.

Micro-determination of carbon by Nicloux' method. B. Braier (Rev. Centr. Estud. Farm. Bioquim., 1931, 20, 149—161; Chem. Zentr., 1931, ii, 1171).—Nicloux' method is suitable for determining C in urine. L. S. Theobald.

Detection of porphyrin in urine. H. T. Schreus and C. Carrié (Klin. Woch., 1931, 10, 1017—1019; Chem. Zentr., 1931, ii, 2362—2363).—Schumm's method for the detection of coproporphyrin in urine is rejected. L. S. Theobald.

Pigment present in the sweat and urine of certain sheep. Isolation, properties, and relationship to bilirubin and the metabolism of hæmoglobin. C. Rimington and A. M. Stewart (Proc. Roy. Soc., 1932, B, 110, 75—91).—From the wool of sheep exhibiting a golden colour a pigment *lanaurin*, $C_{33}H_{36}O_{10}N_4$, has been isolated from the H_2O-sol. suint after removal of the Et_2O-sol. material. This compound resembles bilirubin and is presumably derived from hæmoglobin. It has also been isolated from the urine of a sheep showing golden coloration of the wool, together with two other pigments, one sol. in $CHCl_3$ and the other insol. in $CHCl_3$ and sol. in EtOH, both of which resemble bilirubin more closely than does lanaurin. The excretion of yellow pigment by the sudoriferous gland of sheep has considerable resemblance to familial acholuric jaundice in man. W. O. Kermack.

Effect of uni- and bi-lateral adrenalectomy on blood constituents of rabbits. M. Ohguri (Tohoku J. Exp. Med., 1931, 17, 378—389).—Bilateral adrenalectomy did not affect the blood-total N, -protein-N, -creatine (preformed or total), -uric acid, -inorg. P, -sugar, -hæmoglobin, or -Cl. Chemical Abstracts.

Effect of removal of adrenals and accessory cortical tissues together on blood constituents of rabbits. M. Ohguri (Tohoku J. Exp. Med., 1931, 17, 390—411).—Complete removal of the cortico-adrenal system increases the preformed and total, non-protein-, urea-, and uric acid-N of the blood. The Cl is decreased and the serum-inorg. P increased. Chemical Abstracts.

Allergic skin-test substance. F. S. Smyth and K. Bain (J. Allergy, 1931, 2, 177—180).—On treatment of the serum with saturated $(NH_4)_2SO_4$ the essential antibody fraction is pptd. with the globulins and is associated with the pseudoglobulin. Non-essential lipoid substances may be eliminated by prolonged storage of the serum before treatment with $(NH_4)_2SO_4$. Chemical Abstracts.

Alveolar carbon dioxide tension, alveolar carbon dioxide index in voluntary apnœa, and vital capacity in pulmonary emphysema and bronchial asthma. S. Manca (Arch. Farm. sperim., 1931, 53, 141—165).—The alveolar CO_2 tension is normal in both conditions. The alveolar CO_2 index is elevated in pulmonary emphysema proportionally to the extent of the lesions and is of diagnostic val. Vital capacity is reduced considerably in emphysema and slightly in bronchial asthma. R. K. Callow.

Decomposition of the lecithins of rice and its connexion with beriberi. S. Belfanti (Arch. Ital. Biol., 1931, 85, 190—207; Chem. Zentr., 1931, ii, 2029).—Feeding with polished rice is associated with lack of enzymes, which is considered to be important in connexion with the onset of avitaminosis. Particularly noteworthy is the lack of phosphatase, which decomposes toxic lysocithins. A. A. Eldridge.

Calculus of the tonsil. J. Chabaud and R. Lecoq (J. Pharm. Chim., 1932, [viii], 15, 228—230).—The occurrence of a calculus (0·585 g.) composed of Ca phosphate is described. H. W. Dudley.

Colloidal phenomena in gall-stones. H. B. Weiser and G. R. Gray (J. Physical Chem., 1932, 36, 286—299).—Rhythmic rings of Ca–bile pigment and of Ag_2CrO_4 were obtained in a mass of cholesterol crystals pptd. in the presence of a small amount of a hydrophilic colloid such as gelatin, albumin, or fibrin. The concentric rings in gall-stones are a manifestation of the Liesegang phenomenon. Concentric bands are not formed in either natural or synthetic cholesterol stones in the absence of hydrophilic colloids. F. Saunders (*c*).

Recent biochemical research in cancer with special reference to the metabolism of the normal and malignant cell. E. C. Dodds (Amer. J. Cancer, 1931, 15, 2765—2779).—Derangement of metabolism of malignant tissues is shown by high glycolysis and defect in respiration; the latter is possibly more sp. than the former. The defect lies almost entirely in the carbohydrate metabolism; probably the breaking up of the triose is at fault. Definite growth-promoting substances similar to those obtained from the anterior pituitary lobe are often present in the urine in cancer. Chemical Abstracts.

Intracellular hydrogen-ion concentration studies. V. Colorimetric p_H of malignant cells in tissue culture. R. Chambers and R. J. Lud-

FORD (Proc. Roy. Soc., 1932, **B**, **110**, 120—124).—The cytoplasm of various tumour cells grown in tissue culture has p_H 6·4—7·0, whilst the nucleus has $p_H > 7·2$. Injury of the cell accompanied by cytolysis results in the cytoplasm becoming more acid and developing a $p_H < 5·6$, whilst the nucleus retains a $p_H > 7·2$.

W. O. Kermack.

Lipin content of human serum in cancerous and cancer-free subjects. G. de Voss (Z. physiol. Chem., 1932, **205**, 20—24).—The phospholipin, total cholesterol, and cholesteryl ester showed average vals. of 150·5, 152·2, and 75·7 mg., respectively, per 100 c.c. for cancerous and 178·7, 169·3, and 92·1 mg. for cancer-free subjects. Only 5 of the latter were healthy; these showed higher lipin vals. than the diseased cancer-free subjects. In cases of cancer of liver and pancreas higher vals. for phospholipin and total cholesterol were observed.

J. H. Birkinshaw.

Fermentation-accelerating action of tumour extracts and its relationship with Rosenthal's activator. G. Boström (Biochem. Z., 1932, **245**, 85—101).—Rat's tumour extracts increase the anaërobic lactic acid fermentation of the liver of fed rats by 400% (827—124%). In starving rats the action is small. Perfusion with physiological saline for 30—60 min. before the experiment decreases the fermenting power by 35%, a fermentation activator being probably removed by washing. 48 hr. after subcutaneous injection of tumour extract, the liver respiration is greatly decreased and the anaërobic and aërobic lactic acid acid fermentation increased.

P. W. Clutterbuck.

Micro-determination of nitrogen. Its application in the diagnosis of cancer. H. J. Fuchs and M. von Falkenhausen (Biochem. Z., 1932, **245**, 304—313).—An apparatus and colorimetric method for the micro-determination of N are described.

W. McCartney.

Content and activation of urinary diastase in cancer and other diseases. E. Fränkel, P. Geréb, and R. Simke (Biochem. Z., 1932, **245**, 44—51).—Although there are no characteristic differences in the diastase of the urine in these diseases, it was found that the latter frequently contained a substance which activated diastase. The activator is inactivated above 45°, is active between p_H 4·0 and 7·5, is adsorbed by kaolin, but is not eluted therefrom by phosphate. P. W. Clutterbuck.

Enzymes of chicken sarcoma. E. Somekawa (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, **18**, 23—36).—An aq. extract of Rous sarcoma showed slightly greater and more varied enzyme activity than did a muscle extract. A. Cohen.

Proteins of human serum. Distribution of protein in normal and pathological sera. Diagnosis of tuberculosis and cancer. A. Schmitz and F. Wulkov (Biochem. Z., 1932, **245**, 408—417).—For the separation of globulins from albumins in serum-proteins pptn. with $(NH_4)_2SO_4$ may be used, but for further fractionation other methods must be applied. The procedure of Goldschmidt and Kahn (A., 1929, 951) gives unsatisfactory results. If dil. solutions of serum (1 c.c.) are added to series of $(NH_4)_2SO_4$ solutions (saturation ranging from 5 to 100%) and the degrees of turbidity produced (measured with a step photometer) are plotted against the concn. of $(NH_4)_2SO_4$ which causes them, curves termed "protein spectra" are obtained. In these curves one portion represents the globulins and another the albumins. Sera from healthy persons always gives the same type of curve and hence always contains the same type of protein mol. and neither consumption of large amounts of fat nor addition of Na glycocholate to the serum has any effect on the "spectra." In pathological sera of all kinds variations, from which no conclusions can be reached, appear in the globulin portions of the curves. The albumin portions, however, are always similar except in tuberculosis and cancer (and also, to some extent, in cirrhosis of the liver). This finding applied to the diagnosis of the two first-named diseases yielded correct results in 96% of the cases examined.

W. McCartney.

Catabolism of fats directly introduced into the animal body. Basal metabolism of pancreas-diabetic animals following the infusion of fat. T. Baba (Tohoku J. Exp. Med., 1931, **17**, 274—292).—Intravenous injection of a fat emulsion into diabetic dogs causes the R.Q. to fall below 0·707. With animals in which the pancreas had been incompletely resected the R.Q. fell to a val. above 0·707.

Chemical Abstracts.

Distribution of phosphorus compounds and calcium in the blood of children. M. Sokolovitch (Arch. Dis. Childhood, 1931, **6**, 183—208).—The blood-P of children tends to be higher and to show greater variation than that of adults. Changes in the partition of P are found in nephritis, diabetes mellitus, and infantile tetany, but the total P content is not increased. The serum-Ca of children is normal in diabetes and slightly increased in nephritis.

Chemical Abstracts.

Clinical calorimetry. XLVIII. Nitrogen equilibrium with a low-protein diet. W. S. McLellan and R. R. Hannon (J. Biol. Chem., 1932, **95**, 327—333).—A patient with diabetus mellitus was fed on a diet containing 20 g. of protein per day, and having an energy val. of 50% above the basal heat output. N equilibrium was established during the last month of the period of observation (106 days), and wt. equilibrium during the whole period without any ill effects from the low protein level of the diet. A decrease in the carbohydrate content of the diet produced excretion of ketonic substances, but no increase in body-protein metabolism. A low record of 1·78 g. of N per day excreted in the urine was reached. A. Lawson.

Toxic fraction in certain eczema sera. F. S. Smyth (J. Allergy, 1931, **2**, 173—176).—Toxicity is not due to allergens or to alteration of the colloidal properties by heat or cold; the effect resembles that of the "histamine-like" substance described by Lewis and Harmer. Chemical Abstracts.

Essential fatty acids and goitre-producing substances. F. E. Chidester (Science, 1932, **75**, 106).—A discussion in which the importance of the I–fat balance is emphasised. L. S. Theobald.

Iodine question in Lettland in relation to goitre. J. Kupzis (Z. Hyg., 1932, 113, 551—573).—The I content of inland soils is largely dependent on the ease of leaching and on the fertilisers (notably animal manures) used. The prevalence of goitre is in no way associated with the amounts of Ca, Mg, Fe, or org. matter present in drinking-H_2O.
A. G. Pollard.

Range of effective iodine dosage in exophthalmic goitre. IV. Effect on basal metabolism of daily dose of about 0·75 mg. W. O. Thompson, P. K. Thompson, and A. C. Cohen (Arch. Int. Med., 1932, 49, 199—214).—The percentage approach of basal metabolism to the normal in cases of exophthalmic goitre is proportional to the dose of I and to the amount of I in the thyroid available for the storage of colloid, between the limits of dosage 0·75—6 mg. A certain min. daily dose of I produces a max. effect. H. Davson.

Thiocyanate therapy in hypertension. I. Its toxic effects. W. Goldring and H. Chasis (Arch. Int. Med., 1932, 49, 321—329).—Toxic manifestations occur independently of the amount of drug administered, there being, in some cases, no margin of safety between the toxic and therapeutic doses.
H. Davson.

Effect of insulin therapy on pancreatic enzymes in malnutrition. C. W. Lueders and M. E. Watson (Arch. Int. Med., 1932, 49, 330—342).—Analysis of the pancreatic secretions and the bile salts, together with studies of the stool, before and after doses of 40 units of insulin showed an increase in pancreatic enzymes, improvement in the function of the biliary tract, and a more complete digestion and assimilation of food following the dose. H. Davson.

Calcium and phosphorus metabolism in nephritis. F. J. Ford (Arch. Dis. Childhood, 1931, 6, 209—230).—Retention of Ca and P is approx. normal; excretion tends to be diverted from the urine to the fæces. Chemical Abstracts.

Plasma-proteins and œdema in children presenting nephrotic syndrome. J. K. Calvin and A. H. Goldberg (Amer. J. Dis. Children, 1931, 42, 314—327).—A marked decrease in serum-albumin is usually associated with the œdema of the nephrotic syndrome. The globulin content is only slightly decreased, or may be increased sufficiently to reverse the albumin : globulin ratio.
Chemical Abstracts.

Iron-deficiency hypothesis in pellagra. S. Bliss (Science, 1932, 75, 266).—Critical (cf. Halliday, *ibid.*, 1931, 74, 1931). L. S. Theobald.

Relationship between calcium and potassium balance and rheumatism agents. I. Relationship between uric acid content and calcium and potassium in serum by the use of narcotics. K. In (Folia Pharmacol. Japon., 1931, 12, No. 3, 406—416).—Hypnotics, but not morphine, disturb the ionic balance in rheumatic tissue; the serum-Ca is decreased (often increased by morphine) and the -K increased. Chemical Abstracts.

Experimental scurvy. XI. Glutathione content of tissues of guinea-pigs fed on vitamin-*C*-free diet. R. Sato and S. Ohato (J. Biochem. Japan, 1931, 14, 325—329).—Slight increases occur in the suprarenals and skeletal muscle, but no change is detectable in the liver, kidneys, lungs, heart, spleen, and testicles. F. O. Howitt.

Scurvy and the potassium and sodium content of the urine and the blood. L. Randoin and A. Michaux (Compt. rend., 1932, 194, 565—567).—During the course of scurvy in guinea-pigs fed on a diet containing 1% NaCl, the vol. of urine diminishes very greatly, the Na and K content decreasing proportionately. The Na content of the blood-serum and total blood increases slightly. The K content of the serum diminishes, but, unlike that of the controls, is greater than that of the total blood, this being due to a decrease in the no. of red blood-cells caused by the scurvy. A. Lawson.

Sodium and potassium content of muscles during the development of scurvy. L. Randoin and A. Michaux (Compt. rend., 1932, 194, 647—650).—In guinea-pigs on a diet containing no vitamin-*C*, the content of Na in the muscles increases whilst that of K decreases as scurvy develops. From previous work on the retention of Cl′ (A., 1931, 383), it is concluded that the Na is retained as NaCl.
A. Lawson.

Compound of taurocholic acid with guaiacol. D. Ganassini (Arch. Ist. Biochim. Ital., 1932, 4, 3—8).—*Guaiacol taurocholate*, $OMe\cdot C_6H_4\cdot C_{26}H_{44}O_7NS$, m. p. 110°, is tolerated by the human organism, has no irritant effect on the stomach or kidneys, and appears to be of val. in treating chronic tubercular empyema of the lungs. T. H. Pope.

Embryonic metabolism. VI. The amino-acids of the yolk, white, embryo, and shell membranes during development of the hen's egg. H. O. Calvery (J. Biol. Chem., 1932, 95, 297—300).—In the developing egg, tyrosine decreases, whilst tryptophan and cystine increase in the embryo, but all three remain const. in the white, yolk, and shell membrane. Arginine and lysine remain const., whilst histidine decreases in all fractions except the shell membrane, which is unaffected by the development of the embryo. A. Lawson.

Survival of embryonic tissues of the hen in Ringer's solution at low temperatures. L. Bucciante (Atti R. Accad. Lincei, 1931, [vi], 14, 356—361).—The survival at 5—10° varies with the different tissues. There is a progressive removal of trophic substances, which diffuse from the cells into the liquid. The addition of embryo juice is almost indispensable for the culture of the washed tissues in Ringer's solution; in a culture medium resulting from plasma alone, the tissues grow either not at all or only to a slight extent. T. H. Pope.

