BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

DECEMBER, 1932.

General, Physical, and Inorganic Chemistry.

Series and term values in the arc spectrum of tellurium. J. E. Ruedy (Physical Rev., 1932, [ii], 41, 588—594; cf. this vol., 668).—The region λ 3750—11,287 was photographed. Full data and classifications are tabulated. The ionising potential was 8·96 volts. N. M. B.

Optical dissociation of iodine and enhancement of predissociation by collisions. L. A. Turner (Physical Rev., 1932, [ii], 41, 627—634).—In the region 2100—1514, absorption by the atoms of light of wave-lengths 1830, 1783, 1642, 1618, 1583, and 1515 Å. was found, the lines arising from transitions to the normal state of the atom. A predissociation effect, enhanced by collisions, is described and interpreted. N. M. B.

Collisions of the first and second kind in the positive column of a cæsium discharge. F. L. Mohler (Bur. Stand. J. Res., 1932, 9, 493—508).—Previous measurements (*ibid.*, 95) lead to the conclusion that the no. of excited atoms in the first excited state nearly equals the no. which would exist in equilibrium at the electron temp. T_e. With increasing current, the electron concn. and the no. of collisions of the first and the second kinds increase greatly and the life of the excited states is reduced. With increasing pressure, the electron temp. and the concn. of excited atoms decrease, whilst their no. increases. E. S. H.

Light yield in helium, mercury, and nitrogen spectra excited by electron collision. T. Thieme (Z. Physik, 1932, 78, 412—422).—The relative intensity of 16 He and 13 Hg lines was determined for exciting electrons of 9—400 volts. Measurements on N_2 showed that the laws for the excitation function of at. spectra apply to mol. spectra.
A. B. D. C.

Nuclear spin and magnetic moment of Li^7. L. P. Granath (Physical Rev., 1932, [ii], 42, 44—51).—From measurements on the hyperfine structure of λ 5485 the nuclear spin of Li^7 is 3/2, and the nuclear magnetic moment is 3·29 times the theoretical val. for the proton. N. M. B.

Products of dissociation in nitrogen. J. Kaplan (Physical Rev., 1932, [ii], 42, 97—100).—The products of dissociation from the known triplet states are determined from 4 regions of predissociation in the triplet band systems. N. M. B.

Influence of collisions on the time of decay of Na resonance radiation. F. Duschinsky (Z. Physik, 1932, 78, 586—602).—The time of decay of Na resonance radiation is decreased by addition of N_2, which extinguishes the fluorescence, but not by He, which only broadens the resonance lines. Rise of temp. increases the time of decay.
A. B. D. C.

Further doublets of As V. A. S. Rao (Nature, 1932, 130, 630). L. S. T.

Spark spectrum of arsenic. M. Ram (Indian J. Physics, 1932, 7, 299—305).—Data for 130 lines in the region 5651·29—3780·80 Å. are tabulated. N. M. B.

Interferometric measurements in the spectrum of krypton. C. V. Jackson (Proc. Roy. Soc., 1932, A, 138, 147—153).—The wave-lengths of the 10 bright violet lines of the first spectrum of Kr have been measured with an accuracy of about 0·001 Å., by interferometric comparison with the primary standard. The agreement with previous measurements by Humphries on the Ne scale (A., 1931, 7) is good. This group of lines appears to be suitable as a scale for spectroscopic purposes. It is situated in a convenient part of the spectrum, and the lines are suitably spaced and about twice as sharp as those of Ne. L. L. B.

Intensities of components of hyperfine structure of the more intense lines of the visible spectrum of Hg I. Hyperfine structure of the term (Hg^{199}) 7^3D_2. J. Gilles (Compt. rend., 1932, 195, 579—580).—The hyperfine structures of the lines 5790·66, 5769·60, 5790, 4077, and the triplet $6^3P—7^3S$ of Hg^{199} have been investigated, and the intensities of their components determined. The structure of the term 7^3D_2 is discussed. C. A. S.

Series in the complex spectrum of singly-ionised mercury, Hg II. T. S. Subbaraya (Z. Physik, 1932, 78, 541—554). A. B. D. C.

Singlet principal series of mercury. Y. Ishida and S. Hiyama (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 19, 78—82).—Term classifications are corrected by examination of Stark effect patterns.
N. M. B.

Determination of some spectral properties of element 87. H. Yagoda (J. Amer. Chem. Soc., 1932, 54, 3074—3080).—The ionisation potential and doublet separations of the principal series spectrum have been evaluated by several independent methods. The weighted average val. of the ionisation potential is approx. 4·11±0·2 volts. In spectrographic detection of element 87, an intense line of approx. wave-length 4260±100 Å. is to be expected.
H. S. H. (c)

Cold electric arc in vacuum. F. H. Newman (Phil. Mag., 1932, [vii], **14**, 712—718; cf. A., 1926, 1069).—The conditions for maintaining arcs with electrodes of Hg, Na, or K, and their spectra, have been investigated. H. J. E.

Spectroscopic investigation of some metal electrodes in vacuum arcs. F. H. Newman (Phil. Mag., 1932, [vii], **14**, 718—725).—Additional observations with cathodes of Hg, Na, and K are recorded. H. J. E.

Numerical values of atomic constants and *X*-ray terms. H. R. Robinson (Phil. Mag., 1932, [vii], **14**, 605—612).—A crit. review of recent literature. H. J. E.

Fine structure in *X*-ray absorption spectra. J. D. Hanawalt (J. Franklin Inst., 1932, **214**, 569—584).—The fine structure of absorption edges in *X*-ray spectra of vapours and solids is discussed, especially in connexion with Kronig's theory based on the quantum mechanics of electrons in crystal lattices. This theory explains experimental observations and the close relation that exists between the nature of the fine structure and that of the crystal structure of the substance. A. J. M.

***X*-Ray diffraction from calcite for wavelengths 1·5—5 Å.** L. G. Parratt (Physical Rev., 1932, [ii], **41**, 561—576).—Expressions for the coeffs. of reflexion, % reflexion, and width of line are evaluated for calcite for six lines in the region 1·54—5 Å., and are in agreement with experiment. N. M. B.

***K*-Satellites.** O. R. Ford (Physical Rev., 1932, [ii], **41**, 577—587).—A survey of the α-satellites from Ge to Mg, and the β-satellites from Cu to Cl, shows new lines and resolutions of components. New series $K\beta^{IV}$ for Sc, Ca, and *K* and $K\beta^{V}$ for Ca, K, and Cl were found. N. M. B.

Influence of lattice binding on the K_α lines of carbon. M. Renninger (Z. Physik, 1932, **78**, 510—520).—The shape of the 44·6 Å. line of C was investigated for graphite, diamond, and carborundum; carborundum gives the sharpest line, and graphite the least symmetrical. A. B. D. C.

Intensity ratios in the *L*-region of rare earths. G. von Hevesy and E. Alexander (Z. Physik, 1932, **78**, 576—579).—The ratio of intensity for neighbouring rare earths of the *L*α and *L*β lines, when plotted against at. no., gives a curve similar to that of paramagnetism. A. B. D. C.

Ionisation of neon and argon by positive alkali ions of energies from 650 to 2000 volts. J. C. Mouzon (Physical Rev., 1942, [ii], **41**, 605—612).—A new type of apparatus allowed investigation with accelerating potentials up to 2000 volts. N. M. B.

Ionising action of neon atoms rendered metastable by resonance radiation. F. M. Penning (Z. Physik, 1932, **78**, 454—469).—Addition of 0·003% of A to Ne at 40 mm. pressure and illuminated with resonance radiation increased the current passing between electrodes 24 times, due to ionisation of A atoms by metastable Ne atoms. A. B. D. C.

Photo-electric properties of alkali metal films as a function of their thickness. J. J. Brady (Physical Rev., 1932, [ii], **41**, 613—626).—A mol. beam was used to deposit computed nos. of alkali metal atoms on a Ag surface. The max. threshold, the film thickness of its occurrence, and the thickness for max. total photo-electric emission, in mol. layers were, respectively, K, 5800 Å., 3·0, 12·4; Rb, 6200 Å., 1·5, 5·0; Cs, 6600 Å., 1·5, 5·0. Na showed some anomalous effects. N. M. B.

Thermionic and photo-electric work functions of molybdenum. L. A. Du Bridge and W. W. Roehr (Physical Rev., 1932, [ii], **42**, 52—57).—Photo-electric and thermionic data for outgassed Mo in const. equilibrium condition gave the val. 4·15±0·02 volts for the work function. N. M. B.

Electric current from glowing cathodes in gases and vapours at atmospheric pressure. M. Ruhnke (Ann. Physik, 1932, [v], **14**, 881—904).—The dependence of current intensity on electrode potential, distance between electrodes, temp. of cathode, and the nature of the gases adsorbed was investigated, using a W cathode for Hg vapour, H_2, and mixtures of N_2 and H_2. W. R. A.

Electron emission of metals under the influence of *X*-rays. H. Küstner (Ann. Physik, 1932, [v], **14**, 857—880).—Mathematical. W. R. A.