True metabolic rate of the chick embryo and the respiration of its membranes. J. Needham (Proc. Roy. Soc., 1932, B, 110, 46—74).—The yolk-sac of the hen's egg steadily absorbs 320 cu. mm. O_2 per g. per hr. from the 3rd to the 15th day of development and then the rate of respiration decreases, reaching about 60% of the above val. at the time of hatching. The respiration rate of the allantois rises from 100 cu. mm. O_2 per g. per hr. on the 6th day to a max. of 390 cu. mm. on the 13th day, and then falls to about 250 at the time of hatching. The respiratory rate of the embryo as calculated by subtracting the O_2 consumption of the extra-embryonic membranes from that of the intact egg falls from 1200 cu. mm. O_2 per g. per hr. on the 6th day to 800 cu. mm. on the 19th, the max. rate occurring before the 6th and probably on the 5th day. W. O. Kermack.

Influence of chemical composition on tissue respiration. T. Doxiades (Biochem. Z., 1932, **245**, 52—60).—The O_2 utilisation, CO_2 production, R.Q., and the protein, fat, and carbohydrate contents of slices of rat's liver are determined. The O_2 consumption increases with increasing protein and decreasing fat content of the tissues. P. W. Clutterbuck.

Effect of amino-acids on respiration of tissues. IV. Serine, valine, sarcosine, *iso*leucine, and phenylglycine. B. Kisch (Biochem. Z., 1932, **244**, 451—458; cf. this vol., 82).—With regard to their effect on the respiration of the liver and kidney tissue, serine, valine, sarcosine, and phenylglycine resemble the NH_2-acids previously examined and *iso*leucine resembles leucine, but is somewhat less active. The effect of the acids is greater on old than on fresh tissue; the difference between the two kinds of tissue is slight. The [H$^{\cdot}$] of the nutrient medium has the same effect as with the acids first examined. W. McCartney.

Effect of amino-acids on respiration of retinal tissue. B. Kisch (Biochem. Z., 1932, **244**, 459—463).—The respiration of fresh retina (pig, ox, dog, and other species) is increased, in some cases very greatly, by glycine, phenylglycine, valine, leucine, serine, sarcosine, alanine, and phenylalanine and in the case of the old tissue the increase is greater. Retinal tissue differs from kidney tissue in that with the former the effects of alanine and phenylalanine are less, those of serine, valine, and sarcosine more, pronounced than with the latter. W. McCartney.

Salinity of the medium and its effect on respiration in the sea anemone. C. S. Shoup (Ecology, 1932, **13**, 81—85).—Variations in the salt concn. of the medium on either side of the normal concn. of sea-water decrease respiration in *Metridium marginatum*. In single-salt media, Na, Ca, and K salts have a pronounced effect. A. G. Pollard.

Emission of oxygen by the pelvic filaments of the male *Lepidosiren* with some experiments on *Symbranchus marmoratus*. J. T. Cunningham and D. M. Reid (Proc. Roy. Soc., 1932, B, **110**, 234—248).—When *Lepidosiren* is placed in H_2O with a very low content of dissolved O_2, the dissolved O_2 (determined by Winkler's method) decreases if the specimen is a female or a male with undeveloped pelvic filaments, but definitely increases in the case of a male with well-developed filaments. The decrease is probably due in part at least to the mucus introduced with the fish. The results indicate that the developed pelvic filaments of the male *Lepidosiren* excrete O_2 into the H_2O probably to oxygenate the fertilised eggs. W. O. Kermack.

Nature of metabolic regulation of body temperature and its relation to temperature sensations. J. M. O'Connor (Proc. Roy. Irish Acad., 1932, **40B**, 175—193).—In non-shivering rabbits under urethane anæsthesia O_2 consumption is correlated with rectal temp. Statistical analysis of data shows that the extra O_2 consumption during shivering is independent of head temp. but is max. at a skin temp. of 28°, falling to zero at 35° and at 23°. Cold sensation in the human forearm is abolished at about 21°. Hence chemical temp. regulation is probably a reflex response to cold stimuli from the skin. J. B. Bateman.

Metabolism of cold-blooded animals. D. Goulston (J. Proc. Roy. Soc. New South Wales, 1931, **65**, 51—58).—Measurements on the O_2 absorption and CO_2 expiration of a resting frog show that its metabolic rate falls continuously during starvation. N. H. Hartshorne.

Basal metabolism of Australian merino sheep. E. W. Lines and A. W. Peirce (Bull. Counc. Sci. Ind. Res. Austral., 1931, No. 55, 34 pp.).—The effects of different diets and the duration of fasting on the R.Q. and basal metabolism of ewes are studied. The conditions for standard basal metabolism determinations are defined. A relation between body-wt. and skin-area is obtained. H. Davson.

Fasting metabolism of cattle. E. B. Forbes, W. W. Braman, M. Kriss, and R. W. Swift (J. Agric. Res., 1931, **43**, 1003—1014).—Conditions for the determination of standard basal metabolism are defined. No const. val. is obtained with two steers fasting for 6 days. H. Davson.

Basal metabolism. I. Error of basal metabolism determination and normal range of basal metabolism. II. Basal pulse complex. R. L. Jenkins (Arch. Int. Med., 1932, **49**, 181—187, 188—198).

Carbon dioxide dissociation curve of living mammalian muscle. L. Irving, H. C. Foster, and J. K. W. Ferguson (J. Biol. Chem., 1932, **95**, 95—113).—The CO_2 content and tension (the latter assumed equal to the CO_2 tension of the venous blood leaving the muscle) of the gastrocnemius muscles of the dog were determined for normal and over-ventilation and for ventilation with a CO_2-rich mixture after removal of the first muscle. The CO_2 dissociation curve is expressed by the equation CO_2 (c.c. per 100 g.)= $3{\cdot}4\sqrt{pCO_2}$, where pCO_2 is the tension in mm. of Hg. This curve is used for the construction of a combining-power curve, the solubility coeff. being assumed to be 0·41. Also, accepting the pK'_1 val. as equal to that of serum, *i.e.*, 6·07 (A., 1928, 150), and applying the Henderson–Hasselbalch equation, the reaction of the resting muscle is p_H 6·9—7·0 for CO_2 tensions of 50—60 mm., whilst the buffering power is determined and resolved into its components. F. O. Howitt.

The coupled nature of lactic acid glycogen synthesis in muscle. D. Burk (J. Physical Chem., 1932, **36**, 268—272).—The theory (cf. Bancroft and Bancroft, A., 1931, 513) that glycogen may be synthesised in muscle from lactic acid according to a freely reversible shift in the equilibrium point (caused by adsorption of glycogen on protein) is quantitatively inconsistent. C. T. Snell (*b*).

Amount of lactic and other ether-soluble acids in blood and organs at rest, after muscular work, and when supplied with reduced amounts of oxygen. S. L. Ørskov (Biochem. Z., 1932, **245**, 239—251; cf. A., 1930, 801).—The method for the determination of lactic and other Et_2O-sol. acids in blood can also be applied to tissues (liver, kidney, muscle). The lactic acid content of organs increases during extirpation. The blood, liver, and kidneys of cats and rabbits contain approx. equal amounts of lactic acid, but there is much more of it in the muscles, possibly because production takes place during extirpation. Muscular work results in increase, in organs and in blood, of both lactic and the other acids. The latter disappear from the blood sometimes more, sometimes less, quickly than does lactic acid. In frog muscle also muscular work leads to increase in the amount of the other acids, although this increase is not so great as it is with rabbits. Increase in the amount of the other acids also results from lack of O_2 and in dead organs to which O_2 is not supplied considerable increase takes place. The nature of the acids resulting from muscular work and O_2 lack is not known but they contain neither P nor N. W. McCartney.

Nervous control of carbohydrate metabolism. I. Position of the centre. II. Chemical changes set up in the body during decerebration hyperglycæmia. III. Nature of the mechanism of the nerve control. C. Donhoffer and J. J. R. Macleod (Proc. Roy. Soc., 1932, **B**, **110**, 125—141, 141—157, 158—171).—I. Decerebration of well-fed rabbits during the short period of anæsthesia induced by the intravenous injection of "amytal" almost always causes marked hyperglycæmia within 2 hr., provided that decerebration is effected in the neighbourhood of the pons. It follows that the centre regulating carbohydrate metabolism is situated in or near the pons. While the animals are under "luminal" or "amytal" anæsthesia, puncture of the floor of the fourth ventricle does not affect the blood-sugar level, nor does mechanical asphyxia or Et_2O, whilst injection of adrenaline causes hyperglycæmia.

II. Decerebration in the neighbourhood of the pons besides causing hyperglycæmia increases the blood-lactic acid, decreases the glycogen in the liver if this is initially above about 0·7%, but otherwise usually increases it, and decreases the percentage of glycogen in the leg muscles. Decerebration not at the level of the pons produces only insignificant changes in these factors, except that decerebration at the medulla oblongata usually brings about an increase in muscle-glycogen. The degree of hyperglycæmia is not correlated with the initial concn. of glycogen in the liver and muscles. When the latter is low, the amount of glucose which must be injected into a normal rabbit to raise its blood-sugar to an extent equal to that observed after decerebration through the pons much exceeds that which can be accounted for by the changes in the liver- and muscle-glycogen. When the liver- and muscle-glycogen is initially high most of the increase in the blood-glucose may be accounted for by changes in these. The blood-non-protein-N, the O_2 consumption, and the R.Q. are not definitely altered after decerebration through the pons, although in one experiment a pronounced increase in O_2 consumption took place. Injection of glucose into rabbits decerebrated at the pons does not prevent the disappearance of muscle-glycogen, but may retard the fall in liver-glycogen or bring about an increase.

III. In rabbits containing relatively little liver- and muscle-glycogen, hyperglycæmia following decerebration through the pons is prevented by double adrenalectomy, atropine and section of both vagi, ergotamine and section of both vagi, or amytal. In well-fed animals containing more liver- and muscle-glycogen, hyperglycæmia does occur under these conditions, but it is usually not so pronounced as with simple decerebration. With little glycogen in the liver, hyperglycæmia following decerebration is probably due to stimulation of gluconeogenesis in the liver through the parasympathetic nerves.

W. O. Kermack.

Utilisation of lactose in the rat and the pig. E. A. Fisher (New Zealand J. Sci. Tech., 1931, **13**, 96—103).—The scouring effect of whey is due mainly to the lactic acid. An inverse relationship exists between the live wt. increase of rats and the amount of lactic acid in the diet in excess of that supplying approx. 25% of the calories. With rats, as with pigs, this is accompanied by considerable excretion of reducing sugar in the urine. W. G. Eggleton.

Effect of yeast on liver-glycogen with various diets. H. Aida (Biochem. Z., 1932, **244**, 431—434; cf. A., 1931, 1184).—In rats administration of yeast results in increase in the amount of glycogen in the liver only if a certain min. of sugar is added to the basal diet. W. McCartney.

Influence of yeast on protein metabolism in normal and depancreatised dogs. E. S. Nasset, H. B. Pierce, and J. R. Murlin (J. Lab. Clin. Med., 1931, **16**, 1151—1168).—N-retention is increased when yeast is included in the diet. Ingestion of yeast tends to reduce the D : N ratio of depancreatised dogs. Chemical Abstracts.

Supplementary feeding of carbohydrates to suckling calves in relation to the utilisation of milk-protein. N. Remer (Bied. Zentr., 1932, **B**, **3**, 463—506).—Calves from a few days old were reared satisfactorily on whole milk supplemented with dried potatoes and distillery malt. The proportion of milk was decreased with increasing age. The % utilisation of milk-protein was slightly reduced by potato feeding. A. G. Pollard.

Growth and reproduction on milk diets. J. Waddell, H. Steenbock, E. B. Hart, and E. Van Donk (J. Nutrition, 1931, **4**, 53—65).—On a diet of whole milk and Cu chronic anæmia, due to low Fe intake, occurred. Growth and reproduction were subnormal. On a diet of whole milk, Cu, and Fe no anæmia was observed, but growth and reproduction were still subnormal, possibly owing to low calorific val. Small quantities of Mn and/or I improve the ovulation rhythm in rats on milk, Cu, and Fe diets.

Chemical Abstracts.

Replacement of food protein by ammonium hydrogen carbonate in the feeding of cows. P.

Ehrenberg, E. Ungerer, and H. Klose (Biochem. Z., 1932, 245, 118—145).—In experiments of short duration with cows, the food protein can be replaced considerably or totally by acid slices of beet which have been soaked in NH_4HCO_3. It appears probable that the NH_4-N is utilised in milk formation.

P. W. Clutterbuck.

Intermediate protein metabolism. III. Experiments on dogs with liver injuries and Eck's fistula. F. Silberstein, L. Tuchman, and A. Glaser (Biochem. Z., 1932, 245, 102—117).—The effect of various liver injuries (poisoning with P, tolylenediamine, CCl_4, ligature of the bile duct, and Eck's fistula) on the metabolism of dogs receiving peptone is investigated. In P and tolylenediamine poisoning, the abs. and relative amounts of urea formed are never less and usually greater than in normal animals. With CCl_4 the urea formation is not decreased but the curves are complicated, due to injury of the kidneys. Ligature of the bile duct and Eck's fistula do not affect urea formation.

P. W. Clutterbuck.

Factors which determine renal weight. IX. Endogenous protein metabolism. E. M. MacKay and J. R. Cockrill. **X. Effect of feeding desiccated thyroid.** E. M. MacKay and L. L. MacKay (J. Nutrition, 1931, 4, 25—32, 33—37).—IX. The kidney wts. of male albino rats which received a diet devoid of protein were almost directly proportional to the endogenous protein metabolism as measured by urinary N excretion.

X. Administration of a diet containing 0·4% of desiccated thyroid causes an increase in kidney wt. greater than could be accounted for by the increase in protein intake incidental to the increased food consumption.

Chemical Abstracts.

Cysteine and taurine as substituents for cystine in nutrition. H. H. Mitchell (J. Nutrition, 1931, 4, 95—104).—Cysteine, but not taurine, when added to a rat diet deficient in cystine, improved the growth-promoting val. Conversion of cysteine into cystine probably occurs within the body rather than in the intestinal tract where reducing conditions are present.

Chemical Abstracts.

Physiology of creatinine and creatine. Excretion of creatinine and creatine. I. At the minimum nitrogen level of metabolism and during fasting. II. During the course of benzoic acid, phloridzin, and phosphorus poisoning. E. F. Terroine, R. Bonnet, P. Danmanville, and G. Monrot. **III. During exogenous nitrogen metabolism.** E. F. Terroine and P. Danmanville (Bull. Soc. Chim. biol., 1932, 14, 12—46, 47—67, 68—84).—I. In young pigs, brought to the min. N level of endogenous metabolism by a carbohydrate diet, the weekly excretion of creatinine remains const., whilst that of creatine varies considerably, becoming less as the min. N level is maintained. The ratio creatine-N/total N for the urine varies for different animals of the same species, but is always greater than that for muscle. The substitution of fasting for the carbohydrate diet causes a large increase in creatine excretion corresponding with the increase in total N excreted.

II. Administration of BzOH and phloridzin to young pigs brought to the min. N level of metabolism results in considerable increase of creatine excretion, the creatinine excretion remaining const. Rabbits under similar conditions give parallel results on administration of P. Creatine, therefore, appears to be formed independently of the creatinine–creatine balance.

III. Young pigs fed on various complete diets excrete quantities of creatine which vary inversely with the amount of retained N of the diet. The excretion of creatinine remains nearly const.

A. Lawson.

Origin of creatine. Treatment of progressive muscular atrophy with glycine. K. Thomas, A. T. Milhorat, and F. Teichner (Z. physiol. Chem., 1932, 205, 93—98).—Administration of glycine increases the excretion of creatine in creatinuric patients. In some cases after continued administration the creatine in the urine decreases, and creatinine appears, accompanied by an improvement in the patients' condition. Glycine produced no effect in muscular atrophy.

J. H. Birkinshaw.

Effect of muscular work on the creatine and creatinine content of normal human blood. K. Kácl (Biochem. Z., 1932, 245, 452—458).—In man muscular exercise leads to great increases in the total creatinine and creatine content of the blood and to very slight increase in the content of preformed creatinine. The contents revert to normal (occasionally to slightly below normal) after 3 hrs.' rest; after 1 hr. they are still somewhat above normal. The increases are not proportional to the extent of the exercise taken. In athletic persons the effect of the exercise is less than it is in others.

W. McCartney.

Urea formation in the animal body. IV. A. 2. Urea formation in surviving organs and in their press-juice. S. Salaskin, L. Soloviev, and D. Tiukov (Z. physiol. Chem., 1932, 205, 1—10; cf. A., 1931, 869).—In autolysis of placenta the urea increases, the optimum p_H for its production being 5·64—6·20. Addition of physiological saline and of an AcOH mixture increases urea formation, but autolysis probably does not increase the uric acid. Urea, NH_2-acids, and residual N increase independently. The total urea in placental as in liver autolysis is due to the arginine–arginase system. The arginine content of the protein of fresh placenta is about 7%, about 20% of which is converted into urea on autolysis. Arginase added towards the end of autolysis increases the urea somewhat, but less than the addition of arginine.

J. H. Birkinshaw.

Purine metabolism. P. Rondoni (Arch. Ital. Biol., 1931, 85, 101—108; Chem. Zentr., 1931, ii, 1877).—Determinations of uric acid and allantoin in rat's urine indicate that the purine metabolism of the rat is exceptionally analogous to that of man.

A. A. Eldridge.

Post-mortal formation of ammonia in muscle. J. K. Parnas (Biochem. Z., 1932, 245, 159—165).—The post-mortal formation of NH_3 in frog's muscle kept in physiological fluids at 11—13° amounts only to 1/10—1/15 of the val. assigned by Embden (A., 1931, 1449). P. W. CLUTTERBUCK.

Plasma-lipins in lactating and non-lactating animals. P. J. SCHAIBLE (J. Biol. Chem., 1932, 95, 79—88).—The plasma contents of fatty acids, lipin-P, and neutral fat are higher in lactating than in non-lactating cows or in steers. In both lactating and non-lactating animals the fatty acids of the plasma-lecithin are less unsaturated than those of the cholesteryl esters, whilst the fatty acids of the neutral fat are intermediate. Hence the cholesteryl esters may play a part in fat transportation. The increase in lipin level during the onset of lactation is not accompanied either by a change in character of the fatty acids or by a difference in distribution.

F. O. HOWITT.

Influence of the spleen on cholesterol metabolism. E. LIVERANI (Arch. Farm. sperim., 1932, 53, 166—177).—Stimulation of the spleen provokes a rise in blood-cholesterol in the splenic vein. The spleen regulates the blood-cholesterol level.

R. K. CALLOW.

Composition of the contents of the small intestine in normal dogs after a fatty meal. H. WENDT (Biochem. Z., 1932, 245, 80—84).—The neutral fat, free fatty acid, and soap content of the upper $\frac{2}{3}$ and lower $\frac{1}{3}$ of the small intestine in dogs 3, 4, 5, and 7 hr. after a fatty meal (100 g. of olive oil) is investigated. Only a small portion (26—34%) of the total fat is in the hydrolysed condition.

P. W. CLUTTERBUCK.

Metabolism of tricaprin. M. POWELL (J. Biol. Chem., 1932, 95, 43—45).—Tricaprin fed to rats as the sole source of fat in the diet results in decoic acid forming 15% of the fatty acids of the fat depots. This confirms the view that, whilst C or lower fatty acids tend to disappear or form longer chains, C_{10} or higher acids are deposited in the fat depots unchanged (cf. A., 1929, 596, 1484; 1931, 760).

F. O. HOWITT.

Consumption of foodstuffs and the vitamin requirement of cattle from birth to the age of 2½ years. H. ISAACHSEN (Bied. Zentr., 1932, B, 3, 540—548).—Evidence is presented that in ruminants vitamin-*B* is formed in the digestive tract with the aid of bacteria. 3—4 kg. of roots per day supply sufficient vitamin-*C* for the winter feeding of cattle.

A. G. POLLARD.

Metabolisable energy and net energy values of maize meal. E. B. FORBES, W. W. BRAMAN, M. KRISS, and R. W. SWIFT (J. Agric. Res., 1931, 43, 1015—1026).—The net energy val. of maize meal is greater when fed in combination with lucerne hay that when it is fed exclusively. H. DAVSON.

Nutritive value of cereals. V. FAMIANI (Atti R. Accad. Lincei, 1931, [vi], 14, 306—309).—Growing albino rats, fed with maize and barley, grow more rapidly on small-grained seed than on large-grained, but in other respects no substantial differences are observed. T. H. POPE.

Physiological effect of rations restricted principally or solely to the lucerne plant. III. Influence of various mineral supplements on the calcium, phosphorus, and nitrogen metabolism of dairy cattle. J. R. HAAG, I. R. JONES, and P. M. BRANDT (J. Dairy Sci., 1932, 15, 23—28; cf. this vol., 299).—Use of Na_2HPO_4 as a supplement to lucerne hay resulted in a small positive P balance, and of bone meal in positive Ca and P balances. $CaCO_3$ did not affect the storage of Ca or P. N balances were variable. A. G. POLLARD.

Coefficients of digestibility of the constituents of milk, and the balance of calcium and phosphorus in calves on a milk diet. J. S. HUGHES and H. W. CAVE (J. Nutrition, 1931, 4, 163—169).—Digestion of food including roughage is not impaired by restriction to a milk diet.

CHEMICAL ABSTRACTS.

Utilisation by normal adult subjects of the calcium and phosphorus in raw milk and in ice-cream. M. M. KRAMER, M. T. POTTER, and I. GILLUM (J. Nutrition, 1931, 4, 105—114).—Seven of 10 subjects showed more favourable Ca balances when ice-cream was the chief source of Ca. Normal subjects on an acid-forming diet utilised the Ca in ice-cream made from condensed milk at least as well as that derived from raw milk. In general, P balances followed the trend of the Ca balances.

CHEMICAL ABSTRACTS.

Calcium and phosphorus metabolism. XI. W. T. SALTER, C. FULTON, and F. ANGIER (J. Nutrition, 1931, 4, 1—13).—Calculation of the potential acidity and alkalinity of diets is discussed.

CHEMICAL ABSTRACTS.

Absorption of calcium soaps and relation of dietary fat to calcium utilisation in the white rat. O. F. BOYD, C. L. CRUM, and J. F. LYMAN (J. Biol. Chem., 1932, 95, 29—41).—Ca palmitate, stearate, oleate, and their mixtures together with a fat-free diet were fed to rats and the fæces examined for Ca and fatty acids. The Ca utilisation is greatest with the oleate and least with the stearate. Addition of fat to a diet in which Ca is supplied as $CaCl_2$ results in an increased acidity of the fæces, an increased absorption of Ca and P, and decreased fæcal CO_3'' and soaps. Replacement of $CaCl_2$ by Ca lactate results in a disappearance of this effect.

F. O. HOWITT.

Effect of iodine on individuals with normal metabolism. A. LEMORT (Compt. rend. Soc. Biol., 1931, 106, 1283—1284; Chem. Zentr., 1931, ii, 1877).—Administration of Lugol's solution nearly always lowers the basal metabolism.

A. A. ELDRIDGE.

Effect of [administration of] small amounts of iodine on the metabolism of the dog. C. SALVADORI (Biochem. Z., 1932, 245, 314—344).—Administration of daily doses of 2 or 4 mg. of I to the dog (3 years old) results, always after some days, in a 20% increase in the metabolic rate. When 6 mg. are given daily for 50 days the rate alternately rises and falls, the max. increase being about 25%. Toxic effects sometimes appear when the dose is 6 mg., but not when it is 2 or 4 mg. The last-named dose has a much less pronounced and less lasting effect in the young dog. In the full-grown dog daily doses of 2 and 4 mg. of I result in retention of N.

W. MCCARTNEY.

Fluorescence intra-vital microscopy and photochemotherapy. G. Kögel (Mikrochem., 1932, 10, 450—451). H. F. Gillbe.

Local anæsthetics. K. Miescher (Helv. Chim. Acta, 1932, 25, 163—190).—The prep. and properties of "percain" are described. The essential feature of a local anæsthetic is the presence of a basic or O-containing substituent bound to high aliphatic or hydroaromatic radicals or certain negative groups including CCl_3, alkyl groups, aromatic and unsaturated heterocyclic rings. The CO group in ketonic or ester form and the α-NH_2 group are particularly favourable. Local anæsthetic effect is strengthened by introducing higher alkyl groups in the form of side-chains, by increasing the no. of aromatic or heterocyclic rings, and by introducing alkoxy-groups or basic substituents. Published work on the relation between anæsthetic effect and surface tension and on the variation of the effect with the amount of anæsthetic administered is reviewed. E. S. Hedges.

Micro-detection of soporifics. R. Fischer (Mikrochem., 1932, 10, 409—429).—A sample of urine, blood, or serum is extracted with Et_2O, and barbituric acid derivatives are separated by treating the extract with aq. NaOH. The acidified solution is then extracted with Et_2O, and the soporific is isolated by evaporation of the solution and micro-sublimation of the residue. Identification is effected by observation of the sublimation temp., m. p., and appearance of the sublimate, and by measurements with the polarising microscope. Tables for identification and chemical tests are given for 21 soporifics, together with the results of applying the method to subjects who had taken veronal, noctal, and phanodorm. Veronal has been isolated from 2 c.c. of serum from a patient to whom 4—5 g. had been administered. H. F. Gillbe.

Chronaxie. W. D. Bancroft and G. H. Richter (J. Physical Chem., 1932, 36, 215—228).—A narcotic causes the excitability of an isolated tissue to increase to a max., and then to decrease below normal. Coagulating agents (*e.g.*, salts of heavy metals) produce a similar effect. Min. excitability occurs at the isoelectric point of the protein or proteins present in the tissue. C. T. Snell (*b*).

Oxygen consumption and production of ammonia in brain tissue in presence of narcotics. M. Bülow and E. G. Holmes (Biochem. Z., 1932, 245, 459—465; cf. Loebel, A., 1926, 84).—Narcotics (mixtures of O_2 with C_2H_4, C_2H_2, $CHMe{:}CH_2$, N_2O under pressure, and also ethylurethane and Et_2O), even in concns. often much greater than those required to produce narcosis, have no effect on the O_2 absorption of tissue from rabbit-brain, although still greater concn. may have some effect. Moreover, the narcosis induced does not affect the power of the tissue to produce NH_3. In addition to free NH_3, the lipin- and protein-free filtrate from the tissue contains a substance from which NH_3 is liberated by the action of conc. alkali. W. McCartney.

Distribution of chloroform between erythrocytes and blood-serum. N. V. Lazarev and E. Nusselmann (Biochem. Z., 1932, 244, 417—425; cf. Winterstein and Hirschberg, A., 1927, 893).—*In vitro* in solutions of $CHCl_3$ in blood (pig, dog, ox, wether) the erythrocytes always contain more of the substance than does the serum. In pig's and (to a smaller extent) in dog's and ox blood, the coeff. of distribution (between erythrocytes and serum) decreases as the concn. increases. Wether's blood gives indefinite vals. Equations showing the relation between the concn. in erythrocytes and that in serum are given for pig's and ox blood. As regards the abs. magnitudes of the coeffs. (at low concn.) the bloods form the descending series: pig, dog, ox. The significance of the results for theories of narcosis is discussed. W. McCartney.

Influence of the vegetative nerve poisons on the intermediate protein metabolism. B. Ito (Folia Pharmacol. Japon., 1931, 12, No. 2, 273—303).—As observed by determination of urinary constituents, serum HIO_3 val., and blood-residual N, adrenaline, nicotine, and pilocarpine depress, choline and eserine delay, whilst atropine temporarily increases, the intermediate protein exchange. Muscarine has no action. Chemical Abstracts.

Pharmacological actions of alkyl derivatives of harmol. I. Ethylharmol. J. A. Gunn and R. St. A. Heathcote (Quart. J. Pharm., 1931, 4, 549—565).—Ethylharmol, injected subcutaneously, has a min. lethal dose of 0·15 g. per kg. for the frog and 0·2 g. per kg. for the guinea-pig. Of the various pharmacological actions described, the powerful dilatory action on the coronary vessels is noteworthy. F. O. Howitt.

Pilocarpine hyperglycæmia. T. Inouye (J. Biochem. Japan, 1931, 14, 215—255).—Pilocarpine hyperglycæmia is due to sympathetic stimulation of the adrenals. F. O. Howitt.

Effect of ergotamine on alimentary hyperglycæmia during disease of the liver produced by phosphorus poisoning. Z. Ernst and S. Karády (Biochem. Z., 1932, 245, 299—303)—Since administration of ergotamine to rabbits results in increase in the alimentary blood-sugar even during severe poisoning with P, it follows that, in the healthy organism, the prevention of hyperglycæmia by the drug is due to an increase in the power of the liver to assimilate sugar. W. McCartney.

Hypoglycæmic action of bile acids. K. Tanaka (J. Biochem. Japan, 1932, 14, 463—473).—*apo*-, Dehydro-, and dehydrodeoxy-cholic acids have the same hypoglycæmic activity as cholic or deoxycholic acid, whilst cholanic and cholatrienic acids are inactive. Hence the power to lower the blood-sugar appears to depend on the $:CH\cdot OH$ or $:CO$ group in the bile acids. F. O. Howitt.

Hydrocyanic acid. VII. Hydrocyanic acid hyperglycæmia. F. Kudo (J. Biochem. Japan, 1932, 14, 447—461).—The hyperglycæmia due to HCN poisoning in rabbits is considerably reduced by removal of the medulla of the suprarenals, whilst the poisoning is accompanied by an increase of adrenaline in the blood. Hence the increased blood-sugar is largely due to abnormal liberation of adrenaline. F. O. Howitt.

Influence of trypan on formation of glycogen. Insulin and glycogen. R. Messina (Arch. Farm. sperim., 1932, **53**, 178—191).—Less glycogen is found in the liver, muscle, and myocardium of rats after injection of trypan. Comparison of the effect of glucose, adrenaline, and insulin on trypanised and normal rats shows that trypan retards tissue-glycogen formation. Insulin stimulates tissue metabolism and provokes combustion of available sugar, and glycogenolysis. R. K. Callow.

Sulphonium compounds and the autonomic nervous system. R. Hunt and R. R. Renshaw (J. Pharm. Exp. Ther., 1932, **44**, 63—79).—These show an action similar to though less marked than that of the N-containing compounds. As with the latter, substitution of one or more Me groups by CH_2Ph reduces both the " muscarine " and " nicotine " activities in anæsthetised or pithed cats. P. G. Marshall.

General properties and toxicity of propylene glycol. M. A. Seidenfeld and P. J. Hanzlik (J. Pharm. Exp. Ther., 1932, **44**, 109—121).—This compound exerts a local burning sensation on the tongue without injury to the oral mucosa; it has a more acrid taste than glycerol or ethylene glycol, and leaves no after-effects. It is less toxic than ethylene glycol, being lethal only in 40% of rats injected intravenously with 15 c.c. per kg. body-wt. Continued drinking of even a 10% solution has no effect on growth and body-wt., and no pathological changes are observed. P. G. Marshall.

Toxicity of thiophen. F. Flury and F. Zernik (Chem.-Ztg., 1932, **56**, 149).—Thiophen is slightly more toxic than C_6H_6. E. S. Hedges.

Effect of caffeine and theophylline on the solubility of uric acid and sodium urate. A. Jung and W. Zörkendörfer (Schweiz. med. Woch., 1930, **60**, 503; Chem. Zentr., 1931, ii, 2332).—Caffeine (2%) increases the solubility of uric acid in H_2O seven-fold. Na urate and uric acid also show increased solubility in phosphate-buffered solution after addition of caffeine; for uric acid the solubility decreases with a rise in p_H and for the urate it decreases linearly with an increase in the [Na$^{\cdot}$] of the Na phosphate. Theophylline has an effect similar to but smaller than that of caffeine. L. S. Theobald.

Diuretic action of salicylates on uric acid, and solubility of uric acid. I. Yamaguchi (Folia Pharmacol. Japon., 1931, **12**, No. 3, 397—405).—Alkali (stomach tube) increases whilst acid diminishes the uric acid excretion of rabbits and the diuretic action of salicylates. The solubility of uric acid is increased by salicylates in the (descending) order: Ca, Mg, Li, Na, K; the diuretic action on urinary uric acid was also influenced in this order. Chemical Abstracts.

Reversible coagulation in living tissue. X. W. D. Bancroft, R. S. Gutsell, and J. E. Rutzler, jun. (Proc. Nat. Acad. Sci., 1932, **18**, 8—15).—A morphine addict was successfully treated by the administration of large doses of NaCNS while morphine was gradually withdrawn. The CNS′ probably acts by peptising rapidly the protein colloids agglomerated by morphine and also by displacing the morphine adsorbed in the tissues and thus causing more rapid elimination. W. O. Kermack.