Radiation from cæsium and other metals bombarded by slow electrons. C. Boeckner (Bur. Stand. J. Res., 1932, **9**, 413—418).—The abs. intensity and intensity wave-length distribution of the radiation emitted by Cs, Cr, Ni, Mo, and W, bombarded by slow electrons, is similar in each case. Radiation is much more intense from contaminated surfaces than from clean surfaces. The radiation is probably analogous to the continuous *X*-rays and not due to the excitation of characteristic electron levels. J. W. S.

Analogy between the Dirac electron and the electromagnetic wave: magnetic moment and moment of rotation of the electron. L. de Broglie (Compt. rend., 1932, **195**, 536—537, 577—578).—Mathematical. C. A. S.

Impacts of fast electrons and magnetic neutrons. J. F. Carlson and J. R. Oppenheimer (Physical Rev., 1932, [ii], **41**, 763—792).—Mathematical. The impacts of two free electrons, a fast electron, and a magnetic neutron, the energy transfers, range, and ionising power of the primary electron, and the no. and nature of the impacts of a neutron are considered. N. M. B.

Electron microscope. M. Knoll and E. Ruska (Z. Physik, 1932, **78**, 318—339).—Formation of images by electron and ion beams is discussed, the possible " lens " systems being the pinhole camera, magnetic fields, electrostatic fields between electrodes, and electrostatic fields of space charge. A. B. D. C.

Investigation of the distribution of emission from glowing cathodes with the magnetic electron microscope. M. Knoll, F. G. Houtermans, and W. Schulze (Z. Physik, 1932, **78**, 340—362).—Photographs are reproduced showing the distribution of emission centres on cathodes, and points of intense emission are shown to be surrounded by negative space charge. A. B. D. C.

Inelastic electron scattering in gases. I. C. B. O. Mohr and F. H. Nicoll (Proc. Roy. Soc., 1932, **A**, **138**, 229—244).—Experiments are described on the angular distribution of the inelastic scattering for the case of electrons which have lost energy in raising the atom to the most probable excited state. The investigations were carried out in He, A, and Hg vapour over the angular range 20—160°, using electrons with incident energies between 21 and 196 volts. In the case of A and Hg vapour, the scattering curves show maxima and minima at large angles and are similar to the corresponding elastic curves, whilst at the lower voltages in Hg vapour the resemblance gradually disappears. The results suggest that it is merely the "size" of the atom which is fundamentally important in the explanation of the inelastic, as well as the elastic, scattering of electrons by the heavier atoms. L. L. B.

Scattering of slow electrons. II. E. Feenberg (Physical Rev., 1932, [ii], **42**, 17—32; cf. this vol., 553).—Mathematical. The equations for scattering in He and the inert gases are considered. The former gives good agreement with experiment at the resonance potential; discrepancy at low potentials is due to neglected at. distortion. N. M. B.

Absorption of radiation originating from a beam of electrons in helium. Electron excitation function for the sharp series of orthohelium. L. R. Maxwell (J. Franklin Inst., 1932, **214**, 533—542).—The fact that absorption takes place in excited He from the non-metastable $2P$ and $2p$ states, as well as from the metastable $2S$ and $2s$ levels, is confirmed. Absorption for higher series members is also shown; diffuse series lines are more easily absorbed than the sharp series lines for all the terms of the series. A. J. M.

Reflexion of fast electrons by single crystals. H. Raether (Z. Physik, 1932, **78**, 527—538).—The resolving power of the crystal grating parallel to a beam of electrons is always small, the effective thickness of the crystal being $<10^{-5}$ cm.; this limiting thickness and the deduction of inner potentials are discussed. A. B. D. C.

Electron diffusion, electron attachment, and ageing of negative ions in commercial nitrogen at atmospheric pressure. J. Zeleny (J. Franklin Inst., 1932, **214**, 513—532).—An answer to criticism by Loeb and Bradbury (this vol., 317). New evidence is given for the variation in size and mobility of ions formed in commercial N_2 with age. A. J. M.

Ionisation of helium, neon, and argon under impact of their own atoms and positive ions. C. J. Brasefield (Physical Rev., 1932, [ii], **42**, 11—16).—The no. of electrons liberated from neutral rare-gas atoms under impact was measured as a function of the kinetic energy of the impinging particles; curves show the relative efficiency of atoms and positive ions. N. M. B.

Mobility of alkali ions in gases. C. F. Powell and L. Brata (Proc. Roy. Soc., 1932, **A**, **138**, 117—132).—Previous work (this vol., 670) has been extended to include Li ions and the gases Kr, Xe, N_2, and H_2. In addition, the four-gauze method is applied to (*a*) an investigation of the clustering of impurity mols. around the simple alkali ions; (*b*) an attempt to detect the two isotopes of Li by the difference in their mobility; and (*c*) an unsuccessful search for the missing element no. 87 in samarskite. The results in A, Kr, and Xe are expressed by $k=0{\cdot}55/[\sqrt{\rho(D-1)}](1+m/M)^{\frac{1}{2}}$ (cm., sec., unit e.s. field), where ρ is the gas density at n.t.p., D its dielectric field const., m and M are the masses of the gas atom and ion, respectively. If the factor 0·55 is replaced by a term A, this relation is identical with those deduced by Langevin and Hassé. L. L. B.

Emission of positive ions from hot tungsten. P. B. Moon (Proc. Camb. Phil. Soc., 1932, **28**, 490—496).—Results of measurements of the positive ion currents emitted by W in the temp. range 3000—3200° abs. are in agreement with vals. calc. from the Saha equation. The work function associated with the ionic evaporation lies between 10 and 11 electron-volts. N. M. B.

Reflexion of thallium, lead, and antimony atoms from sodium chloride crystals. J. M. B. Kellogg (Physical Rev., 1932, [ii], **41**, 635—640).—Tl and Pb are in part scattered and in part specularly reflected; Sb shows reflexion deviating from the specular, which may be explained by the interchange of momentum between the incident particle and the crystal. N. M. B.

Polarisation of light originating from moving and stationary particles of hydrogen canal rays. (Miss) W. A. Lub (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 826—837).

Determination of at. wt. of osmium. R. Gilchrist (Bur. Stand. J. Res., 1932, **9**, 279—290).—A method for the extraction and purification of Os is described. The at. wt. obtained from the ratio $(NH_4)_2OsCl_6$: Os is 191·53 and that from the ratio $(NH_4)_2OsBr_6$: Os is 191·57. $(NH_4)_2OsCl_6$ and $(NH_4)_2OsBr_6$ have d^{25} 2·93 and 4·09, respectively. J. W. S.

Atomic mass of potassium. I. End-point of potassium chloride–silver titration. C. R. Johnson and G. W. Low, jun. (J. Physical Chem., 1932, **36**, 2390—2394).—Both potentiometric and nephelometric analyses have been made of KNO_3–HNO_3 solutions saturated with AgCl. The potentiometric titration method is applicable in at. mass measurements, and avoids liquid junction and activity difficulties. C. T. S. (*c*)

Isotopes of uranium. T. R. Wilkins and W. M. Rayton (Nature, 1932, **130**, 475—476).—Evidence of several isotopes of U (from Colorado carnotite) which emit α-rays has been obtained. L. S. T.

Isotopic weight of H^2. K. T. Bainbridge (Physical Rev., 1932, [ii], **42**, 1—10; cf. Urey, this vol., 554).—The mass of neutral H^2 was $2{\cdot}01351\pm0{\cdot}00006$, and $2{\cdot}01351\pm0{\cdot}00018$ relative to He, and $O^{16}=16$, respectively. The equiv. packing fraction was 0·675%. The structure of the nucleus and interpretation of lines in the mass spectra are discussed. N. M. B.

Photochemical separation of isotopes. W. Kuhn and H. Martin (Naturwiss., 1932, 20, 772).—On irradiation of $COCl_2$ with light of wave-length 2816·179 Å. from an Al arc (filtered through Cl_2+Br in CCl_4, barbituric acid in H_2O, and CS_2 in C_6H_{14}), the Cl_2 liberated shows slight excess of Cl^{35}. J. W. S.

Isotopy. F. Paneth (Z. Elektrochem., 1932, 38, 496—504).—A review. G. Hertz has prepared, by diffusion for only 8 hr., a 1 c.c. sample of Ne in which the ratio $Ne^{20} : Ne^{22}$ is 1 : 1 (normally 9 : 1); the lightest fraction obtained contained only 1% of Ne^{22}. H. F. G.

Relation between the periodic system and chemical classifications. I. N. Longinescu (Bul. Chim. Soc. Române, 1931, 34. Reprint, 4 pp.).—Similarities between the periodic system and electrochemical, thermochemical, photochemical, and analytical classifications of the elements are discussed. J. W. S.

Ionising power of artificial H-rays. K. Diebner (Z. Physik, 1932, 77, 581—600).—H-rays were obtained by bombardment of Al and F with α-rays, and the expression $v^3=a(R-x)$ was found to give the velocity in terms of range for ranges between 3 and 33 cm.; in the formula $K=K_0(R-x)^{2/3}$, relating total ionisation with range, K_0 is $2{\cdot}06\times10^4$ for CO_2, or approx. 1/4 that for α-rays. The sp. ionisation near the end of an H-ray path rises to seven times that at a range of 50 cm. A. B. D. C.