Coagulation of proteins in marine borers. W. D. Bancroft (J. Physical Chem., 1932, **36**, 546—548; cf. A., 1931, 657).

Amount of adrenaline secreted from the suprarenal glands of dogs in hæmorrhage and poisoning. Y. Satakè (Tohoku J. Exp. Med., 1931, **17**, 333—344).—Hæmorrhage or poisoning by guanidine, peptone, or camphor causes a sudden increase in the adrenaline output of dogs; caffeine and tetrahydro-β-naphthylamine have a slight effect, whilst urethane and strychnine cause a slow increase. Chemical Abstracts.

Influence of piqûre on the adrenaline discharge, blood-sugar, and blood-pressure. T. Yen, T. Kaiwa, and M. Wada (Tohoku J. Exp. Med., 1931, **17**, 345—377).—Piqûre of the floor of the fourth ventricle of dogs caused a 50% elevation in blood-sugar within 30 min.; the blood-adrenaline increased from 0·00001—0·00002 to 0·00001—0·00005 mg. per min. per kg. Et_2O anæsthesia obscured the changes. Chemical Abstracts.

Relationship between chemical constitution and taste. A. L. Fox (Proc. Nat. Acad. Sci., 1932, **18**, 115—120).—The bitter taste of many derivatives of phenylthiocarbamide, *s*- and *as*-diphenylthiocarbamide, and certain other derivatives of thiocarbamide, such as *s*-dibenzylthiocarbamide, is felt only by certain individuals; to others they are tasteless. This failure in taste perception, which it is proposed to call " taste blindness," is apparently not correlated with age, sex, or race. The failure of taste in these individuals may be due to the insolubility of the compounds in their saliva. W. O. Kermack.

Genetics of sensory thresholds for phenylthiocarbamide. A. F. Blakeslee (Proc. Nat. Acad. Sci., 1932, **18**, 120—130).—The threshold concns. of aq. solutions of phenylthiocarbamide at which the bitter taste is distinguishable is different for different individuals and in certain instances is so high that a conc. aq. solution of the substance or the dried powder applied to the tongue does not evoke the taste. These taste differences appear to be innate and to be inherited by the offspring. The thresholds for other tastes also differ according to the individual and, further, certain individuals are unable to distinguish between certain tastes such as bitter and acid. W. O. Kermack.

Liposelection of cations. A new method in experimental hydrology. M. Loeper and A. Mougeot (Compt. rend., 1932, **194**, 575—576).—It is suggested that the property of fatty acids of destroying the prophylactic power of mineral waters by pptn. of the cations might be used to determine the effective ions in toxiphylactic or zymosthenic material. A. Lawson.

Physiological effect of trihydrol in water. T. C. Barnes (Proc. Nat. Acad. Sci., 1932, **18**, 136—139).—The growth of *Spirogyra* is increased by the presence of trihydrol, $(H_2O)_3$, in the culture medium.

A similar effect of trihydrol is probably of wide importance in biological processes.

W. O. Kermack.

Calcium gluconate solutions for hypodermic use and control of their titre. G. C. Gualdoni (Boll. chim.-farm., 1932, **71**, 45—47).—Discussion of de Carli's results (this vol., 16, 22, 44).

T. H. Pope.

Sorption of intestinal gases by "adsorgan," 'silargel," "argocarbon," and preparations 779 f and 1112. K. H. Bauer and K. Rauscher (Pharm. Zentr., 1932, **73**, 129—133).—The sorption of CO_2, CH_4, H_2S, CO, air, and H_2 by the above adsorbents in presence of H_2O has been measured. The prep. 1112 (a highly active Ca silicate) has an extraordinarily high sorption capacity for CO_2. Adsorgan and silargel adsorb intestinal gases strongly.

E. S. Hedges.

Loss of calcium from blood in oxalate and fluoride poisoning. Transport of calcium in the organism. A. Jodlbauer (Arch. exp. Path. Pharm., 1932, **164**, 464—468).—In rabbits on a Ca-poor diet subcutaneous administration of large doses of $Na_2C_2O_4$ or NaF causes a fall in blood-Ca which, although not fatal, may nevertheless be greater than the smaller fall brought about by the administration of a series of small doses of these compounds sufficient to cause the death of the animal. The development of tetanic symptoms does not run parallel with the level of the blood-Ca. In the nucleated red blood-corpuscles of the fowl the fall in Ca concn. following administration of $Na_2C_2O_4$ is much greater than in the plasma.

W. O. Kermack.

[Physiological] action of calcium. V. Autonomous equilibrium in the ox in relation to the composition of the blood-serum in experimental and pathological hypocalcæmia. Toxic action of intravenous injections of oxalates and citrates. L. Seekles, B. Sjollema, and F. C. van der Kaay (Biochem. Z., 1932, **244**, 258—267).—In cattle the decrease in the Ca content of the blood-serum following intravenous injection of $Na_2C_2O_4$ reaches its max. in a few min. The extent of the decrease and the severity of the accompanying toxic symptoms are relatively greater in cows than in young calves. Injection of even a large excess of oxalate does not ppt. all the serum-Ca: 30—40% of it is present in non-ionised form and is only incompletely and with difficulty pptd. by oxalate. If only a small part of this fraction is pptd. by a large excess of oxalate, death ensues. As a rule the injections cause decreases of about 10—15% in the inorg. P and Mg content of the serum. No decrease in the Ca content of the serum follows intravenous injection of Na citrate.

W. McCartney.

Distribution of chlorides and iodides in the skin and muscles of the rabbit after administration of potassium iodide. H. A. Shoemaker and F. P. Underhill (J. Pharm. Exp. Ther., 1932, **44**, 23—42).—A single dose of 0·5 g. of KI per kg. body-wt. administered *per os* causes an increase in the I content of tissues which reaches a max. 3 hr. after administration. Multiple doses do not further increase the I content of tissues. The Cl : I ratio is const. in the same animal and I shows no tendency to displace Cl.

P. G. Marshall.

Can iodides replace chlorides in chloride deficiency? H. A. Shoemaker and F. P. Underhill (J. Pharm. Exp. Ther., 1932, **44**, 43—46).—When there is a demand for Cl′, as in the case of superficial burns, this cannot be replaced by I′.

P. G. Marshall.

Parenteral resorption of colloids. IV. M. Murata (Biochem. Z., 1932, **245**, 67—70).—With sufficiently large doses of NaI, after oral and intraperitoneal administration, I appears in the serum. After administration of lipoiodine orally, I slowly appears in the serum and remains detectable for a long time. After subcutaneous administration, I appears in the serum very late and transiently and after intraperitoneal administration it does not appear in the serum, although detectable in the urine for a long time. With iodised caseinogen I never appeared in the serum, but was present in the urine.

P. W. Clutterbuck.

Effect of feeding titanium oxide to sheep. H. O. Askew (New Zealand J. Sci. Tech., 1931, **13**, 76—77).—Daily ingestion by sheep of large quantities (2—3 g.) of TiO_2 produces no ill-effects after 3 months. The complete elimination of the TiO_2 in the excreta suggests its suitability for use as a reference substance for digestibility trials.

W. G. Eggleton.

Oxygen-transporting enzyme of respiration. O. Warburg (Angew. Chem., 1932, **45**, 1—6).—A lecture.

Histochemical detection of peroxidases. L. Lison (Compt. rend. Soc. Biol., 1931, **106**, 1266—1268; Chem. Zentr., 1931, ii, 2022).—A reagent prepared from acid-violet or -fuchsin (1·5 g.), Zn dust (5 g.), AcOH (2 c.c.), and H_2O (100 c.c.), a further 2 c.c. of AcOH being added after cooling, remains colourless for days; before use, 10 c.c. of the filtered solution are treated with 1 c.c. of H_2O_2 and the tissue is immersed in it for 10 min. "Leucozinc" is particularly suitable for the detection of hæmoglobin.

A. A. Eldridge.

Action of peroxidases. I. Determination of activity by means of benzidine. K. L. Zirm, F. Reuter, and H. Wallstaedt (Biochem. Z., 1932, **245**, 290—298).—The coloured solution obtained by the action of peroxidase on benzidine in AcOH in the presence of H_2O_2 yields with excess of NaOH a dye sol. in EtOH and capable of being used for colorimetry. This dye (termed purpurobenzidine) can be obtained in the same way by the action of $KMnO_4$ on benzidine in AcOH. The peroxidase of hæmin and of horse-radish can be determined colorimetrically with the help of solutions of the dye, units similar to those given by Willstätter and Pollinger (A., 1923, i, 262) being used to express the activity.

W. McCartney.

Action of carbon monoxide on peroxidase. K. A. C. Elliott and H. Sutter (Z. physiol. Chem., 1932, **205**, 47—54).—The apparent inhibition of peroxidase by CO (A., 1931, 1455) is an unsp. effect due to agitation by the gas stream and is also given by N_2, air, and H_2. If a saturated solution of CO is used in place of a stream of gas, no inhibition is observed, even with a CO/H_2O_2 quotient of 14, using the malachite-green method (A., 1926, 1275).

J. H. Birkinshaw.

Lipin-oxidase in the soya bean. E. André and K. Hou (Compt. rend., 1932, **194**, 645—647).—Exposure to air of the unboiled residue from the prep. of soya-bean " milk " causes an increase in *d* and Ac val. and a decrease in I val. of the Et_2O extract as compared with the corresponding vals. for the boiled material. This is believed to indicate the presence of a lipin-oxidase.

A. Lawson.

o-Quinones as enzyme models. II. Experiments with various substrates. B. Kisch (Biochem. Z., 1932, **244**, 440—450; cf. this vol., 90).—Of the pyrocatechol derivatives investigated for oxidative deamination of NH_2-acids, the most active, between p_H 6·9 and 8·0, are, for glycine and phenylglycine, adrenaline; for glycine Et ester, glycylglycine, serine, and leucine, hydroxyquinol. The [H$^{\cdot}$] has a great effect on the activity. Isatin and alloxan do not effect deamination under the conditions chosen. *iso*Leucine differs from leucine and resembles valine and α-aminobutyric acid in not being appreciably deaminated by any of the catalysts. From the notable specificity of the latter it is concluded that within the mol. of org. substances groups apparently exactly similarly constituted differ as a result of the influences of other parts of the mol.

W. McCartney.

Influence of chlorine ions on salivary amylase. T. Omori (J. Biochem. Japan, 1931, **14**, 339—342).—Electrodialysis of saliva yields a liquid which exhibits no amylolytic activity except when NaCl is added. This activity is proportional to the amount of Cl′ bound by the constituents of the solution. PO_4''' and SO_4'', which do not activate the enzyme, do not reduce the total conductivity of the system. Hence neutral salts such as NaCl and to a smaller extent $NaNO_3$, which activate amylase, combine chemically with the enzyme.

F. O. Howitt.

Activation of amylase. R. H. Clark, F. L. Fowler, and P. T. Black (Trans. Roy. Soc. Canada, 1931, [iii], **25**, III, 99—105).—The rate of hydrolysis of dil. starch solutions (0·1—5%) at 25° by " malt diastase, U.S.P." is increased by " activators " such as ethylene chlorohydrin, KCNS, and thiourea. The increase in enzyme activity is approx. proportional to the concn. of the " activator " for low concns. There is an optimum concn. for each " activator " which gives the max. rate of hydrolysis. The course of the reaction was followed by (*a*) using 0·005*N*-I solution to detect the presence of starch, (*b*) determining the reducing substances in the sample. The activation of the enzyme cannot be attributed to small changes in p_H.

J. L. D'Silva.

Effect of reaction on the destruction of ptyalin. R. Ege (Biochem. Z., 1932, **244**, 243—257).—The ptyalin of different individuals varies very greatly in its power to resist destruction. p_H 6·5 is the reaction optimum for the enzyme; at p_H 5·9 and 7·5 the resistance falls to about half and beyond these vals. further loss of power to resist occurs. For equal changes in [H$^{\cdot}$] the change in the resistance is the greater the further the [H$^{\cdot}$] is removed from the optimum. It follows that ptyalin cannot be regarded as an ampholyte with isoelectric point at p_H 6·5 and having a stable undissociated mol. but very labile ions. The destruction of ptyalin at $p_H <$ about 3·2 is not a unimol. process, but is very nearly so at other reactions.

W. McCartney.

Hydrolytic and synthetic action of preparations from the pancreas of pigs receiving different diets. E. Bach and L. Lovas (Biochem. Z., 1932, **245**, 345—349).—As regards their power to hydrolyse and synthesise esters, pancreas preps. from fat pigs are two or three times as effective as are those from thin animals. Inactivated pancreas powder from fat pigs contains material which promotes enzymic esterification.

W. McCartney.

Enzymic fission of dehydrogenated peptides. Discovery of a dipeptidase. M. Bergmann and H. Schleich (Z. physiol. Chem., 1932, **205**, 65—75).—Glycyldehydrophenylalanine (I) with $CH_2Cl{\cdot}COCl$ yields *chloroacetylglycyldehydrophenylalanine*, m. p. 212° (corr.), which in aq. NH_3 gives *diglycyldehydrophenylalanine* (II), becomes brown at 214°, decomp. 226°. Extracts of pig's and sheep's kidney hydrolyse (I). The enzyme responsible, *dehydrodipeptidase*, is stable in glycerol extracts and is very sensitive to HCN. The optimum p_H is 7·5. The enzyme does not hydrolyse the tripeptides glycyldehydrophenylalanylglycine and glycyldehydrophenylalanyl-*d*-glutamic acid (in which the dehydroamino-acid has no free CO_2H), but mixed with other enzymes it does attack (II), yielding 2 mols. of glycine and 1 mol. each of NH_3 and phenylpyruvic acid. In the last case the first stage of the hydrolysis is due to the aminopolypeptidase.

J. H. Birkinshaw.

Histochemistry of enzymes. II. Distribution of peptidase in roots and sprouts of malt. K. Linderstrøm-Lang and H. Holter (Compt. rend. Lab. Carlsberg, 1932, **19**, No. 6, 39 pp.).—Microtome sections of the primordial root and leaf-shoot of sprouting barley are examined for peptidase activity by a micro-method in which alanyl- or leucyl-glycine is used as substrate and the hydrolysis is followed by titration (cf. A., 1931, 1455). The activity varies strongly along the primordial root, being at a max. at a distance of 0·8 mm. from the root-tip, but only slightly along the leaf-shoot. The ratio of the velocities of hydrolysis of the two substrates also varies along the root and has a min. val. at the growth region of the tip.

F. O. Howitt.

Salicylaldehyde-phosphoric acid and oxidative dephosphorylation. C. Manaka (J. Biochem. Japan, 1932, **14**, 481—487).—Salicylaldehyde-phosphoric acid is hydrolysed by taka- or kidney-phosphatase, the p_H optima being 3 and 10, respectively. In presence of oxidising agents such as H_2O_2 the aldehyde forms the corresponding acid, which spontaneously undergoes dephosphorylation. The p_H optima of these reactions are 10 and 5·6, respectively, that of the complete process being 7.

F. O. Howitt.

Influence of bile acids on glycerophosphatase. II. H. Takata (J. Biochem. Japan, 1932, **14**, 439—445).—The *in vitro* synthesis of glycerophosphoric acid

in liver- and, to a greater extent, in kidney-tissue is increased by addition of Na cholate.
F. O. Howitt.

Influence of thiol compounds on phosphatase. E. Waldschmidt-Leitz and A. Schäffner (Naturwiss., 1932, **20**, 122).—Catheptic enzymes are activated by SH-compounds (this vol., 85). The hydrolysis of org. esters of H_3PO_4 is also influenced by SH-compounds. The rate of hydrolysis of glycerophosphate by kidney-phosphatase is diminished considerably by cysteine, whilst its synthesis is only slightly affected by this substance. W. R. Angus.

Allantoinase. K. Ro (J. Biochem. Japan, 1932, **14**, 405—411).—An aq. extract of soya bean is pptd. with $COMe_2$, the ppt. extracted with 70% aq. EtOH followed by 90% aq. EtOH and finally Et_2O, yielding a powder containing allantoinase. This prep. hydrolyses allantoin quantitatively to allantoic acid, the reaction being unimol. with p_H and temp. optima of 7·3 and 50—60°, respectively. F. O. Howitt.

Isolated liver-cells. I. Vitality of the cells and their enzymes. II. Effect of dyes. S. Kodajima (J. Biochem. Japan, 1931, **14**, 279—289, 291—304).—I. The peptidase, lipase, and, to a greater extent, the amylase of liver-cells in physiological saline retain their activities for some days. The nucleus-staining capacity is lost after 14 days. No enzyme capable of hydrolysing NH_2-acids could be detected.

II. The vitality of the cells is reduced more by acidic than by basic dyes. Amylase is the least affected of the cell-enzymes, whilst neutral-red has a marked action on the lipase activity. F. O. Howitt.

Uricase. K. Ro (J. Biochem. Japan, 1931, **14**, 361—390).—Uricase is prepared from ox-kidney by $COMe_2$-pptn. of an aq. extract, the ppt. being washed with aq. EtOH followed by Et_2O and finally dried. Such a prep. contains proteins closely associated with the enzyme, which is readily extracted by solutions at p_H 9·4, the optimum reaction. The temp. optimum is 45°, the activity being destroyed by heating to 70° and by the presence of 12% EtOH or Et_2O. During its action on uric acid oxidation–reduction potentials indicate the presence of an intermediary of high oxidation potential between the substrate and the allantoin produced. The enzyme is inhibited by KCN or by absence of O_2 and is accelerated by small concns. of $CuSO_4$. Injection into rabbits results in the formation of an anti-enzyme in the serum.
F. O. Howitt.

Kinetics of carboxylase action and its significance in controlling the biological decomposition of carbohydrates. K. Wetzel (Planta [Z. wiss. Biol.], 1932, **15**, 697—738).—The action on org. acids of carboxylase from yeast and from seeds is largely restricted to the decomp. of α-keto-acids. Oxalacetic and pyruvic acids are readily decomposed. Mesoxalic acid is not attacked and tends to inhibit the action of the enzyme on pyruvic acid. Carboxylase action is depressed by aldehydes which may be adsorptively combined with the enzyme. The reactive group of carboxylase is probably an NH_2-group. Regulation of carbohydrate decomp. and acid production in plants is probably related to the inhibitory action of certain products (*e.g.*, MeCHO and methylglyoxal) on carboxylase. The production of lactic acid rather than EtOH from methylglyoxal by yeast and the action of " ketone–aldehyde mutase " are similarly explained. Relationships between carboxylase activity and the temp. and reaction of the substrate are examined. The autolytic decomp. of carboxylase at const. temp. and p_H is of the nature of an irreversible unimol. reaction. A. G. Pollard.

Oxygen consumption and carbon dioxide production during the growth of yeast. O. W. Richards and F. W. Haynes (Plant Physiol., 1932, 7, 139—144).—The O_2 consumption of yeast cultures reached a max. during the equilibrium interval between the first and second cycles of growth. The utilisation of O_2 for the oxidation of metabolic products in the culture medium is suggested. CO_2 production declines as the sugar remaining in the medium decreases. A. G. Pollard.

Nature of zymase fermentation. W. A. Belitzer and E. N. Gorkin (Biochem. Z., 1932, **245**, 146—148).—The prep. of an active yeast juice from powdered dried yeast without maceration is described. The view that the fermentation of yeast juice is due to the activity of ultramicroscopic micro-organisms which are not removed by centrifuging is discredited, since the unpowdered yeast always gave an inactive extract. P. W. Clutterbuck.

Fermentation of trehalose. A. J. Kluyver and F. L. W. van Roosmalen (Biochem. Z., 1932, **245**, 13—24).—The fermentation velocities of glucose, fructose, maltose, and trehalose with dried yeast under comparable conditions and the effect of phosphate are investigated. It is probable that the formation of trehalosemonophosphate in the fermentation of fructose and glucose by dried yeast is due at least partly to the phosphorylation of trehalose pre-existing in the yeast, but the results leave open the possibility of formation of the ester by synthetic processes.
P. W. Clutterbuck.

Action of iodine on yeast. II. K. Scharrer and W. Schwartz (Biochem. Z., 1932, **245**, 218—233).—I′ and IO_3' under determined conditions increase the growth and the germinating power of yeast. Mol. I is more toxic than I′. " Uroselectan " and " yatren " show the stimulatory action and " alivan " gives an increased growth, but only in very low concn. (10^{-6}%). Iodoethylthiosinamine gives a small increase in growth at concns. of 5×10^{-5} to 5×10^{-6}, larger amounts being toxic and causing rapid diminution of yield. (Cf. A., 1927, 903.) P. W. Clutterbuck.

Nomenclature of catalysts involved in alcoholic fermentation. A. J. Kluyver and A. A. Stheeman (Biochem. Z., 1932, **244**, 366—369).—Since the simultaneous action of several activators, of which Euler's co-enzyme is merely one, is necessary in the fermentation of hexoses by yeast, the nomenclature suggested by Neuberg and Euler (A., 1931, 1333) is inapplicable. The names holozymase and apozymase may logically be retained for the present, but the term cozymase should be abandoned. W. McCartney.

Biological gas reactions. II. Formation of acetic acid in the biological conversion of carbon

mon- and di-oxide into methane. F. Fischer, R. Lieske, and K. Winzer (Biochem. Z., 1932, **245**, 2—12).—The biological conversion is described of $CO+H_2O$ in presence of a colloidal substance into CO_2+H_2 and of CO_2+H_2 into AcOH, which in presence of colloidal substance is further converted into CO_2+CH_4. The formation of AcOH from $H_2CO_3+H_2$ is an essential stage in the biological formation of CH_4. P. W. Clutterbuck.

Conversion of lactic into pyruvic acid by means of *Bacterium Delbrücki*. E. Simon (Biochem. Z., 1932, **245**, 488—493).—When *B. Delbrücki* is cultivated in a suitable medium containing pure Ca lactate pyruvic acid is produced and consequently the view of Kostytschev and others (A., 1930, 960) that this acid is an intermediate stage in the conversion of methylglyoxal into lactic acid is disproved. Also, there is no production, in the circumstances mentioned, of acetoin, diacetyl, or βγ-butylene glycol. *B. Delbrücki* lives and grows for at least 12 days in the medium, eventually destroying the pyruvic acid. W. McCartney.

Bacteria producing trimethylene glycol. C. H. Werkman and G. F. Gillen (J. Bact., 1922, **23**, 167—182).—Trimethylene glycol is produced from glycerol by many organisms. A. G. Pollard.

Fermentation of glyceraldehyde. A. I. Virtanen and J. von Hausen (Z. physiol. Chem., 1932, **204**, 235—246).—*B. coli* I ferments only the *l*-form of *dl*-glyceraldehyde. No acclimatisation of the organism to glyceraldehyde was observed. Glyceraldehyde had a definitely toxic action on the bacteria. In broth containing glyceraldehyde no growth was observed although the bacteria grew in broth alone. As with dihydroxyacetone the main portion is probably converted by a Cannizzaro reaction into glycerol and glyceric acid (which is further fermented to AcOH, HCO_2H, CO_2, and H_2), whilst a parallel reaction gives lactic acid (25%) by way of methylglyoxal. J. H. Birkinshaw.

Aërobic pectin fermentation. A. I. Makrinov (Zentr. Bakt. Par., 1932, II, **85**, 339—348).—Anaërobic fermentation of pectin substances by *Granulobacter pectinovorum* yields butyric acid and AcOH with small amounts of CO_2 and H_2. With aërobic organisms (*Pectinobacter amylophilum*) 75% of the pectin is converted into CO_2 and H_2 with smaller proportions of HCO_2H and AcOH. During the retting of flax by the latter organism pigment and extractive matter are destroyed and retting can be completed in one operation. A. G. Pollard.

Decomposition of pentosans by soil bacteria. J. Ziemięcka (Rocz. Nauk Roln. Lés., 1931, **25**, 313—332; Chem. Zentr., 1931, ii, 2470).—*B. xylanophagus*, which decomposes xylan in non-acid medium, but not cellulose, was isolated from soil, straw, and stable manure. A. A. Eldridge.

Metabolism of bile acids. IV. Influence of bacteria and of ultra-violet and *X*-rays on bile acids. H. Mikami (J. Biochem. Japan, 1932, **14**, 489—500).—Bile acids in sterile aq. solution experience gradual decomp. on keeping at room temp., a decomp. which is slightly greater following inoculation with *B. coli*. EtOH solutions are more stable. Ultraviolet but not *X*-irradiation of aq. solutions accelerates the decomp. F. O. Howitt.

Secretion and thermostability of bacterial proteases. A. I. Virtanen and J. Tarnanen (Z. physiol. Chem., 1932, **204**, 247—258).—Young proliferating cells of *B. fluorescens liquefaciens* and *B. subtilis* excrete practically all their proteinase into the medium, since after filtration the bacterial mass shows only 0·4—0·6% of the activity of the filtrate. The bacterial mass contains polypeptidase and dipeptidase, which are liberated only after autolysis. The proteinase is stable at 100° for several min. in cultures containing protein and is not immediately inactivated at 110°. In protein-free cultures, the enzyme is inactivated at 60° in 30 min. The apparent thermostability at 100° is due to protective action of protein and may be imitated by addition of caseinogen, with which the protection is minimal at 60°, but marked above 70°. J. H. Birkinshaw.

Mechanism of the reduction of nitrates [by bacteria]. IV. M. P. Korsakova (Bull. Acad. Sci. U.S.S.R., 1931, 833—846; cf. A., 1930, 251; 1931, 265).—*B. turanicum* grows well at first in solutions in which the source of N is solely inorg., but gradually loses the ability to do so. When this organism is grown in yeast water–glucose solutions containing KNO_3 it activates the system org. compound–nitrate to an oxidation–reduction process, during which CO_2 is evolved and KNO_3 is apparently reduced to $H_2N_2O_2$ or HNO. T. H. Pope.

New autotrophic bacterium which oxidises ammonia directly to nitrate and decomposes petroleum. C. B. Lipman and L. Greenberg (Nature, 1931, **129**, 204—205).—An organism, which grows under autotrophic conditions in an inorg. salt medium with $(NH_4)_2SO_4$ or KNO_3 as the source of N, oxidises NH_3 directly to NO_3 and more quickly than do the nitrifying bacteria. It also decomposes petroleum completely without forming gases other than CO_2. Cellulose is not decomposed. L. S. Theobald.

Intake of dissolved substances by bacteria. I. H. Habs (Z. Hyg., 1932, **113**, 239—272).—Under uniform conditions the I-absorbing capacity of an individual species of bacteria is const. Variations among different strains of the same species are small, but between different species differences in I fixation are significant. The intake of I probably results from physical adsorption followed by chemical combination. The I absorption of bacterial cultures increases with age and is not entirely accounted for by the additional amount of bacterial substance formed. Killing bacteria by heat does not destroy their I-fixing power provided the bacterial substance is not destroyed. Products of bacterial metabolism affect the I intake, especially if they tend to change the [H˙] of the suspension. The proportion of "loosely combined" I is not related to the nature of the organism nor to the total surface exposed, but definite amounts of "chemically combined" I can be associated with particular species of organisms. A. G. Pollard.

Bacterial fluorescence in various media. II. Production of fluorescence in peptone media. F. R. Georgia and C. F. Poe (J. Bact., 1932, 23, 135—145; cf. this vol., 198).—Peptones vary considerably in their ability to cause pigmentation in bacterial cultures. The production of fluorescence was not facilitated by the use of media containing high concn. of peptone, nor by the presence of purines, meat bases, or asparagine. A. G. Pollard.

Agglutination. E. Freund and R. Katz (Biochem. Z., 1932, 245, 35—43).—The behaviour of normal serum and serum in various cases of sepsis against bacteria is investigated, and tables summarise the amount of agglutination with various organisms in different pathological conditions. The agglutination obtained with normal is not obtained with septic serum. P. W. Clutterbuck.

Bacterial agglutination and its relation to colloidal theory. S. Mudd, R. L. Nugent, and L. T. Bullock (J. Physical Chem., 1932, 36, 229—258).—The addition of electrolyte to a suspension of bacteria reduces the electrokinetic potential, ζ, but does not necessarily cause pptn., since the stability of the suspension depends also on the degree of hydration of the bacterial surface, which is different for different bacteria. The stability of a bacterial or other suspension depends on the relation between the repulsive forces, principally ζ, and the work of cohesion, W, which is the product of the interfacial tension, γ, between particle and medium, and the area of contact. Hydration reduces W by reducing γ. Agglutination by antibodies may be due to changes either in W or in ζ. Non-sp. agglutination by tannin produces a high negative charge on the particles, but also a relatively hydrophobic surface with a high W. K. V. Thimann (c).

Bacterial substances isolated from *B. typhosus* and *B. paratyphosus*. K. Nagase (Japan J. Exp. Med., 1930, 8, 365—369).—Nucleoproteins and residue antigens were prepared. The latter gave only ninhydrin and Molisch reactions; they showed no antigenic activity *in vivo*, but gave sp. precipitin reactions with homologous antibacterial sera. The nucleoproteins were antigenic *in vivo*, but gave only group precipitin reactions. Chemical Abstracts.

Bacterial substances isolated from dysentery bacilli. K. Nagase (Japan. J. Exp. Med., 1930, 8, 371—378).—The nucleoprotein and residue antigen prepared from *B. dysenteriæ* are analogous to those from *B. typhosus*. Chemical Abstracts.

Unitarian hypothesis of antibodies. I. II. Quantitative relationship among antibodies of serum and different serum-protein fractions. T. Takayama (Sei-i-kwai Med. J., 1930, 49, No. 7, 21—57, 58—85).—All the antibodies in the serum immunised against cholera vibrio and goat corpuscles are in the serum-globulin fractions, the greater amount being sometimes found in the pseudo-globulin. The concns. of the antibodies in the serum are the same as the sum of those in serum-globulin fractions. When immune cholera serum and serum immune against goat corpuscle are heated, all the antibodies decrease as the temp. rises, those in the pseudo-globulin being more resistant than those in the euglobulin. Probably all the antibodies are the same substance. Chemical Abstracts.

Antigens and antibodies of the staphylococcus. O. Gengou (Ann. Inst. Pasteur, 1932, 48, 135—143).—Neither washed suspensions of pyogenic staphylococci killed with CH_2O nor cultures of staphylococci which have been lysed by bacteriophage contain demonstrable toxin and neither of these preps. when injected into rabbits produces antibodies to the toxins of the staphylococci. These antitoxins can be produced only by the injection of free toxin or of anatoxin. W. O. Kermack.

Hæmolysis of blood-cells by staphylotoxin. O. Gengou (Ann. Inst. Pasteur, 1932, 48, 19—26).—Hæmolysis of blood-cells caused by staphylotoxin does not destroy the ability of the leucocytes to transform cholera vibrios into granules, or their power to immunise rabbit serum against *B. anthracis*, or to prevent the participation of the blood-platelets in the coagulation of the blood. A. Lawson.

Hæmotoxin of bacteria. K. Nagase (Japan. J. Exp. Med., 1930, 8, 379—389).—Purified hæmotoxins, giving negative protein and positive Molisch reactions, produced sp. antihæmotoxins *in vivo*, but gave negative precipitin and anaphylactic reactions. They were destroyed by taka-diastase, but not by proteolytic enzymes. Chemical Abstracts.

Detoxication of bacterial toxins and their antigenic properties. Y. Nishiura (Sei-i-kwai Med. J., 1930, 49, No. 11, 10—34).—Toxoid formation from vibrio toxin differs from that of tetanus and diphtheria toxins. Many aldehydes and the salts of aromatic acids can detoxicate vibrio toxin without destroying its power to produce immunity; these reagents are detoxicants to the others without (except for CH_2O and furfuraldehyde) producing toxoids. The differences are attributed to different chemical structures of the toxins. Chemical Abstracts.

Precipitation between tetanus toxin and tetanus antitoxin. T. Inoue (Arb. med. Univ. Okayama, 1931, 2, 369—395).—There are indications that the pptn. of tetanus toxin by antitoxin is not sp. Serum and bacterial precipitins show the same phenomena. There is no parallelism between the pptn. reaction and the toxity of toxins prepared in different ways and subjected to different treatments (*e.g.*, CH_2O). Chemical Abstracts.