Natural hydrogen rays. K. Philipp [with L. Meitner] (Z. Elektrochem., 1932, 38, 545).—The range of the H-rays emitted from a thin film of paraffin on bombardment with α-rays ($2{\cdot}9-3{\cdot}4\times10^6$ volts) varies according to the third power of the velocity. The branching effect observed in the Wilson chamber with Be neutrons has been found to occur also with neutrons derived from B and Li. H. F. G..

Early days of radioactivity. (Lord) Rutherford (Z. Elektrochem., 1932, 38, 476—480).—A lecture. H. F. G.

Development of research on radioactivity, and its influence on related subjects. S. Meyer (Z. Elektrochem., 1932, 38, 480—488).—A lecture. H. F. G.

Radioactivity and elementary chemical processes. O. Hahn (Z. Elektrochem., 1932, 38, 511—518).—A review, dealing mainly with applications of radioactive phenomena in the study of pptn. processes, mixed crystal systems, and adsorption, and in the investigation of structure by the emanation method. H. F. G.

Relation of polonium and thorium-*B* to other metals. G. Tammann (Z. Elektrochem., 1932, 38, 530—532).—The photographic method of studying the distribution of a radioactive element in an alloy is described. When Cu, Ag, Sb, Bi, Zn, Cd, Sn, or Te containing Po crystallise, the Po separates on the surfaces of the nuclei. The solubility of Po in these metals is extremely small: 10^{-10}% in Te, and $5{\cdot}28\times10^{-10}$% in Bi. Th-*B* disperses homogeneously in Pb, but is insol. in other metals, even when 5—10% Pb is present. H. F. G.

Neutron. J. Chadwick (Z. Elektrochem., 1932, 38, 546).—A note of recent work. H. F. G.

Possible existence of multiply-charged particles of mass one. M. Delbrück (Nature, 1932, 130, 593).—Theoretical. It is suggested that the particle of mass 1 may have arbitrary, positive, and negative vals. of its charge. L. S. T.

Enfeeblement of nuclear radiation from beryllium in material screens. J. Thibaud and F. D. la Tour (Compt. rend., 1932, 195, 655—657; cf. this vol., 672).—The log I_x/x curve is convex to the axis of x only if the aperture closed by the Pb screen is small; with a large aperture it is concave. This is attributed to dispersion by the Pb, the less penetrating neutrons being most strongly dispersed. To determine the coeff. of extinction, μ, a narrow aperture, 2·5—3·0 cm., must be used; this gives for recoil atoms producing 8000—10,000 pairs of ions the approx. relation $\mu=0{\cdot}3\sqrt{x}$, a result explicable either by the neutrons having a continuous spectrum of velocities or by their consisting of two principal components of coeff. $\mu_1=0{\cdot}040$ and $\mu_2=0{\cdot}065$. The particles producing $>$22,000 pairs of ions (N nuclei) are unaffected by thicknesses $\not>$7—8 cm. Pb; for greater thicknesses their no. falls rapidly. Extinction in Hg is similar to that in Pb, but for that in medium and light elements the curve is almost a straight line. $\mu_{at.}$ for screens of Sn, Fe, S, and Al containing the same nos. of atoms shows little variation with at. no. C. A. S.

α-Rays and research on atomics. H. Geiger (Z. Elektrochem., 1932, 38, 488—490).—A survey. H. F. G.

Ranges of α-particles from polonium, uranium I, and uranium II with the Wilson chamber. F. N. D. Kurie (Physical Rev., 1932, [ii], 41, 701—707).—Using a new method, the ranges were $3{\cdot}690\pm0{\cdot}005$, $2{\cdot}58\pm0{\cdot}015$, and $3{\cdot}11\pm0{\cdot}01$ cm., respectively. N. M. B.

Energy distribution curves of the disintegration electrons. B. W. Sargent (Proc. Camb. Phil. Soc., 1932, 28, 538—553).—A method for calculating the absorption curve of β-rays forming a continuous spectrum is developed, and gives satisfactory agreement when applied to available data. Distribution curves with momentum of the β-rays from Ac-*C*″, U-X_2, Th-*C*, and Th-*C*″ are found. N. M. B.

Significance of β- and γ-rays for research on atomics. (Frl.) L. Meitner (Z. Elektrochem., 1932, 38, 490).—A note of the difficulties of correlating quantitatively an α- or β-ray change with the state of excitation of the atom, of explaining the continuous energy distribution of emitted nuclear electrons, and the scattering of short wave-length radiation. H. F. G.

Theory of emission of β-rays by radioactive nuclei. A. Schidlof and H. Saini (Helv. phys. Acta, 1932, 5, 73—91; Chem. Zentr., 1932, ii, 15).

Numerical calculation of scattering correction of γ-ray absorption measurements. G. T. P. Tarrant (Proc. Camb. Phil. Soc., 1932, 28, 475—489).

Distinction between neutrons and γ-rays. H. Becker and W. Bothe (Naturwiss., 1932, 20, 757—758).—Experiments are described by which neutrons and γ-rays can be distinguished by using a tube containing paraffin and utilising the radiation from Be excited by α-rays from Po. W. R. A.

Spectrum of the solar corona. T. L. de Bruin (Proc. K. Akad. Wetensch. Amsterdam, 1932, 35, 286—294).—The three red coronal lines 6776, 6704, and 6374 Å., and the green line 5303 Å. are shown, by a crit. examination of available data, to be due to neutral O. M. S. B.

Visible spectrum of Northern lights. L. Vegard (Z. Physik, 1932, 78, 567—575).—A large-aperture prism spectrometer revealed several new lines, the most important appearing beyond 6000 Å. A. B. D. C.

Spectrum of cosmic radiation. A. S. Skąpski (Nature, 1932, 130, 472—473). L. S. T.

Spectrum of cosmic radiation. A. W. Conway (Nature, 1932, 130, 581; cf. preceding abstract). L. S. T.

Interpretation of cosmic-ray phenomena. T. H. Johnson (Physical Rev., 1932, [ii], 41, 545—552).—Schindler's data (cf. this vol., 5) on the transition effect is interpreted on the assumption that the equilibrium between the primary radiation and its secondary corpuscular rays is different in different media. Absorption coeffs. in Pb, Fe, and air are calc. N. M. B.

Dissociation of hydrogen molecules by collision with optically excited xenon atoms. H. R. Calvert (Z. Physik, 1932, 78, 479—485).—Excited Xe atoms dissociate H_2, indicating that no intermediate product is required for this sensitised reaction. A. B. D. C.

Penetration of atoms by photons. V. Posejpal (J. Phys. Radium, 1932, [vii], 3, 390—407).—Theoretical. The propagation of photons in a hypothetical corpuscular ether permeating the atom is investigated, and deductions are compared with various experimental data. N. M. B.

Relativistic Thomas–Fermi atom. M. S. Vallarta and N. Rosen (Physical Rev., 1932, [ii], 41, 708—712).—A solution of the equation for inner at. potential and charge distribution is applied to the case of Hg. N. M. B.

Nuclear structure. E. G. Jones (Nature, 1932, 130, 580; cf. this vol., 894).—Quantised spins and orbital momenta appear to be associated with neutrons and protons in the nucleus. A model built on certain further assumptions accounts for all the observed moments of the nuclei up to O^{16}. L. S. T.

Analytic atomic wave functions. J. C. Slater (Physical Rev., 1932, [ii], 42, 33—43).—Mathematical. N. M. B.

Fundamental particles. R. M. Langer (Science, 1932, 76, 294—295).—The electron and the Dirac magnetic pole can be regarded as fundamental particles. The photon is considered to be a combination of an ordinary and a negative energy electron, whilst the neutron is built from a positive and negative magnetic pole. The proton is a combination of a neutron and a positive electron. L. S. T.

Most probable values of e, e/m, and h. K. Shiba (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1932, 19, 97—121).—Available data are reviewed critically. The val. of e must be revised by correcting for the coeff. of viscosity of air; the X-ray val. of e gives consistent vals. of h by eight methods. The most probable fully corrected vals. are: $e=(4{\cdot}803\pm0{\cdot}004)\times10^{-10}$; $e/m=(1{\cdot}7605\pm0{\cdot}0010)\times10^{7}$; $h=(6{\cdot}624\pm0{\cdot}007)\times10^{-27}$. N. M. B.

Band spectrum of chromic oxide. C. Ghosh (Z. Physik, 1932, 78, 521—526).—CrO bands between 7100 and 4800 Å. were investigated; the heat of dissociation of the lower electronic state is 3·78 volts. A. B. D. C.

Rotational analysis of some CO_2 emission bands. I. R. F. Schmid (Physical Rev., 1932, [ii], 41, 732—750).—Full data are tabulated for the P and R branches composing the red degraded bands at λλ 3254, 3377, 3511, 3534, 3839, 3247, 3370, 3503, 3545, and 3674 Å. The lines of the first five bands show staggering; none shows Zeeman effect. N. M. B.