Relation of copper and iron to the production of toxin and enzyme action. A. Locke and E. R. Main (J. Infect. Dis., 1931, 48, 419—435).—The production of diphtheria toxin in proteose medium is inhibited by substances [cysteine, $K_4Fe(CN)_6$] which diminish the available Cu content of the medium or augment its available Fe content. Addition of Fe and Mn to cysteine-treated broth is followed by an abnormally great depression of toxin production. Broth treated with H_2S behaves similarly to cysteine-treated broth. The production of neurotoxin by the tetanus bacillus is partly inhibited by cysteine. The hæmotoxin of *B. welchii* is unaffected by cysteine, CN', or $Fe(CN)_6''''$, inhibited by $Fe(CN)_6'''$

and stimulated by $Fe^{\cdot\cdot}$. The neurotoxins appear to be dispersions of bacterial protoplasm containing fragments of a cationic respiratory substance having Cu as the predominant catalyst. The hæmotoxins appear to contain fragments of an anionic respiratory substance having Fe^{II} as the predominant catalyst.

Chemical Abstracts.

Cultivation of anaërobic bacteria with the help of leucocytic and bacterial products. H. Goldie (Ann. Inst. Pasteur, 1932, 48, 179—186).—By the addition of leucocytes to anaërobic growths of bacteria (*B. botulinus*) very rapid growth is induced which may continue even under aërobic conditions. A small quantity of the actively growing culture is in turn able to stimulate other cultures so that a type of transmissible activation is obtained. The activating substance is stable to heat, but is destroyed by Et_2O. Old cultures of *B. botulinus* contain substances, one thermolabile, stable to acids, and enzyme-like in nature, which when added to cultures of anaërobes allows them to be grown aërobically and is probably catalase, and a thermostable substance readily destroyed by acid, which is growth-inhibiting. W. O. Kermack.

Effect of iron oxides on the growth of bacteria. O. Baudisch (Biochem. Z., 1932, 245, 265—277).—Since the catalytic and biocatalytic properties of the Fe oxides vary greatly according to degree of purity and physical state, various samples of the oxides prepared from Fe carbonyl, Fe nitrate, and spectroscopically pure Fe have been examined. All of these samples except one, prepared in an electric arc, behave either like catalase or like peroxidase or in both ways. The experiments of Webster and Baudisch (J. Exp. Med., 1925, 42, 473) have been repeated using *B. hæmoglobinophilus* and *B. influenzæ*.

W. McCartney.

Catalase action of iron compounds in culture media. O. Baudisch and R. Dubos (Biochem. Z., 1932, 245, 278—281; cf. preceding abstract).—The life of pneumococci in culture media can be prolonged by addition of Fe oxides or certain Fe compounds: these destroy the peroxides which kill the organisms.

W. McCartney.

Virus problems. G. Pyl (Naturwiss., 1932, 20, 131—134).—The chemical and physico-chemical methods of purifying and concentrating virus preps. are discussed with some reference to a lymph infected with foot-and-mouth disease. Such a virus is most effectively preserved by glycerol, whilst purification up to ×1000 is achieved by adsorption methods when consideration is given to the $[H^{\cdot}]$ of the medium. The ultra-filtration and the electrophoretic separation of an activating agent are briefly discussed.

F. O. Howitt.

Tubercle ultra-virus. I. G. Sanarelli and A. Alessandrini (Ann. Inst. Pasteur, 1932, 48, 144—178).—Ultrafiltrates through collodion of cultures of tubercle bacilli when injected intraperitoneally into guinea-pigs give rise to a definite but a typical tuberculous pathological condition, leading ultimately to the death of the animal and due apparently to the existence in the ultrafiltrate of tubercle ultra-virus. The disease may be transmitted to other guinea-pigs and although tubercle bacilli do not appear in the first guinea-pig these usually may be observed, at first in an attenuated form, after a no. of passages. W. O. Kermack.

Acceleration of the dehydrogenation of mercaptans by metals. Oligodynamic action of metals. T. Bersin (Biochem. Z., 1932, 245, 466—472; cf. Tammann and Rienäcker, A., 1928, 675).—In presence of O_2 and in an alkaline medium the conversion of the SH group of thioglycollanilide into the ·S·S· group is accelerated by metals in the order $As > Cu > Sb > Zn > Cd > Ag > Fe > Ni$; this series agrees well with that showing extent of oligodynamic activity. The results of Harrison (A., 1928, 44) and of Labes and Freisburger (A., 1931, 120) concerning the effect on the conversion of the disulphide itself and of alloxan are confirmed and a method for the alkalimetric titration of aliphatic mercaptans is given. W. McCartney.

Effects of salts on disinfection by alkalis. O. E. Lowman, J. H. Buchanan, and M. Levine (Iowa State Coll. J. Sci., 1931, 5, 251—268).—Experiments were performed at 60° with an organism resembling *B. subtilis* and 0·25*N*-NaOH alone or with 0·342*N*-NaCl, -NaBr, -NaI, or -NaF (p_H 12·92—12·83). The solution containing NaI was the most effective germicidal agent.

Chemical Abstracts.

Bactericidal action of mixtures of different monochloro-derivatives of homologues of phenol. R. Etinger-Tulczynska and W. Ulrich (Z. Hyg., 1932, 113, 437—444).—Various mixtures of chlorocresols, -xylenols, and -thymols have greater bactericidal power than either constituent used alone.

A. G. Pollard.

Effect of $[H^{\cdot}]$ on the toxicity of several preservatives to micro-organisms. W. V. Cruess, P. H. Richert, and J. H. Irish (Hilgardia, 1931, 6, No. 10, 295—314).—The min. concn. of solutions of NaOBz, Na salicylate, Na_2SO_3, and KOAc necessary to prevent the growth of micro-organisms was greater at p_H 5·0—9·0 than at p_H 2·0—4·5. The influence of these solutions on rates of fermentation was similarly affected by p_H but to a smaller extent. The retarding effect of NaOBz on the reproductivity of yeast was less at neutrality than at p_H 3·0—2·9. The action of solutions of NaCl and of CH_2O on *Saccharomyces ellipsoideus* was affected only to a small extent by $[H^{\cdot}]$. The effective concn. of NaOBz solutions in food preservatives was in some cases 200 times as great at p_H 7·0 as at p_H 3·0.

A. G. Pollard.

Is the hyperinsulinæmia following injection of adrenaline of pancreatic origin? E. Zunz and J. La Barre (Compt. rend. Soc. Biol., 1931, 106, 1241—1244; Chem. Zentr., 1931, ii, 1873).—Experiments on dogs indicate that adrenaline, or a substance mobilised by it, stimulates the insulin production of the pancreas. A. A. Eldridge.

Mechanism of insulin and synthalin action. K. Ochiai (Nagoya J. Med. Sci., 1931, 5, 110—124).—The liver-glycogen of the normal rat decreases gradually after injection of insulin and disappears in hypoglycæmic convulsions; the muscle-tissue

glycogen is increased. After starvation for 24 hr. the liver and skeletal muscle of rats contained no appreciable quantity of glycogen. On administration of insulin with glucose little glycogen is deposited in the liver and much in the muscle of rats and guinea-pigs. In rabbits the reverse holds. Synthalin gives similar results. Histological changes in the liver and kidney after administration of synthalin are identical with those occurring in cases of severe poisoning, *e.g.*, by P, As, $CHCl_3$, $HgCl_2$, or EtOH.
Chemical Abstracts.

Form of the insulin particle. K. Freudenberg (Z. physiol. Chem., 1932, **204**, 233—234; cf. this vol., 96).—A corrected calculation of the dimensions of the insulin particle. The smallest mol. aggregate appears to consist of a double mol.
J. H. Birkinshaw.

Induced oxidation of glucose in presence of insulin acting as an inductor. H. L. Dube and N. R. Dhar.—See this vol., 346.

Variations of the secretion of insulin in intra- and extra-pancreatic hyperglycæmia. J. La Barre (Compt. rend. Soc. Biol., 1931, **106**, 1244—1246, 1247—1248; Chem. Zentr., 1931, ii, 1873).

"Heart hormones." P. B. Rehberg (Dansk Tidsskr. Farm., 1932, **6**, 41—54).—A lecture.
H. F. Harwood.

Nature of the so-called circulatory hormone preparations. T. Brugsch, H. Horsters, and H. Rothmann (Med. Klinik, 1931, **27**, 1378—1379; Chem. Zentr., 1931, ii, 2346).—Co-enzyme characteristics were detected in Eutonin, Auriculin, Padutin, Lacarnol, and muscle-adenylic acid. The so-called hormone preps. should therefore be regarded as co-enzyme preps. L. S. Theobald.

Effect of cortico-adrenal extract on energy output. E. Eagle and S. W. Britton (Science, 1932, **75**, 221—222).—Intraperitoneal injection of cortico-adrenal extract increases the working capacity of a dog; a similar effect is observed with man.
L. S. Theobald.

Determination of thyroxine in the thyroid. J. P. Leland and G. L. Foster (J. Biol. Chem., 1932, **95**, 165—179).—The gland is hydrolysed for 18 hr. with boiling 2*N*-NaOH. Thyroxine is then separated from other I compounds in the hydrolysate by extraction with BuOH, I being determined in the BuOH extract. The alkaline hydrolysis is accompanied by a destruction of thyroxine not exceeding 15% of the total amount. Comparison with the method of Harington and Randall (A., 1930, 504) indicates that the latter method gives results exceeding the true vals. by approx. 100%. The average thyroxine content of 52 human thyroids was 25·2% of the total I when no correction was applied for destruction during hydrolysis. F. O. Howitt.

Thyroid action and tissue catabolites. I. Abelin and R. Sato (Sei-i-kwai Med. J., 1930, **49**, No. 8, 1—16).—Small quantities of thyroid fed continuously to dogs and sheep slightly decrease the blood viscosity; the serum-albumin decreases slightly, then rises, and again decreases. Chemical Abstracts.

Hormone of the anterior lobe of the pituitary and the magnesium, calcium, and phosphorus contents of blood. L. Cannavó (Biochem. Z., 1932, **245**, 234—237).—The influence of prolan on the Ca, P, and Mg contents of blood-serum in man, dog, and rabbit is investigated. In man, the Ca and P concn. and the acid–base equilibrium remained unchanged. In dogs and rabbits, the Mg content was considerably, the P content slightly, increased and the Ca content remained unchanged.
P. W. Clutterbuck.

Influence of anterior pituitary substances on the total iodine content of the thyroid gland in the young duck. J. A. Schockaert and G. L. Foster (J. Biol. Chem., 1932, **95**, 89—94).—Injection of fresh saline emulsions of anterior lobes of ox-pituitary glands into young male ducks induces a rapid decrease in the total I of the thyroid gland. This decrease ceases after a few days, but the percentage of I continues to fall for some weeks owing to hypertrophy of the gland. A similar action is brought about by the growth-promoting hormone of the anterior lobe of the pituitary gland (A., 1931, 268).
F. O. Howitt.

Pituitary hormone. Intermedin, a hormone of the pars intermedia. B. Zondek and H. Krohn (Naturwiss., 1932, **20**, 134—136).—The anterior pituitary hormone of warm-blooded animals is not identical with that of cold-blooded. The formation of the "mating cloak" in fish is not influenced by female or male sexual hormone, whilst pituitary extracts will cause its formation. Vasopressin and to a smaller extent oxytocin produce increase in melanophore area in frogs; it is concluded, however, that the dark coloration in frogs due to expansion of melanophores is not sp. for one hormone. The formation of erythrophores in the fish *Phoxinus lævis* is sp. for a definite pituitary hormone, negative responses being given by corpus luteum extracts, male and female sexual hormones, insulin, thyroxine, yohimbine, etc. A certain standard increase in erythrophore area in this fish is defined as a "*Phoxinus* unit." This sp. hormone is prepared from the pituitary by extraction of the powdered, $COMe_2$-dried gland with 0·25% AcOH at the b. p. It is present also in the tuber cinereum and the thalamus, but seldom in the fluid of the third ventricle. From ox-pituitary glands were obtained 2857 units per g. from the anterior lobe, 80,000 from the pars intermedia, and 11,904 from the posterior lobe. This hormone of the pars intermedia is designated "intermedin." Human pituitary glands contain 4000—7000 units per gland. Intermedin is prepared as a solution, free from proteins, vasopressin, and oxytocin, which has no action on the heart, vessels, blood-pressure, or smooth musculature, but produces a rise in O_2 consumption of warm-blooded animals. Intra-vital microscopy of the thyroid gland in rats following injection of the hormone reveals a marked attenuation of the colloid matter.
F. O. Howitt.

Action of hypophysin and its fractions on water and salt metabolism. F. Robert (Arch. exp. Path. Pharm., 1932, **164**, 367—382).—In a young male subjected to H_2O diuresis, the antidiuretic action and the effect on the NaCl metabolism of "tonephin" and "orasthin," fractions separated from hypophysin, are qualitatively the same as those of the latter, but the first is possibly more and the second considerably less active. The diuretic action of these substances appears to be primarily on the kidney.

W. O. Kermack.

Pituitary hormones. IV. Relation between the hypophysis and vitamin-*C*. V. Influence on the germination of *Lupinus albus*, L. R. T. Agnoli (J. Pharm. Exp. Ther., 1932, 44, 47—53, 55—62).—IV. Hormones of the anterior lobe cannot be substituted for vitamin-*C* in a *C*-deficient diet, although a slightly greater initial increase in wt. occurs in guinea-pigs than with other pituitary hormones.

V. Only lipoidal pituitary hormone affects growth of *L. albus*, producing a slight increase.

P. G. Marshall.

Sex hormone in butterflies. S. Loewe, W. Raudenbusch, H. E. Voss, and J. W. C. van Heurn (Biochem. Z., 1932, **244**, 347—356).—The fresh sex organs of freshly hatched sexually mature female butterfles (*Attacus atlas*) contain 90—130 mouse units of œstrin per kg.

W. McCartney.

Production of mucification of the vaginal epithelium of rodents by the œstrous hormone. R. K. Meyer and W. M. Allen (Science, 1932, 75, 111—112).—Theelin produces mucification in guinea-pigs, rats, and mice. This indicates that previous mucifications produced by corpus luteum extracts are due to the œstrin present and not to other sp. hormones such as progestin and relaxin. Mucification in mice has also been produced by œstrin extracted from male urine with C_6H_6.

L. S. Theobald.

New crystalline sexual hormone from the urine of pregnant mares. A. Girard, G. Sandulesco, A. Fridenson, and I. J. J. Rutgers (Compt. rend., 1932, **194**, 909—911).—From the middle fractions of theelin cryst. from EtOH ($[\alpha]_D >$ $+250°$) a new hormone is extracted by Et_2O and purified by fractionation from EtOAc. From 7 tons of urine 100 mg. of *hormone*, m. p. 238—240°, $[\alpha]_D^{15}$ +308° (1% in dioxan), were obtained, closely resembling theelin in chemical properties. The name "*equilin*" is proposed. The following const. are reported for theelin: m. p. 259—260°, $[\alpha]_D^{15}$ +163° (*semicarbazone*, m. p. 266—267°; *oxime*, m. p. 241—242°; *benzoate*, m. p. 218—219°, $[\alpha]_D^{15}$ +128°; *Me ether*, m. p. 173—174°).

A. Cohen.

New plant source of vitamin-*A* activity. D. H. Cook and J. Axtmayer (Science, 1932, 75, 85—86).—Extraction of the crude red annatto powder from *Bixa orellana* with cold 80—90% EtOH gives a reddish-brown solution which yields a dark-coloured, resinous material. Administration of this fraction, which is practically free from bixin, to rats fed on a vitamin-*A*-free diet results in increased growth. The seeds contain approx. 2% of active material, the nature of which is not yet definitely ascertained.

L. S. Theobald.

Vitamin-*A* content of ghee. A. L. Bacharach (Brit. Med. J., 1930, II, 141—142).—Low vals. were obtained.

Chemical Abstracts.

Variations in vitamin-*A* and chemical composition of maize. G. S. Fraps (Texas Agric. Exp. Sta. Bull., 1931, No. 422, 46 pp.).—Yellow maize was rich and white maize poor in vitamin-*A*. Different varieties of maize showed no significant variation in protein, fat, N-free extract, ash, Ca, Mg, or PO_4''' contents. Maize grown in different localities varied in Ca, PO_4''', and notably in protein content. A significant correlation between protein content and rainfall is indicated.

A. G. Pollard.

Carotenoids and vitamin-*A* in the blood-serum and organs of higher animals. H. von Euler and E. Virgin (Biochem. Z., 1932, **245**, 252—264).—Results of determinations of carotenoids (xanthophyll etc.) and vitamin-*A* in the serum of cattle, rats, and guinea-pigs, in the livers of cattle, rats, hens, fresh- and salt-water fish, and in the kidneys of guinea-pigs are recorded. In rats the vitamin-*A* content of the liver decreases with age, and feeding with hæmin results in a great reduction in the amount of the carotenoids in the liver. To obtain the best yield of vitamin-*A* from the livers of marine fish fresh organs should be used.

W. McCartney.

Effect of ultra-violet light on the vitamin-*A* of butter. C. L. Shrewsbury and H. R. Kraybill (Science, 1932, 75, 86).—Butter-fat exposed to the light of a quartz–Hg arc in air loses its colour and vitamin-*A* potency; exposure in N_2 results in no loss of colour, but in some loss of growth-promoting power. Loss of potency does not appear to be a direct effect of ultra-violet light. Oxidation produced indirectly may destroy the vitamin-*A*, and irradiation in air and, to some extent, in N_2 appears to produce a substance which retards the growth of rats.

L. S. Theobald.

Vitamin-*A* and -*D* studies with growing chicks. H. S. Gutteridge (Sci. Agric., 1932, **12**, 327—337).—Pilchard oil had a similar antirachitic efficiency to cod-liver oil, but in the proportion of 1% of the ration did not provide sufficient vitamin-*A*. Vitamin-*D* in the oil was reduced by purification.

A. G. Pollard.

Reserves of vitamins-*A* and -*D* of some elasmobranchs. E. André and R. Lecoq (Compt. rend., 1932, **194**, 912—914).—The relative vals. of the liver oils of *Scymnus Lichia*, *Centrina vulpecula*, and *Raia batis* are 90, 40, and 30 for vitamin-*A*, and 40, 35, and 25 for vitamin-*D*, as determined by rat tests. The elasmobranchs can therefore store these vitamins without affecting the nature of the skeleton.

A. Cohen.

Antineuritic vitamin. V. Empirical formula of the antineuritic vitamin. VI. Properties of the antineuritic vitamin of rice-bran. A. G. van Veen (Rec. trav. chim., 1932, **51**, 265—272, 279—283).—V. Numerous analyses of the vitamin hydrochloride (and chloroaurate), obtained essentially by the method previously described (A., 1931, 880), indicate the probable formula $C_6H_{10}O_2N_2$,HCl.

VI. A dil. (1 in 10,000) aq. solution of the vitamin hydrochloride gives a definite ppt. with tungstic acid or $AuCl_3$. The biuret reaction is negative, and NH_2, CO_2H, $\vdots$NH, $\vdots$NMe, OH, OMe, and CO groups are absent. The activity is destroyed by conc. H_2SO_4 at 0° but not by warm dil. H_2SO_4 or dil. HCl. Reduction with Zn, Sn, Mg, or Fe in acid gives inactive oily or resinous products; at least 1 mol. of H_2 is absorbed during catalytic (PtO_2) reduction, but the resulting product is freed from Pt only with difficulty. The hydrochloride is oxidised readily by $KMnO_4$, NaOBr, and H_2O_2 at room temp., and slowly by CrO_3 in AcOH. The pure vitamin, unlike the crude product, is largely destroyed by HNO_2 at 30—40°. Adsorption on protein occurs readily. H. Burton.

Concentration of vitamins-B_1 and -B_2. P. A. Levene (J. Biol. Chem., 1932, 95, 317—326).—Large variations in the growth from month to month of rats fed on a normal diet are recorded. The effect on the growth of the administration of progressively increased amounts of dried yeast, EtOH extract of yeast, and the $COMe_2$ ppt. from yeast press-juice is studied, the two last-named materials being the most potent. Adsorption from the EtOH extract and the press-juice with SiO_2 gel gave preps. more active in promoting normal growth, but less active in producing growth above normal. Further concn. of the adsorbed material by pptn. with 70% aq. KI in EtOH caused decrease in activity, but by combination of this prep. with the EtOH crude extract heated to 140°, the SiO_2 adsorption was shown to have produced a highly active prep. of the B_1 (heat-labile) factor. Pptn. of the solution remaining after the SiO_2 adsorption with $COMe_2$ and treatment of the aq. solution of this ppt. with aq. KI and EtOH gave a ppt. (B_2 factor) inactive alone, but highly active with the above B_1 concentrate. A. Lawson.

Vitamin-B_1 and -B_2 requirements of lactation. D. L. Hussemann and R. A. Hetler (J. Nutrition, 1931, 4, 127—140).—Lactation in the rat depends on vitamins-B_1 and -B_2, between which a quant. relationship may exist. The latter is probably the more important. Chemical Abstracts.

Vitamin-B_2 and the growth factor in tomato juice. R. G. Daggs and A. G. Eaton (Science, 1932, 75, 222—223).—Experiments on rats showing the absence of vitamin-B_2 from tomato juice are recorded, and evidence for the differentiation of this vitamin and a purely growth-promoting factor is advanced.

L. S. Theobald.

Effect of heat on vitamin-B_2 in protein-free milk at varying hydrogen-ion concentrations. N. Halliday (J. Biol. Chem., 1932, 95, 371—385).—Protein-free milk prepared from skim-milk powder by pptn. of the caseinogen with 1% HCl has p_H 4·3, and contains the total vitamin-B_2 content of the milk powder. Heating the protein-free milk at p_H 4·3, 7, and 10 for 1 hr. causes 10, 30, and 40% loss in B_2 activity, respectively, and for 4 hr., 30, 50, and 75% loss; keeping for 1 week at p_H 4·3 and 7 causes no loss but at p_H 10, 75% of the vitamin is destroyed. Evidence is shown of the presence of some growth factor in the milk powder which is destroyed in the prep. of the protein-free milk. Results for vitamin content based on the cure of dermatitis in rats were different from the above results, which were obtained from a study of the growth. A. Lawson.

Nitrogenous metabolism during unbalanced nutrition. III. Nitrogenous metabolism of pigeons during the development of polyneuritic avitaminosis. B. A. Lavrov and N. Jarussova (Biochem. Z., 1932, 244, 390—402; A., 1928, 1161).—Experimental avitaminosis in pigeons produces a negative N balance, although there is no connexion between the loss of N, which increases regularly as the disease develops, and the under-nourishment involved. In normal pigeons the N content of the body is greater at the end of the experiment than at the beginning, whilst in the diseased birds the reverse is the case. It follows that the avitaminosis leads to increased degradation of the N compounds in the body.

W. McCartney.

Antiscorbutic vitamin in home-canned carrots. A. Spohn and A. Hunter (J. Agric. Res., 1931, 43, 1101—1108).—A daily dose of 15—20 g. of raw carrot protects guinea-pigs (350 g.) from scurvy. Canned carrots, heated at 100° for 90 min. with a little vinegar, or under 10 lb. pressure for 40 min., with or without acid, were fed to guinea-pigs in daily doses of up to 50 g. All the animals developed scurvy and died within the test period. Carrots canned with and without added acid gave similar results.

A. Cohen.

Antiscorbutic vitamin in the juice of home-canned tomatoes. A. Spohn (J. Agric. Res., 1931, 43, 1109—1113).—The protective daily dose of raw tomato juice for guinea-pigs (300—400 g.) is 3·5 c.c. After heating at 100° for 20 min., 4 c.c. of juice daily does not prevent scurvy. A. Cohen.

Action of irradiated ergosterol and its relationship to parathyroid function. I, II. H. B. Taylor, C. B. Weld, H. D. Branion, and H. D. Kay (Canad. Med. Assoc. J., 1931, 24, 763—777; 25, 20—34).—Similarity is revealed. The study has been extended to rats, mice, rabbits, and fowl.

Chemical Abstracts.

Prevention of convulsions. E. J. Sheehy (Science, 1932, 75, 81).—Convulsions appeared in pigs fed on a non-vitamin-D diet and confined to a compartment lighted through glass. Animals receiving vitamin-D did not develop convulsions.

L. S. Theobald.

Growth-promoting vitamin (M). L. P. Rosenov (Biochem. Z., 1932, 244, 413—416).—Hay contains a vitamin (vitamin-M) which, in addition to those already known, is necessary for normal growth. A vitamin present in yeast is similar or identical. The growth produced by the new vitamin proceeds according to the law of mass action.

W. McCartney.

Growth-promoting vitamin (M). A. Scheunert (Biochem. Z., 1932, 245, 494—495).—Rosenov's experiments (preceding abstract) provide no evidence for the existence of a vitamin-M.

W. McCartney.

Vitamin-E in iron-treated dry rations. J. Waddell, H. Steenbock, and E. Van Donk (J. Nutrition, 1931, 4, 79—93).—The Fe-treated stock ration produces male and female sterility; treatment with Fe produces an anti-vitamin-E. Fe is also apparently pro-oxygenic. Chemical Abstracts.

Reproduction and lactation on simplified diets. M. W. Taylor (Iowa State Coll. J. Sci., 1931, 5,

No. 4, 355—356).—Cod-liver oil contains vitamin-*E*. Mineral oil prevents reproduction even when wheat-germ oil is included in the diet. Crude cane molasses, beet molasses, and sorghum contain vitamin-*E*. Vitamins-*A* and -*E* are destroyed by $FeCl_2$. Vitamin-B_2 is the limiting factor in lactation on these diets.
CHEMICAL ABSTRACTS.

Male sterility on milk diets. J. WADDELL and E. VAN DONK (J. Nutrition, 1931, 4, 67—77).—Sterility, not due to lack of vitamin-*E*, was observed in rats fed on whole cow's milk, Fe, and Cu.
CHEMICAL ABSTRACTS.

Influence of temperature on the rate of accumulation of chlorophyll in etiolated seedlings. V. N. LUBIMENKO and E. R. HUBBENET (New Phytologist, 1932, 31, 26—57).—The greening of etiolated wheat seedlings takes place between 2° and 48° with a max. rate at 26—30°. The effect of temp. on the process depends on its influence on the synthesis of leucophyll and its transformation into chlorophyllogen. Diminution in the rate of chlorophyll production above 30° is associated with the formation of a colourless substance instead of chlorophyllogen from leucophyll. Technique for the spectrocolorimetric determination of chlorophyll is appended.
A. G. POLLARD.

Action of carbon monoxide on fresh plants. Absorption spectra of chlorophyll-*a* and -*b* in presence of carbon monoxide, nitrogen, oxygen, and carbon dioxide. M. PADOA and N. VITA (Biochem. Z., 1932, 244, 296—302).—Spectroscopic examination of C_6H_6 solutions of chlorophyll-*a* and -*b* treated with N_2, O_2, CO_2, and CO shows that these gases (N_2 excepted) form labile compounds with the pigments, that with CO being the most stable. The result is in agreement with findings concerning the suppression by CO of assimilation in green plants.
W. MCCARTNEY.

Black raspberry. I. Expressed tissue fluids. II. Rates of water movement through excised parts of fruiting canes and current season shoots. III. Growth and yield as influenced by fertilisers. R. E. MARSHALL (Michigan Agric. Exp. Sta. Tech. Bull., 1931, No. 111, 3—9, 9—17, 18—32).—I. The f.-p. depression of the tissue fluids of leaves and shoots increased with the advancing season, changes being greater in leaves than in shoots.

II. The rate of movement of H_2O under 0·5 atm. pressure through sections of old and fruiting canes decreased and in stems and new shoots increased as the season advanced.

III. Early applications of $(NH_4)_2SO_4$ increased yields during the first part of the picking season, but max. yields followed autumn or spring dressings of the fertiliser. Increased yields were associated with the production of smaller berries. Rainfall largely influenced both yield and berry size. Early applications of $(NH_4)_2SO_4$ resulted in an increased no. of shoots per plant, but smaller elongation per shoot. Superphosphate produced an increased shoot elongation after harvesting. Fertilisers did not affect the no. of canes per crown nor the diameter of the canes.
A. G. POLLARD.

Changes accompanying fruit development in the garden pea. C. S. BISSON and H. A. JONES (Plant Physiol., 1932, 7, 91—105).—The abs. wts. of N, total sugars, starch, and ash contents of the pods reached a max. early in development (20—24 days) and subsequently declined with advancing maturity. Acid-hydrolysable polysaccharides (other than starch) and crude fibre increased steadily throughout. In the peas the abs. wt. of N, starch, crude fibre, and ash increased throughout growth. The max. abs. wt. of sucrose was reached about the 32nd day and subsequently declined rapidly, whereas that of acid-hydrolysable polysaccharides was attained towards the end of the development period (40 days). Peas were of harvesting size when the total sucrose content was a max., but the highest % of the sucrose was attained at an earlier date. A. G. POLLARD.

Ripening [of fruit]. L. MOREAU and E. VINET (Compt. rend. Acad. Agric. France, 1932, 18, 197—202).—The sugars which accumulate rapidly in grapes during ripening are derived not only from material synthesised in the leaves, but also from reserves translocated from stems and trunk. A. G. POLLARD.

Biochemistry of the ripening of fruits of the Japanese medlar (*Eriobotrya japonica*). A. L. KURSSANOV (Planta [Z. wiss. Biol.], 1932, 15, 752—766).—Ripening of the fruit is characterised by an accumulation in the pericarp of fructose, sucrose, and malic acid and the almost complete disappearance of maltose, tartaric acid, and amygdalin. The glucose content increases slightly and that of citric acid increases in the early stages of the development of the pericarp and subsequently declines as full ripeness approaches; the proportions of dextrin, starch, hemicellulose, cellulose, proteins, and non-protein-N compounds decrease as ripening advances. In the seed, ripening is accompanied by an increase of amygdalin, starch, hemicellulose, and cellulose and the elimination of maltose. There is a characteristic periodic inversion and synthesis of sucrose and a decrease in I val. The dextrin content remains practically const. and N matter declines. A. G. POLLARD.

Early and late ripening and the acids of fruit. R. NUCCORINI (Annali Chim. Appl., 1932, 22, 10—16).—A study of the variation in the amount of tartaric, citric, and malic acids obtained at three stages of ripening in early and late varieties of cherries, peaches, and plums confirms previous observations (A., 1930, 1482). O. F. LUBATTI.

Variation in fruiting ability of oil palms. H. W. JACK and R. B. JAGOE (Malay. Agric. J., 1932, 20, 14—19).—Comparison of crops from naturally- and artificially-pollinated young palms, grown under average conditions, show a coeff. of variability of 47 for the yield. E. LEWKOWITSCH.

Movement of organic materials in plants. F. C. STEWARD and J. H. PRIESTLEY (Plant Physiol., 1932, 7, 165—171).—A criticism of Crafts (A., 1931, 774). A. G. POLLARD.

Variation of the oxygen content of culture solutions. W. A. CANNON (Science, 1932, 75, 108—109).—When certain plants, *e.g.*, willow, sunflower, and cotton, are exposed to sunlight, a movement of O_2 takes place from shoot to root when the latter is in a culture solution, particularly in pure H_2O. O_2

liberated during photosynthesis thus appears to move downward to supply, wholly or partly, the O_2 requirements of the root. L. S. THEOBALD.

Life-history and composition of the soya-bean plant. H. L. BORST and L. E. THATCHER (Ohio Agric. Exp. Sta. Bull., 1931, No. 494, 88 pp.).—The % of N in soya-bean leaves was much greater than in the stems. As maturity approached the N content of leaves, stems, and pods decreased considerably and that of seeds to a smaller extent. The % of N in the whole tops decreased during the period of active growth and increased towards maturity. At maturity more than one half of the total N was stored in the seed. The P content of leaves and stems decreased as the plants matured. The % of P in mature seeds was approx. four times that of leaves, stems, and pods. The storage of K in the leaves reached a max. in the early stage of pod formation and decreased later. In stems, leaves, and pods there was a decline in K content as the plants matured. The % of K in ripened seeds was greater than that of any other part of the plant. The proportion of Ca and Mg in the whole tops decreased towards maturity. The % of Ca in the various plant organs was in the order leaves>pods>stems>roots>seeds. In leaves and pods the total and % of Mg were much lower than those of Ca. A. G. POLLARD.

Utilisation of atmospheric nitrogen by germinating (lupin) seeds. N. VITA (Biochem. Z., 1932, **245**, 210—217).—The absorption of N by lupin seeds which were germinated in an atm. containing CO was investigated. The absorption of N is related to the development of the seeds and not to bacterial activity. The influence of the concns. of CO_2, O_2, and CO on the absorption is tested. The absorption is not obtained with the seed-meal.