Spectra of the alkali halide vapours. H. Beutler and H. Levi (Z. Elektrochem., 1932, 38, 589—591).—The absorption spectra (2300—7000 Å.) at 1270°, emission spectra between Ni electrodes in an atm. of He or Ne, and chemiluminescence spectra produced when a stream of halogen enters a vessel containing the vapour of the metal have been determined. A new NaI absorption band system between 3050 and 5000 Å. is reported. H. F. G.

Absorption spectrum of nitrous oxide and heat of dissociation of nitrogen. A. K. Dutta (Proc. Roy. Soc., 1932, A, 138, 84—91).—Gaseous N_2O shows continuous absorption, beginning at 2750 Å., corresponding with 104·0 kg.-cal. Assuming the photochemical reaction to be $N_2O+h\nu=NO+N$, the heat of dissociation of N_2 is calc. to be 8·7 volts. A second absorption, indicating photochemical decomp. of N_2O into NO and excited N atoms, is expected near 1840 Å. Previous work on the heat of dissociation of N_2 is discussed. L. L. B.

Absorption spectrum of nitrogen dioxide. A. Herrmann (Ann. Physik, 1932, [v], 15, 89—108).—The absorption spectrum of NO_2 has been mapped afresh from 2491 to 2459 Å. The effect of an electric field on the spectrum and that of PhCl was investigated. There was no effect up to 36,000 volts per cm. The bands in the neighbourhood of 2459 Å. do not change their sharpness with temp. between −15° and 500°, nor appreciably by addition of another gas up to 3 atm. pressure. A. J. M.

Near ultra-violet bands of silicon chloride. A. C. Datta (Z. Physik, 1932, 78, 486—491).—The heat of dissociation for the lower level associated with these bands is 4·9 volts. A. B. D. C.

Absorption spectra of the samarium ion in solids. I. Absorption by large single crystals of $SmCl_3,6H_2O$. II. Conglomerate absorption of $SmCl_3,6H_2O$ and a partial energy level diagram of the Sm^{+++} ion as it exists in crystalline $SmCl_3,6H_2O$. F. H. SPEDDING and R. S. BEAR (Physical Rev., 1932, [ii], **42**, 58—75, 76—85).—Full data for absorption lines and bands at 20°, 78°, 112°, and 298° abs. are tabulated. The influence of temp. on the positions of lines and multiplets and on the width and intensity of lines is explained by three direct effects of temp. change on the crystal.

II. Additional lines from conglomerates of crystal fragments are reported for 20°, 78°, 169°, and 298° abs., and with those above are used to establish the existence of lower energy levels. N. M. B.

Absorption of substituted benzenes. I. Chlorine series. H. CONRAD-BILLROTH (Z. physikal. Chem., 1932, **B**, **19**, 76—83).—The ultra-violet absorption of all the Cl-derivatives of C_6H_6 in hexane solution has been measured. With increase in the no. of substituents the spectra shift towards the visible. All the spectra exhibit three strong bands, from which two nuclear frequencies are deducible. In a group of isomerides two absorb at almost the same place and have about the same extinction in the strongest band, whereas the absorption of the third, the 1 : 4, 1 : 2 : 4, or 1 : 2 : 4 : 5 derivative, is nearer the visible; extinction in the strongest band is much greater than for the others. R. C.

Influence of substitution on the absorption and reactivity of the carbonyl group. W. HEROLD (Z. Elektrochem., 1932, **38**, 633).—Previous work (this vol., 461) has been extended to solutions of various aldehydes, halogenated and hydroxylated ketones, esters, acid chlorides, and amides in H_2O and alcohols. In all cases when two groups attached to the CO group are positive, in the alternating polarity sense, the normal CO band at 32,000—36,000 cm.$^{-1}$ is observed; if one group is negative, the carbonyl band at $>$40,000 cm.$^{-1}$ appears instead, whilst with two negative groups the absorption lies beyond the range of quartz. When one positive and one negative group are present, there is no change with time of the absorption spectrum, *i.e.*, no semiacetal type of compound is formed by union with the solvent. Chloroacetamide shows gradual change of the absorption with time. H. F. G.

Photochemical changes of histidine and histamine. J. P. BECKER (Pflüger's Archiv, 1931, **228**, 751—754; Chem. Zentr., 1932, i, 2959).—The absorption curves are too close for spectro-analytical use. Glyoxalinylethyl alcohol and glyoxalinyl-lactic acid produce similar curves. A. A. E.

Absorption distribution in solutions with two absorbing constituents. K. WEBER [with E. DRESNER and B. AGRAS] (Z. physikal. Chem., 1932, **B**, **19**, 30—34).—The validity of the absorption distribution formula (A., 1930, 288) has been demonstrated experimentally, the extinction of fluorescence by mol. collisions in fluorescing systems being taken into consideration. R. C.

New isotopic effect. L. GOLDSTEIN (Compt. rend., 1932, **195**, 703—706).—Theoretical. The total isotopic effect on the Raman spectrum of a compound *AB*, where *B* consists of two isotopes, *B′* and *B″*, *B′* being more abundant, is $\Delta\nu_R=(\rho^2-1)(\nu_{n'}/2-\nu_{m'})$, where ρ^2 is the product of the reduced masses of the isotopic mols. and $\nu_{n'}$, $\nu_{m'}$ are respectively the vibrational and rotational frequencies of *AB′* (cf. A., 1931, 1353). C. A. S.

Production of infra-red spectra with electric fields. E. U. CONDON (Physical Rev., 1932, [ii], **41**, 759—762).—The occurrence and intensities of a mol. spectra effect in a strong electric field, analogous to the Stark at. effect, are considered mathematically. N. M. B.

Simplified registering infra-red spectrometer. C. LEISS (Z. Physik, 1932, **78**, 704—706). A. B. D. C.

Infra-red arc spectra photographed with xenocyanine. M. F. MEGGERS and C. C. KIESS (Bur. Stand J. Res., 1932, **9**, 309—326).—Using xenocyanine-sensitised plates, the infra-red arc spectra of Ti, Fe, Co, Ni, and Zr have been measured over the wave-length range 8000—11,000 Å. Most of these lines are interpreted as combinations of previously known terms of the neutral atom. A new Ti term a^5D has been identified. Ti and Fe form suitable comparison spectra for wave-length measurements in the region investigated. J. W. S.

Infra-red spectrum of water and the change of polymerisation caused by dissolved salts. R. SUHRMANN (Z. Elektrochem., 1932, **38**, 627—628).—The dissociation of complex H_2O mols. produced on addition of sol. salts varies, not according to the degree of hydration of the ions of the salt, but in the order of the ionic vols. Certain salts, *e.g.*, alkali halides, cause the bands to become sharper but only slightly displaced, whilst others ($MgSO_4$) cause flattening and the appearance of a new band at 1·4—1·8 μ. Acids and alkalis produce considerable flattening and strong absorption above 1·4 μ. $H^{\cdot}$ and OH' unite with the more strongly dissociated $(H_2O)_n$ mols. H. F. G.

Absorption of carbon tetrachloride in the infra-red. C. SCHAEFER and R. KERN (Z. Physik, 1932, **78**, 609—629).—38 bands observed in the spectrum of CCl_4 between 1 and 22 μ are expressed as harmonic and combination frequencies of the four Raman bands at 215, 304·5, 439·5, 757·5, and 792·5 cm.$^{-1}$ The intensities of the bands are discussed. A. B. D. C.

Raman effect in solutions of cupric salts. A. DA SILVEIRA (Compt. rend., 1932, **195**, 652—653; cf. this vol., 1075).—Solutions of $CuSO_4$ and $Cu(NO_3)_2$ show respectively a new line at 450 cm.$^{-1}$ with a triplet around 1110, attributed to SO_4'' (a case of destruction of degeneration), and lines closely resembling those of $Ca(NO_3)_2$. C. A. S.

Raman and infra-red spectra of carbon dioxide. A. LANGSETH and J. R. NIELSEN (Z. physikal. Chem., 1932, **B**, **19**, 35—46).—Mecke's interpretation of the Raman spectrum of CO_2 (this vol., 559) is unacceptable; Fermi's theory (A., 1931, 1111) satisfactorily accounts for the two strong lines. The

Raman spectrum of gaseous CO_2 has proved to be more complex than had been supposed, several weak lines being present in addition to the two strong lines. The moments of inertia of the mol. in the excited states corresponding with the two latter have been calc. A partial energy diagram of the CO_2 mol. is reproduced. R. C.

Raman effect in molecules and crystals. E. Fermi (Mem. R. Accad. Italia, 1932, 3, [Chim.], 5—22).—Exceptions to the ordinary selection laws for the Raman effect in polyat. mols. are discussed for the case of CO_2. The weak continuous Raman spectrum of NaCl and the spectrum of $CaCO_3$ can also be explained. O. J. W.