P. W. CLUTTERBUCK.

Physiological significance of hydrocyanic acid glucosides in plant metabolism. N. J. STEKELENBURG (Proc. K. Akad. Wetensch. Amsterdam, 1931, **34**, 1179—1189).—HCN or the corresponding cyanohydrin arises in the leaves, not as the first assimilation product of N, but as a secondary product of protein metabolism. It has no essential significance in the N cycle. No appreciable transport of HCN occurs and the HCN glucosides can act as carbohydrate and N reserve. J. W. SMITH.

Seasonal changes in the composition of the non-protein-nitrogen in the current year's shoots of Bartlett pears. A. S. MULAY (Plant Physiol., 1932, **7**, 107—118; cf. A., 1931, 990, 1197).—The distribution of amide-, humin-, basic, NH_2-, and residual N in pear shoots is recorded. Commencement of new growth is associated with high amide- and NH_2-N contents in both wood and bark. These subsequently decline, reaching a min. in autumn and winter, and rising again as the growing season approaches. During growth amide-N is >NH_2-N in the wood. Basic N is at a min. in June, rising to a max. some time before growth starts and then falling rapidly. Hydrolysis of the humin-N of the bark and the residual N in wood results in an increase of the amide-, NH_2-, and basic N fractions.

A. G. POLLARD.

Local variation in nitrogen content of vine leaves. H. LEGATU, L. MAUME, and L. CROS (Compt. rend., 1932, **194**, 679—681).—Heavy phosphate manuring inhibits the initial absorption of N by growing leaves. The variation in N content of the base leaves is the same for different stocks in the same environment, a finding which justifies the usual method of sampling. P. G. MARSHALL.

Natural regulation of protein metabolism in plants. K. MOTHES (Naturwiss., 1932, **20**, 102—103).—A substance, rich in NH_2-acids, which regulates protein metabolism occurs in the onion. Synthesis of protein induced by this medium is favoured by the presence of O_2. Protein-fission and -synthesis is inhibited by narcosis, but such an inhibition is less in an atm. of H_2. Extraction by $COMe_2$ yields a substance which when in the reduced state activates and when oxidised inhibits proteases. Towards the proteolysis of autolysates $Cu^{\cdot\cdot}$ and $Fe^{\cdot\cdot\cdot}$ exhibit an inhibition which is supported by the reduced but not by the oxidised form. The reduced form gives a positive nitroprusside reaction for -SH and hence its similarity to or identity with glutathione is indicated.

F. O. HOWITT.

Biology of tobacco alkaloids. J. CHAZE (Compt. rend. Acad. Agric. France, 1932, **18**, 239—240).—Nicotine in the tobacco plant occurs in the actively dividing cells. In mature plants there is a translocation towards the periphery of the leaves. The nicotine content decreases in etiolated leaves and in the plant generally after fertilisation of the flowers. Nicotine appears in the aleurone grains of germinating seeds. A proportion of nicotine is exuded from the leaf surface and is considered as a metabolic by-product. A. G. POLLARD.

Distribution and variation of the æsculin content of *Aesculus hippocastanum*, L. G. KLEIN and H. LINSER (Planta [Z. wiss. Biol.], 1932, **15**, 767—816).—Æsculin occurs mainly in the bark, bud scales, and in the pith. The amount in the wood is small and decreases with age. Leaves and leaf-stems contain but little. Roots have a considerable proportion but less than the trunk. The total æsculin content reaches a max. in summer, declining before leaf-fall, and rising to a second max. in early spring. With advancing age the proportion increases. Æsculin is regarded as a reserve material.

A. G. POLLARD.

Glucosides of oleander leaves. G. TANRET (Compt. rend., 1932, **194**, 914—916).—Neriin ($[\alpha]_D$ $-32{\cdot}5°$) and oleandrin ($[\alpha]_D$ $-5°$) have been isolated and separated. Neriin differs from strophanthin ($[\alpha]_D$ $+30°$) in its colour reactions and in yielding glucose as one of its hydrolytic degradation products. Its designation as *l*-strophanthin is unjustified.

A. COHEN.

Celluloses of two water plants, *Ottelia ovalifolia* and *Eichornia crassipes*. J. C. EARL and T. M. REYNOLDS (J. Proc. Roy. Soc. New South Wales, 1931, **65**, 75—79; cf. A., 1930, 1415).—The celluloses are probably identical with cotton cellulose.

N. H. HARTSHORNE.

***l*-Fucose in *Pelvetia canaliculata*, Dec. and Thur.** H. COLIN and P. RICARD (Compt. rend., 1932,

194, 643—645).—After preliminary washing with EtOH, H_2O, and dil. aq. alkali, the dried material is hydrolysed with 2% H_2SO_4 for 1 hr. at 120°. The solution is neutralised with $BaCO_3$, conc., and taken up in EtOH, the *l*-fucose being isolated as the phenylhydrazone. Besides *l*-fucose, a dextrorotatory carbohydrate (osazone, m. p. 225°) is produced by the hydrolysis.
A. LAWSON.

Determination of glucose and fructose in maize tissues. V. H. MORRIS and E. F. WESP (Plant Physiol., 1932, **7**, 47—62).—Comparison is made of the I oxidation method for determining glucose and Nyn's method for fructose with the combined reduction–polarimetric method for mixed sugars in expressed maize juices and EtOH extracts. With pure sugar solutions there is good agreement, but in saps etc. the latter method gave consistently higher results (8%). The separate determination of glucose and fructose as above yielded vals. corresponding with total reducing sugars indicated by Fehling's method.
A. G. POLLARD.

Intake of sugar from hypotonic solutions by *Elodea*. T. WARNER (Planta [Z. wiss. Biol.], 1932, **15**, 739—751).—Shoots of *Elodea*, under uniform conditions of temp., light intensity, and nutrition, contain practically const. amounts of mono- and di-saccharides. Immersion in hypotonic (5%) solutions of glucose or sucrose results in a rapid intake of sugar. After 6 hr. the proportional distribution of mono- and di-saccharides in the tissues becomes normal irrespective of the nature of the sugar taken up. Exclusion of light does not affect the sugar distribution, although the total intake is reduced.
A. G. POLLARD.

Productivity and sugar content of the sugar beet, and the reactive power of its plasma. G. HAFEKOST (Z. Ver. deut. Zucker-Ind., 1931, **81**, 813—824).—Increase of osmotic pressure in a liquid with which living and growing plant cells are in contact causes a corresponding increase inside the cells and contraction of the protoplasm. The highest osmotic pressure of the external liquid at which the contracted plasma is still able to function normally and effect growth is termed the max. osmotic power of the plant, and is a measure of capacity for growth and resistance to drought and cold. It is the same for all living cells in a given plant, and the same for a seed as for the plant grown therefrom. It is transmitted in greater measure to the earliest blooms of a plant than to later ones, and is therefore probably not a Mendelian character. In sugar beets it determines not only capacity for growth and resistance, but also the max. sugar content which the plasma can produce in the cell juice. In beet strains having a high max. osmotic power, high sugar content is possible with high wt. of roots, but in those of low max. osmotic power there is less ability to absorb moisture from the soil, and high sugar contents are the result of restricted root growth. A knowledge of the max. osmotic power is therefore of val. in the selection of seeds.
J. H. LANE.

Ergosterol contents of several edible mushrooms. M. SUMI (Bull. Inst. Phys. Chem. Res. Tokyo, 1932, **11**, 120—123).—Ergosterol contents of 0·1—0·4% of the dry wt. have been found. The amount of ergosterol in *Cortinellus shiitake* increases during growth.
R. CUTHILL.

Carotene and dihydroergosterol in green tea. M. TSUJIMURA (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, **18**, 13—21).—From a light petroleum extract, α- and β-carotenes and a sterol, probably dihydroergosterol, were isolated.
A. COHEN.

Isolation of carotene. H. N. HOLMES and H. M. LEICESTER (J. Amer. Chem. Soc., 1932, **54**, 716—720).—The following carotene contents are reported (mg. per 100 g.): lucerne (cured) 2·3; dehydrated spinach 1·5; fresh spinach 4·8; canned spinach (drained) 15·6; yellow maize gluten 0·3; canned carrots (drained) 6·5. Carotene (+xanthophyll) can be obtained free from chlorophyll by treating (during 3 hr.) green leaves with sufficient 3*N*-NaOH to form a thick paste; the mixture is diluted with an equal vol. of H_2O and extracted with $CHCl_3$. This method is not quant. and the subsequent separation of the two pigments is troublesome. A modification of the usual method of isolation of carotene from (canned) carrots is given, the yield being 0·037 g. per kg. of carrots.
C. J. WEST (*b*).

Are leaf-lipins responsive to solar radiation? W. E. TOTTINGHAM (Science, 1932, **75**, 223—224).—Irradiation of the tomato under "Vitaglass" appears to increase the carotenoid and sterol contents of the leaf tissue, which suggests a causal relation between lipins and increased vegetative development.
L. S. THEOBALD.

Biochemical examination of fertile soil. VII. Soil bacteria and plant germination. A. J. J. VANDE VELDE and A. VERBELEN (Natuurwetensch. Tijds., 1932, **14**, 11—16).—During the germination of carrots and lettuce, the [H˙] of the soil falls; with parsley it rises. There is no definite relationship between the [H˙] of the soil and that of the plant sap, and none was observed between soil acidity and no. of microbes.
S. I. LEVY.

Microbiology of the soil. V. S. VINOGRADSKI (Ann. Inst. Pasteur, 1932, **48**, 89—134).—The technique of a method of studying the bacterial content of soil is described. The method consists essentially in the examination of the cultures of single species of bacteria obtained by the use of media infected with all the species in the soil, but containing only one substrate of a type on which that species exercises its natural function. The cultures are made on discs of SiO_2 gel impregnated with mineral salts and the chosen substrate. If a source of N is required, NH_4Cl or NH_4NO_3 is included. To study the fixation of N, no combined N is introduced, and in the case of the nitrifying bacteria, NH_4Cl or NH_4NO_3 is used as substrate. The media thus prepared are treated with definite quantities of soil, varying according to the bacterial content, and incubated for definite periods, after which a morphological and, if necessary, chemical examination is carried out.
A. LAWSON.

Fixation of protein by the soil. A. DEMOLON and J. BRIGANDO (Compt. rend., 1932, **194**, 311—313).—Colloidal solutions of humus and clay suspensions adsorb considerable quantities of protein.

Nitrification of protein incorporated in soil proceeds at the same rate when the protein is free as when it has been adsorbed on humic acid, whilst humic acid alone or in combination with protein does not undergo nitrification. W. O. Kermack.

Alleged permeability of *Fontinalis* cells to alkaloid cations. R. Collander and K. Sommer (Protoplasma, 1931, 14, 1—10; cf. Boresch, A., 1920, i, 800).—Addition of HCl reduced the toxic action of quinine hydrochloride on leaf cells of *Fontinalis*. The emulsifying action of the salt on the fat of the leaf cells increases regularly with the proportion of undissociated mols. in the solution. Alkaloids enter the cell principally in the form of undissociated mols. of the free base. A. G. Pollard.

Abstraction of ions from salt solutions by higher plants. K. Pirschle and H. Mengdehl (Jahrb. wiss. Bot., 1931, 74, 297—363; Chem. Zentr., 1931, ii, 256).—In salt or nutrient salt solutions the abstraction of cations and anions by pea seedlings is not equiv. The change in p_H of the solution, calc. on equiv. H˙ or OH′, does not accord with that corresponding with the excess of one or other ion; hence ion exchange must have taken place at most on a small scale. A. A. Eldridge.

Toxic action of aqueous sodium chlorate on *Nitella*. H. R. Offord and R. P. d'Urbal (J. Agric. Res., 1931, 43, 791—810).—The toxicity of $NaClO_3$ is due to the anion and is decreasingly effective to *Nitella* at p_H vals. ranging from 4·8 to 8·2. Admixture of $CaCl_2$ reduces toxicity. NH_4Cl and $NaClO_3$ are together more toxic than $NaClO_3$ alone. Neither $NaClO_3$ nor ClO_3' accumulates in the cytoplast of *Nitella*; penetration is slow, and still slower in reduced light intensity. Injury of *Nitella* cells by solutions of $NaClO_3$ is manifested by the outward diffusion of Cl′ from the vacuolar sap, loss of turgidity, and appearance of opalescence in the immersion solution. W. G. Eggleton.

Potash manuring and susceptibility [of plants]. Arland (Ernähr. Pflanze, 1931, 27, 470—474).—The sensitiveness of plants to fungal infection is associated with the no. of active stomata per unit leaf area and with transpiration rates. K fertilisers, while increasing crop yields, decrease transpiration whether expressed per g. of tissue or per unit of leaf area. The actual H_2O content of the tissues is but little affected. A. G. Pollard.

***Penicillium* injury to maize.** H. Johann, J. R. Holbert, and J. G. Dickson (J. Agric. Res., 1931, 43, 757—790).—*P. oxalicum* is essentially a saprophyte. $H_2C_2O_4$, the production of which by *P. oxalicum* depends on the amount and availability of nutrient substances, kills or injures the host cells. Low relative humidity, rather than high temp. alone, may accelerate blighting by increasing the transpiration rate of the host. W. G. Eggleton.

Nutritional disorders in maize grown in sand cultures. N. A. Pettinger, R. G. Henderson, and S. A. Wingard (Phytopath., 1932, 22, 33—51).—Three types of chlorosis are distinguished: *A*, due to Mg deficiency, causes chlorotic streaks from leaf base to tip with irregular margins; *B*, due to excess of Na, similar streaks with smooth margins, and *C*, due to Mn deficiency, discontinuous streaks. Absence of B produces sterility in flowers. Addition of Mn, Zn, Cu, B, and As to nutrients increase the frost-resistance of young plants. A. G. Pollard.

Plant cancer and potassium. M. Viala (Compt. rend. Acad. Agric. France, 1932, 18, 63—67).—Deficiency of K favours the development of plant cancer caused by *B. tumefaciens* in geranium plants. A. G. Pollard.

Mosaic disease in *Solanum tuberosum*. R. C. Malhotra (J. Biochem. Japan, 1931, 13, 473—487).—The effect of a potato mosaic disease on the wt., org. constituents, ash, and calorific val. of its host was investigated. F. O. Howitt.

***X*-Ray analysis of the structure of the wall of *Valonia ventricosa*. I.** W. T. Astbury, T. C. Marwick, and J. D. Bernal (Proc. Roy. Soc., 1932, B, 109, 443—450).—*X*-Ray analysis indicates the presence in the cell wall of *V. ventricosa* of two main sets of cellulose chains crossing at an angle $>60°$ and usually about 80°. The fine crossed striæ on the surface of the wall are parallel to the directions of the chains. W. O. Kermack.

Fluorometric determination of hydrogen-ion concentration. H. Linser (Biochem. Z., 1932, 244, 157—164).—A method is described for determination of the p_H of solutions in terms of the intensity of fluorescence of various substances (æsculin, fluorescein, umbelliferone) at a known p_H. The accuracy is 0·05 p_H. P. W. Clutterbuck.

Volumetric determination of small quantities of phosphorus. M. Odin (Acta Pæd., 1930, 9, 392—404; Chem. Zentr., 1931, ii, 602).—The total, acid-sol., and lipin-P of the blood or cerebrospinal fluid is pptd. as NH_4 phosphomolybdate, which is determined titrimetrically. The suspension of the ppt. in ice-cold H_2O is filtered through a hardened filter secured to the end of a tube 6—8 mm. in diameter. 0·015—0·5 mg. of P can be accurately determined. A. A. Eldridge.

Determination of residual nitrogen by direct Nesslerisation. R. Stöhr (Z. physiol. Chem., 1931, 203, 154—156; cf. A., 1931, 1437).—Lublin's method is very similar to a modification (A., 1924, ii, 871) of Folin's method. "Perhydrol" often contains N, for which tests should be made. J. H. Birkinshaw.

Modification of the Van Slyke nitrogen distribution method. J. W. Cavett (J. Biol. Chem., 1932, 95, 335—343).—A modification of the method requiring only 0·5 g. of protein and less than half the time of the previous method is described. Micro-Kjeldahl determinations are used, cystine is determined by a slight modification of the method of Folin and Marenzi (A., 1929, 1093), and histidine directly by that of Koessler and Hanke (A., 1920, ii, 67). A. Lawson.