Raman spectra of iodides. I. Phosphonium iodide and methyl iodide. N. G. Pai (Indian J. Physics, 1932, 7, 285—297).—The lines for PH_4I are 930, 1040, 1113, 1259, 1416, 2304, and 2370 cm.$^{-1}$, attributed to the PH_4 ionic group distorted by the I ions. Lines for MeI are 524, 895, 1028, 1242, 1434, 1760, 2050, 2461, 2557, 2796, 2849, 2950, and 3050 cm.$^{-1}$; correlation with infra-red absorption data is given. N. M. B.

Raman effect. Allenic hydrocarbons. Preparation of $\alpha\alpha$-dimethylallene. M. Bourguel and L. Piaux (Bull. Soc. chim., 1932, [iv], 51, 1041—1062).—The characteristic of the Raman spectra of allene, and methyl-, propyl-, butyl-, and $\alpha\alpha$-dimethylallenes is a strong line at about 1100 (cf. this vol., 109). The Raman spectra of β-methyl-Δ^{β}-butene (I) (alone and admixed with β-methyl-Δ^{α}-butene), isoprene (II), and β-bromo-γ-methyl-Δ^{β}-butene (III) are also given. The Raman spectrum of the product, b.p. 35—36·5°, obtained in about 25% yield [together with (III)] from $\beta\gamma$-dibromo-β-methylbutane (IV) and quinoline shows that it is a mixture of (I) and (II); (I) results by elimination of 2 Br (not 2 HBr) from (IV). H. B.

Specific heat and dissociation of simple hydrocarbons. R. Ruedy (Canad. J. Res., 1932, 7, 328—336).—The vals. of C_v for CH_4, C_2H_4, and C_2H_2 calc. from the Raman and infra-red spectra agree with experimental data. The calc. heat of dissociation of CH_4 into CH_3 and H is 101 g.-cal. per mol., whilst thermochemical data indicate 110—130 g.-cal. The no. of collisions in which the energy could be transferred from mol. to mol. is too small to account for the dissociation of CH_4 into CH_3 and H when passed through a SiO_2 tube at 1000°. Dissociation into CH_2 and H_2 is probable. The fact that a mol. remains in any given vibrational state for a finite time is important in the elucidation of thermal decomp., the investigation of the velocity of ultrasonic waves in gases being of val. in this connexion. The possible modes of vibration in the C_2H_6, C_2H_4, and C_2H_2 mols. are considered. D. R. D.

Resonance fluorescence of benzene. G. B. Kistiakowsky and M. Nelles (Physical Rev., 1932, [ii], 41, 595—604).—The fluorescence of C_6H_6 vapour, excited by the 2536 Å. Hg line, for the pressure range 25—0·01 mm. is described and interpreted. Full data are tabulated; vibrational frequencies found for the normal mol. are: 160, 793(?), 988, 1200, 1354, 1663, and 3139 cm.$^{-1}$ N. M. B.

Theory of fluorescence extinction. K. Weber (Z. physikal. Chem., 1932, B, 19, 22—29).—Experimental evidence against Baur's desensitisation theory (this vol., 578) is described. Electrolytes both extinguish the fluorescence of pinakryptol-yellow and cause pptn. There is no direct connexion between these two effects, for extinction by chlorides, unlike pptn., is almost independent of the cation, and pptn. is retarded by org. and inorg. deactivators. R. C.

Luminescence of solid nitrogen. J. Kaplan (Physical Rev., 1932, [ii], 42, 86—96).—An explanation is proposed for the radiations observed by McLennan in the luminescence of solid N. N. M. B.

Colour of silver as a function of its surface nature. A. Kutzelnigg (Kolloid-Z., 1932, 61, 48—50).—With repetition of reflexions, caused by looser packing of the crystallites, the colour of Ag passes from mirror-like silver, through matt-white, yellowish-grey, brownish-black, to black. A yellowish colour can be recognised photometrically in all these forms. E. S. H.

Photo-electric method for detecting Gurwitsch's mitogenetic rays. L. Petri (Atti R. Accad. Lincei, 1932, [vi], 15, 919—925).—Very short ultra-violet waves are emitted by living, but not by dead, vegetable matter. D. R. D.

Becquerel effect on selenium electrodes. M. Volmer and W. Moll (Z. physikal. Chem., 1932, 161, 401—410).—The effect on a Pt electrode thinly coated with Se and exposed to monochromatic light is a max. at a potential near that of the dropping electrode, the quantum yield then agreeing approx. with the principle of photochemical equivalence. The photo-electric current is accompanied by the formation of H_2Se in approx. the amount required by Faraday's law if the Se were univalent. The primary process is probably $Se+H^{\cdot}+\ominus=HSe$, the electron being released from within the Se, followed by $2HSe=Se+H_2Se$. A Becquerel effect has been detected in a Pt electrode thinly coated with S. R. C.

Emission mechanism of oxide cathodes. H. Kniepkamp and C. Nebel (Wiss. Veröff. Siemens-Konz., 1932, 11, No. 2, 75—87).—An oscillograph method was used to study the change of activity with time of a BaO cathode. The change in activity is to be ascribed to the varying surface covered with O atom-dipoles. A. J. M.

Nature of spontaneous currents on illumination of various detector substances. F. Waibel (Z. Physik, 1932, 78, 423—429).—Semi-conductors act as detectors through thermal effects, and not through barrier layer photo-effects. A. B. D. C.

New experiments on the photo-electric effect. Q. Majorana (Rend. Accad. Sci. Ist. Bologna, 1931, 35, 62—72; cf. this vol., 898).—The photo-electric effect produced when a metal, *e.g.*, Zn, and other metals are illuminated by the light of a Hg-vapour lamp can be demonstrated by the attraction of the metal towards a positively-charged silvered quartz thread or Al needle. No movement of thread or needle occurs when they are negative with respect to the metal. O. J. W.

Crystal photo-effect in clear zinc blende. H. Dember (Naturwiss., 1932, 20, 758).—The effect has been observed in raising the temp. to 365°. W. R. A.

Photographic study of growth of electrolytic striations. R. Taft and O. R. Bingham (J. Physical Chem., 1932, 36, 2446—2454).—The striations of Cu deposited in presence of gum arabic have been studied. The formation and growth of the striæ are explained by assuming adsorption of a gum arabic–copper hydroxide complex on the surfaces of the electro-deposited Cu crystals. Gum arabic increases the cathode polarisation of Cu. R. H. C. (*c*)

Electrical conductivity of deformed rock-salt crystals. Z. Gyulai (Z. Physik, 1932, 78, 630—638).—Sudden compression of NaCl in the form of pastilles causes a sudden increase in conductivity; at high temp. NaCl has a large diminishing conductivity. These changes indicate that the conductivity of NaCl has a stable and a labile component, the labile component appearing on mechanical deformation of the crystal. A. B. D. C.

Variation with temperature of dielectric constant and density of nitrobenzene in vicinity of m.p. H. Braune and W. Giertz (Z. physikal. Chem., 1932, **161**, 389—394).—Wolfke and Mazur's observations (this vol., 329), suggesting transition in the liquid phase, could not be confirmed. R. C.

Dipole moments and molecular structure. III. Oxychlorides of sulphur. J. W. Smith (Proc. Roy. Soc., 1932, A, **138**, 154—161).—The mol. polarisations and refractions of $SOCl_2$ and SO_2Cl_2 have been calc. from data derived from measurements of the dielectric consts. and densities of C_6H_6 solutions of the two chlorides at 25° and 45°, and the vals. of n^{15} and d^{15} for the same solutions. The electric moments calc. from the change in the mol. polarisation with temp. are 1·38 and $1·64 \times 10^{-18}$, respectively, whilst those calc. from the mol. polarisation at 25° and the mol. refraction are 1·58 and $1·86 \times 10^{-18}$, respectively. The discrepancy indicates either that the dipole moments increase with rise of temp., or that the at. polarisations of these mols. are high. L. L. B.

Variation of dielectric constant with temperature. II. Electric moments in the ethylene halides. E. W. Greene and J. W. Williams (Physical Rev., 1932, [ii], **42**, 119—140).—Theoretical expressions for free rotation are discussed. Dielectric const. and density measurements at various temp. by a new method are recorded for $C_2H_4Cl_2$ and $C_2H_4Br_2$ vapour, and are used to calculate the electric moments. The vals. deviate at lower, and converge at higher, temp. N. M. B.

Oxygen valency angle and structure of glucose and related compounds. H. Hibbert and J. S. Allen (J. Amer. Chem. Soc., 1932, **54**, 4115—4116).—The electric moment and O valency angle are: ethylene oxide 1·88, 77°; propylene oxide, 1·88, 77°; trimethylene oxide 2·01, 102°; tetrahydrofuran 1·71, 105°; tetrahydropyran 1·87, 88°. The "normal" O valency angle is 90±5°. From these results the pyranose ring of carbohydrates and related compounds represents a "strainless" puckered ring system and the furanose ring structure a strained flat ring. C. J. W. (*c*)

Molecular and atomic volumes. XLII. Revision of the densities of the aluminium halides. W. Biltz [with O. Hülsmann]. **XLIII. Densities of crystalline nitric, sulphuric, and phosphoric acids, and related substances at low temperature.** W. Biltz and O. Hülsmann (Z. anorg. Chem., 1932, **207**, 371—376, 377—384).—XLII. Data are recorded for $AlCl_3$, $AlBr_3$, and AlI_3 at 18° to −180°; the zero mol. vols. are 53·3, 78·0 (lit. 83·88), and 98·3 (lit. 102—103), respectively. No evidence could be obtained for the existence of two forms of $AlCl_3$.

XLIII. Data are recorded for HNO_3, SO_2, SO_3, H_2SO_4, SeO_2, P_2O_5, HPO_3, H_3PO_4, I_2O_5, and HIO_3, and the zero mol. vols. are given. The calc. val. for O is 10·9. The mol. vol. of vitreous P_2O_5 is smaller than that of the cryst. form. SO_2 and SO_3 have approx. the same mol. vol. From vol. relationships the oxy-acids cannot be regarded as hydrates of the corresponding oxides. H. F. G.

Influence of molybdates on rotatory power of xylose. E. Darmois and (Mlle.) M. Murgier (Compt. rend., 1932, **195**, 707—709).—Addition of varying proportions of MoO_3 and NaOH to aq. xylose has a much greater effect on the rotatory power than in the case of glucose, but indicates the existence of the similar compound, $NaHMoO_4,2C_5H_{10}O_5$ (cf. A., 1921, i, 498; 1931, 939). The equilibrium const. at 20° for xylose+molybdate $\rightleftharpoons$ complex is 0·10. C. A. S.

Magnetic birefringence in solutions of sodium chlorate and sodium bromate. S. W. Chinchalkar (Indian J. Physics, 1932, 7, 317—321).—A feeble negative magnetic birefringence is shown. N. M. B.

Electronic structures of polyatomic molecules and valency. II. Quantum theory of the double linking. R. S. Mulliken (Physical Rev., 1932, [ii], **41**, 751—758; cf. this vol., 902).—The structure, in terms of mol. orbitals, and formation from two excited CH_2 radicals of C_2H_4 and its derivatives, the C:N, N:N, C:C, O:O, and BH_3:BH_3 groups are discussed. The *cis* $\rightleftharpoons$ *trans* change by ultraviolet light is explained by the variation of the angles of the planes of the CH_2 radicals. N. M. B.

Chemistry in space. S. S[ugden] (Nature, 1932, 130, 567).—A summary of the application of the electronic theory of valency to the tetrahedral atom model and of the problem of the optical activity of living matter. L. S. T.

Modified ionic states in crystals. C. P. Snow and F. I. G. Rawlins (Proc. Camb. Phil. Soc., 1932, **28**, 522—530).—The band spectra of Cr and some other transitional elements contain lines which must be of ionic or quasi-ionic origin, and can be explained as due to inter-combination transitions, in agree-

ment with theoretical intensity conditions, which apply also to the case of the rare-earth spectra.
N. M. B.

Nature of chemical linking. IV. Energy of single linkings and relative electronegativity of atoms. L. Pauling (J. Amer. Chem. Soc., 1932, **54**, 3570—3582; cf. this vol., 561).—Extreme ionic and normal covalent linkings are defined. The energy of 21 single linkings can be calc. from data for heats of formation and combustion of gaseous mols. on certain assumptions. Deviations from additivity of the energies of normal covalent linkings (*ibid.*, 901) are positive for all linkings but one, and increase with the ionic character of the linking. Vals. of the energy of 20 linkings for which experimental data are not available are predicted.
G. M. M. (*c*)

Quantum theory of double linking. R. S. Mulliken (J. Amer. Chem. Soc., 1932, **54**, 4111—4112).—Preliminary note. C. J. W. (*c*)

Electron affinity of free radicals. IV. Compounds not aromatic hydrocarbons. H. E. Bent, M. Dorfman, and W. F. Bruce (J. Amer. Chem. Soc., 1932, **54**, 3250—3258; cf. this vol., 680).—ΔF is the same for the addition of Na to diphenylanisylmethyl or CPh_3. ΔF for the addition of Na to 9-chloro-10-phenanthroxyl is more negative than for C-free radicals. Pentaphenyl*cyclo*pentadienyl, tri-*p*-anisylmethyl, and αα-diphenyl-β-trinitrophenylhydrazyl do not form additive compounds when treated with 1% Na amalgam. R. H. F. (*c*)

Electronic constitution of some simple and complex derivatives of copper in relation to their magnetic properties. S. S. Bhatnagar, B. Singh, and A. Ghani (Indian J. Physics, 1932, **7**, 323—330).—Susceptibilities in the solid and liquid state are given for Cu acetate, propionate, butyrate, valerate, hexoate, acetylacetonate, acetylacetate, and dimethylglyoxime, and for bisethylenediamminocupric nitrate, thiosulphate, and hypophosphite. The compound, when the central atom or ion contains completed sub-groups, has zero magnetic moment and is diamagnetic, and where the sub-groups are incompletely filled it is paramagnetic.
N. M. B.

Affinity capacity, affinity, and electroaffinity. G. Urbain (J. Chim. phys., 1932, **29**, 325—338).—A lecture. J. G. A. G.

Reversible processes in a magnetic material with strong inner tension. R. Becker (Wiss. Veröff. Siemens-Konz., 1932, **11**, No. 2, 1—11).—Mathematical. A. J. M.

Mechanism and experimental determination of magnetic multiplets. R. Forrer and J. Martak (J. Phys. Radium, 1932, [vii], **3**, 408—436).—The multiplets were investigated by a study of hysteresis cycles of Fe, Ni, and Co. Ni shows a doublet, Fe two types of triplet, and Co a quadruplet. The deformation by intense fields, orientation, and inversion of the multiplets are described.
N. M. B.

Relation between the electric and diamagnetic susceptibilities of monatomic gases. J. P. Vinti (Physical Rev., 1932, [ii], **41**, 813—817; cf. Kirkwood, this vol., 215).—Mathematical. N. M. B.

Variation of the principal magnetic susceptibilities of certain paramagnetic crystals with temperature. B. W. Bartlett (Physical Rev., 1932, [ii], **41**, 818—832).—The Curie and Weiss consts. for the temp. range 60° to —45° were determined for $CoSO_4,7H_2O$, and for 5 crystals of the series $MR_2(SO_4)_2,6H_2O$, where M=Co, Cu, or Ni, and $R=NH_4$ or K, using EtOH as solvent for the auxiliary paramagnetic salt at low temp. The Curie const. showed small, and the Weiss const. considerable, variation; both decreased progressively with change of metal ion $Co \longrightarrow Ni \longrightarrow Cu$. The effect of the change $NH_4 \longrightarrow K$ was slight.
N. M. B.

Magnetic behaviour of bivalent copper, nickel, and cobalt compounds. W. Klemm and W. Schüth (Z. Elektrochem., 1932, **38**, 621).—The magnetic properties of the halides, oxides, sulphides, and selenides indicate that the tendency to the formation of metallic-type compounds increases with increasing ionisation potential of the cations. There is no abrupt change of magnetic behaviour on passing from highly complex salts to simple binary compounds. H. F. G.

Change of paramagnetic susceptibility due to absorption of light. D. M. Bose and P. K. Raha (Nature, 1932, **130**, 544).—Absorption of light increases the paramagnetic susceptibility of $CrCl_3$ solution (cf. A., 1931, 670). L. S. T.

Diamagnetism of molecules. D. P. Ray-Chaudhuri (Nature, 1932, **130**, 579—580).—As a first approximation for diat. homopolar mols. the loss in diamagnetism on mol. formation is proportional to the binding energy. L. S. T.

Magnetic properties of isotropic ferromagnetic substances. R. Gans (Ann. Physik, 1932, [v], **15**, 28—44).—Mathematical. A. J. M.

Magnetic susceptibility of carbamides, *iso*carbamides, and sulphamide. G. Devoto (Atti R. Accad. Lincei, 1932, [vi], **15**, 973—976).—The magnetic susceptibility and sp. gr. of the following solid compounds have been measured: $R\cdot CO\cdot NH_2$ (where $R=NH_2$, NHMe, NHEt, NHPr, and NMe_2), $CO(NHMe)_2$, $CO(NEt_2)_2$, $NH{:}C(NH_2)\cdot OMe$, $NH{:}C(NH_2)\cdot OEt$, and $SO_2(NH_2)_2$. Isomeric compounds have almost identical susceptibilities.
D. R. D.

Growth of metal crystals in metal vapour. II. M. Straumanis (Z. physikal. Chem., 1932, B, **19**, 63—75; cf. A., 1931, 1115).—In the sublimation of Zn in a H_2 atm. at < 4 mm. pressure, small crystals are formed, the habit of which agrees with Stranski's theory (cf. this vol., 986). The crystals have no definite orientation relative to the glass on which they are deposited. On rapid sublimation in a high vac. a coherent film is formed instead of a cryst. powder. Apparently no dimorphic regular form of Zn exists. R. C.

Swelling of graphite. H. Thiele (Z. anorg. Chem., 1932, **207**, 340—352).—Some samples of graphite exhibited pronounced unilateral swelling when moistened with HNO_3 and heated. The phenomenon is due to union of the laminæ at the edges, with the production of a concertina-shaped mass. It is inhibited by pressure. No oxidation of the C occurs during the swelling, and the nature of the gas filling the spaces between the laminæ is of no significance. Fuming H_2SO_4, anhyd. $FeCl_3$, and Br produce the effect, which in the case of the last-named is to some extent reversible. H. F. G.

Geometrical method of determining the crystal axes of single-crystal wires. B. Chalmers (Phil. Mag., 1932, [vii], **14**, 612—616).—The specimen is stretched, and the axes are calc. from measurements made on the surface markings accompanying glide. H. J. E.

Diffraction of *X*-rays by liquid metals. J. T. Randall and H. P. Rooksby (Nature, 1932, **130**, 473—474).—Liquid Na, K, Rb, and Cs diffract *X*-rays in one main direction, giving a single narrow band the spacing of which is approx. equal to that of the strongest line in the corresponding solid. L. S. T.

Distribution of crystal lattice in stretched aluminium. Y. Tani (J. Fac. Eng. Tokyo, 1932, **20**, 133—146).

Lattice dimensions of niobium, tantalum, and some niobates and tantalates. L. L. Quill (Z. anorg. Chem., 1932, **208**, 257—272).—The following consts. have been determined for Nb and Ta (tempered at 800°), $NaNbO_3$, $NaTaO_3$, $KNbO_3$, and $KTaO_3$, in the order named: a 3·299, 3·298, 3·889, 3·881, 4·005, 3·981, all ±0·002 Å.; $d_{\text{calc.}}$ 8·575, 16·69, 4·609, 7·141, 4·634, 7·022. F. L. U.

***X*-Ray examination f lanthanum, cerium, and neodymium.** L. L. Quill (Z. anorg. Chem., 1932, **208**, 273—281).—La (hexagonal) has a $3·75\pm0·010$, c $6·06\pm0·030$ Å., $d_{\text{calc.}}$ 6·194. Ce, face-centred cubic, a $5·143\pm0·004$ Å., $d_{\text{calc.}}$ 6·799. Nd, hexagonal close-packed, a $3·66\pm0·010$, c $5·88\pm0·030$ A., $d_{\text{calc.}}$ 6·991. F. L. U.

Precision measurements of lattice constants by the powder method. M. C. Neuburger [with G. Masing] (Z. Elektrochem., 1932, **38**, 631—632).—The error caused by incomplete parallelism of the *X*-rays used is noted; it may be obviated by a method of calibration due to F. Regler. By using a calibration curve derived from 4 rock-salt powder diagrams, the total error may be reduced to 0·01%. Be has a $2·2680\pm0·0002$, c $3·5942\pm0·0003$ Å., $d_{\text{calc.}}$ 1·857. H. F. G.

Structure of electrodeposited metals. II. L. B. Hunt (J. Physical Chem., 1932, **36**, 2259—2271). E. H. (*c*)

Charge distribution in ions and the grating constant of rubidium bromide according to the statistical method. H. Jensen (Z. Physik, 1932, **77**, 722—745).—A detailed application of a method previously described (Lenz, this vol., 1078); repulsive forces in these lattices are due to superposition of electric charge clouds, and consequent increase in the kinetic energy of the mol. Fermi gas, rather than to electrostatic repulsions. A. B. D. C.

Transformation of β-quartz into cristobalite. A. N. Schukarev (J. Gen. Chem. Russ., 1932, **2**, 231—237).—Not $<$ 2 mols. of β-quartz take part in the reaction of transformation into cristobalite. R. T.

Crystal structure of potassium dithionate. M. L. Huggins and G. O. Frank (Amer. Min., 1931, **16**, 580—591).—$K_2S_2O_6$ has a 9·82, c 6·36 Å.; space-group D_3^2. $Rb_2S_2O_6$ has a 10·0, c 6·3 Å. Both are hexagonal (trigonal trapezohedral). Ch. Abs.

***X*-Ray examination of chrome ores. I. Lattice dimensions. II. Theoretical densities.** G. L. Clark and A. Ally (Amer. Min., 1932, **17**, 66—74).—Vals. of a vary inversely with the Al_2O_3 content; $d_{\text{calc.}}=d_{\text{obs.}}\pm\ngtr1·3\%$. Ch. Abs.

***X*-Ray study of the polymorphism of normal saturated fatty acids.** F. D. La Tour (Ann. Physique, 1932, [x], **18**, 199—284).—The monoacids with an even no. of C atoms from C_{12} to C_{18} show α and β forms, the transition temp. $\beta\longrightarrow\alpha$ varying, as a function of the no. of C atoms, similarly to m.p. Transition points for oriented layers differ from those for whole crystals. Similar dimorphism is shown by the first members (malonic, succinic, and glutaric) of the di-acid series, and for the higher di-acids with an odd no. of C atoms. Full data are tabulated. N. M. B.

Crystallographic examination of αα′-di-*p*-tolylacetone. H. L. Piotrowski (Arch. Min. Soc. Sci. Varsovie, 1931, **7**, 1—7).—The monoclinic crystals have $a:b:c=1·4373:1:5·6247$, β 116° 50′; n_D 1·65. R. T.

Crystalline structure of α-methylxyloside. E. G. Cox (J.C.S., 1932, 2535—2543).—Comparison of the lattice consts. of this compound with those of β-methylxyloside and α-xylose indicates close relationship. The mol. arrangement of α-methylxyloside is discussed. The pyranose sugar ring is probably not completely planar or of *trans*-strainless form. A. J. M.

Thermo-electromotive force between magnetic and non-magnetic iron. T. Kousmine (Helv. phys. Acta, 1931, **4**, 364—366; Chem. Zentr., 1932, i, 3390).

Non-conducting modifications of metals. J. Kramer and H. Zahn (Naturwiss., 1932, **43**, 792).—By cathode sputtering or by distillation under suitable conditions, Fe, Ni, Pt, Zn, Cd, Sn, Sb, and probably W can be obtained in forms of abnormally low conductivity which are stable only below a certain temp. characteristic of each metal. D. R. D.

Magnetic effects in iron crystals. A. G. Hill (Phil. Mag., 1932, [vii], **14**, 599—604).—Between −190° and 162° the magnetisation curve is linear for fields below 2 gauss, and non-linear for fields up to 20 gauss. The magnetic lag is greater at lower temp. H. J. E.

Effect of strain on magnetostriction and magnetisation in nickel. C. W. Heaps (Physical Rev., 1932, [ii], **42**, 108—118).—Large discontinuities in the magnetisation curve and small Barkhausen jumps may be due to magnetic instability produced in small regions by local strains. N. M. B.

Magnetostriction and magnetisation of single crystals of the iron–nickel series. F. Lichtenberger (Ann. Physik, 1932, [v], **15**, 45—71).—The magnetisation curves and magnetostrictions of single crystals of the Fe–Ni series of various compositions were determined. The unique position occupied by "permalloy" is discussed. It seems to be due to the fact that its composition is approx. the mean of that at which the direction of easiest magnetisation changes (71% Ni), that at which the polycryst. magnetostriction disappears (83% Ni), and that at which there is equal magnetostriction in all directions (85·5% Ni). A. J. M.

Influence of impurities on the cohesion limits and on the ultra-microscopic sol formation of synthetic rock-salt crystals. III. Addition of heavy metal chlorides. W. Metag. **IV. Density determinations for pure salt crystals and for rock-salt with heavy metal impurities.** J. Köhler (Z. Physik, 1932, **78**, 363—374, 375—382).—III. Increase in strength of crystals is always due to impurity in the disperse phase. Doubly-charged foreign cations give a greater increase in strength than singly-charged.

IV. A displacement method was used to determine the densities of NaCl, KCl, and KBr to an accuracy of 0·01%; the method can be used to determine impurities. A. B. D. C.

Plastic extension of α-iron crystals. W. Fahrenhorst and E. Schmidt (Z. Physik, 1932, **78**, 383—394).—Stretching of Fe was studied at room temp. and at −185°; crystallographic translation with $T=\{123\}$ and $t=[111]$ is the probable mechanism. A. B. D. C.

Incidence of lattice distortion and orientation in cold-rolled metals. W. A. Wood (Phil. Mag., 1932, [vii], **14**, 656—665).—The degree of distortion of Cu, an alloy 70% Ni, 25% Fe, 5% Cu, Fe-Al (4% Al), and Fe-Si (4% Si) initially increases rapidly with reduction in thickness of the metal, reaching a const. val., characteristic of the metal and unchanged by further reduction. Lattice distortion, when it occurs, reaches a max. val. before preferred orientation appears. H. J. E.

Mechanism of the allotropic transformation of cobalt and thallium. U. Dehlinger (Metallwirt., 1932, **11**, 223—225; Chem. Zentr., 1932, i, 3150).—The hexagonal lattice is converted at 231° into a face-centred cubic lattice; conditions of the change are discussed. A. A. E.

Influence of impurities on the transformation point of liquid allotropic modifications. S. Dobinski (Nature, 1932, **130**, 662—663).—A theoretical treatment of the possible effects of slight impurities in relation to recent work on $PhNO_2$ (cf. this vol., 1081). L. S. T.

Thermal variations in the mol. wt. of halogens. A. Jouniaux (Bull. Soc. chim., 1932, [iv], **51**, 1062—1069).—A review of published data from which may be deduced the mol. wt. of Cl_x, Br_x, and I_x at different temp. D. R. D.

Mol. wt. in different states of aggregation. I. G. Antonoff (J. Physical Chem., 1932, **36**, 2406—2436).—It is concluded theoretically that all systems exerting outwardly the same pressure at the same temp. are equimol., irrespective of their states of aggregation. Accordingly, two or more phases in thermal equilibrium have the same mol. density. From the mol. wt. of the vapour of a pure substance the degree of association in another phase is calc. as the ratio of the densities of the two phases. The mol. wt. of a liquid attains high vals. at low temp. Liquid and vapour densities vary with temp. in a discontinuous manner. Between any two successive discontinuities the curves follow a single equation the consts. of which vary for different portions of the curve. At temp. of discontinuity the degree of association is a whole, simple no., showing that association takes place according to the law of multiple proportions, and consists of a no. of successive reactions. At discontinuities the liquid consists of only one kind of mol. The mol. wt. of a solid at its m.p. can be calc. from the ratio of the densities of the solid and liquid phases. R. H. C. (*c*)

Electrical resistance and the critical point of mercury. F. Birch (Physical Rev., 1932, [ii], **41**, 641—648).—Relative resistance, and instantaneous pressure and temp. coeffs. in the regions 0—1200° and 1—4000 atm. are given. All vals. increase with rise of temp. and decrease with rise of pressure. The crit. consts. are 1460±20°, and 1640±50 kg. per sq. cm. N. M. B.

Theory of thermoelectricity. B. Bružs (Z. Elektrochem., 1932, **38**, 777—779).—In the thermodynamic treatment of the Thomson theory with reference to thermoelectric effects in metallic and electrolytic systems (Peltier and Seebeck effects), use is made of the postulate previously employed (this vol., 123) according to which the heats of reaction in a stationary system represent latent (secondary) heat. M. S. B.

Superconductivity with alternating currents of high frequency. J. C. McLennan, A. C. Burton, A. Pitt, and J. O. Wilhelm (Proc. Roy. Soc., 1932, **A**, **138**, 245—258).—Observations have been made on the resistance of a conductor at low temp. when both a.c. (frequency 12×10^6) and d.c. are flowing simultaneously. The crit. points for the high-frequency and d.c. resistances are the same, and the position of this common crit. point on the temp. scale is determined by the ratio d.c./a.c. Two effects have thus been established, viz., the depression of the crit. point for the a.c. resistance by the application of high-frequency currents, and the raising of the crit. point for the high-frequency resistance in the presence of a d.c. L. L. B.

Increase in thermo-electric force of oxides by the use of multiple oxide systems. F. Fischer, K. Dehn, and H. Sustmann (Ann. Physik, 1932, [v], **15**, 109—126).—The increase of thermo-electric force is determined for various oxide systems up to five components. The greatest e.m.f. is obtained with a 5-oxide system. The increase may be due to reduction of resistance, or higher e.m.f. of mixed crystals of different oxides. A. J. M.

Conduction of heat of lead–thallium alloy at low temperatures. W. J. de Haas and H. Bremmer (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 323—328).—The thermal resistance of the superconducting alloy, $PbTl_2$, below its transition point 4·09° abs., increases linearly with rise of temp. for magnetic fields $<$ the threshold val. for the alloy and remains practically const. when that val. has been reached. This behaviour is not in accordance with that of pure metals. An explanation is based on the possible non-homogeneity of the alloy. M. S. B.

Halides of the rare earths. VI. Terbium and erbium groups. G. Jantsch, H. Jawurek, N. Skalla, and H. Gavalovski (Z. anorg. Chem., 1932, **207**, 353—367).—The following m.p. are recorded: $GdCl_3$ 609°±2°; $GdBr_3$ 765—786°; GdI_3 926°±2°; $DyCl_3$ 654°±2°; $DyBr_3$ 881°±2°; DyI_3 955°±5°; $HoCl_3$ 718°±2°; $HoBr_3$ 914°±4°; HoI_3 1010°±10°; $ErCl_3$ 774°±2°; $ErBr_3$ 950°±10°; ErI_3 1020°±10°; YCl_3 721°±2°; YBr_3 904°±3°; YI_3 1000°±10°. With increasing at. no. there is a min. in the m.p. of the chlorides at $TbCl_3$; for the iodides the min. is at PrI_3. Beyond Nd the m.p. falls in the order iodide, bromide, chloride, but for La, Ce, and Pr the chloride has the highest m.p. The connexion between these relationships and the cryst. structure and form is discussed. The iodides of Ga, Dy, Ho, Er, and Y begin to sublime without decomp. at 650—700°/0·03 mm., and even at 800—850° no I is liberated. H. F. G.

Variation of the m.p. and volume of carbon tetrachloride with thermal pre-treatment. W. Brüll (Z. Elektrochem., 1932, **38**, 601—611).—The m.p. of CCl_4 increases (by up to 0·5°) with rise of the temp. at which the material has previously been maintained and with reduction of the time which elapses after cooling commences; the lowest m.p. is observed by maintaining the liquid for several hr. at −20°. The rate of cooling has little influence on the reading if the total time of cooling is const. The normal val. is approached slowly by any given specimen, the rate of change being accelerated by certain substances, *e.g.*, anhyd. $CuSO_4$, but not by H_2O. The sp. vol. of the specimen at just above the m.p. is the smaller (by up to 0·05%) the higher is the temp. of pre-treatment. Ordinary solid CCl_4 undergoes a change of sp. vol. (up to 3·6%) with time, and on melting, the liquid also has an abnormal sp. vol. (1·7% max.). It is suggested that in normal liquid CCl_4 two forms are present, the exothermic form amounting to about 3 mol.-% of the total, and that two allotropic modifications exist in the solid state. H. F. G.

M.p. in very narrow capillaries. P. Kubelka (Z. Elektrochem., 1932, **38**, 611—614).—Theoretical. The f.p. of a liquid may be influenced by surface forces at the crystal–liquid, crystal–vapour, and liquid–vapour interfaces. The case of liquid–vapour forces is considered in detail in its application to the f.p. of a liquid adsorbed by an inert porous material; f.-p. depressions of as much as 100° may be anticipated for liquids in contact with active C. H. F. G.

Melting of dissociable compounds. A. Tian (Bull. Soc. chim., 1932, [iv], **51**, 1088—1089).—It is shown theoretically that the addition of a small quantity of either of its dissociation products to a dissociating compound has no effect on its m.p. The effect of dissociation is to lower the m.p. below the normal val. Consequences of these facts are considered. D. R. D.

[Nitrosyl and nitryl fluorides] NOF and NO_2F. O. Ruff, W. Menzel, and W. Neumann (Z. anorg. Chem., 1932, **208**, 293—303).—Physical consts. have been redetermined on carefully purified materials. NOF, m.p. −132·5°, b.p. −59·9°, $d_{liq.}$ $1·919—0·00278T$; NO_2F, m.p. −166°, b.p. −72·4°, $d_{liq.}$ $2·143—0·00323T$. V.p. were also determined. Chemical properties are described. F. L. U.

Relations between b.p. and chemical constitution. IV. Energy relations. Sublimation. Heat of dissociation. K. Billig (Svensk Kem. Tidskr., 1932, **44**, 235—241; cf. this vol., 901).—Trouton's rule is derived, assuming that the b.p. is proportional to the true mol. wt. of the associated liquid in the neighbourhood of the b.p. The energy val. of the linking between the O atoms in $(H_2O)_6$, calc. from the heat of vaporisation of H_2O, is 7·8 kg.-cal., in agreement with the val. calc. for the similar linking in liquid HCO_2H; the corresponding val. for $(MeOH)_2$ is 9·2 kg.-cal. Assuming that the heat of sublimation is proportional to the degree of association, Forcrand's law is derived. Similar considerations are applied to the thermal dissociation of a series of ammoniates of $CaCl_2$ and the carbonates of H, Ag, Ca, Ba, and Na. The general inference is that the heat of vaporisation, sublimation, or thermal dissociation is directly proportional to the mol. wt. in the ideal gaseous or dissolved state, multiplied by the degree of association or other attractive property of the mols. E. S. H.

Correction for incomplete thermal insulation in measurements of small heat capacities. W. H. Keesom and J. A. Kok (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 294—300).—An accurate method is described for correcting for heat exchange with the surroundings in the measurement of small heat capacities, by Nernst and Eucken's method, at the lowest liquid He temp. M. S. B.

Specific heat of liquid helium. W. H. Keesom and K. Clusius (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 307—320).—The sp. heat curve for liquid He under saturation pressure rises from 1·4° to 2·19° abs., where there is a sharp max. (at. heat approx. 9 g.-cal.); it then falls quickly to a flat min. at approx. 2·6° abs. and again rises very slowly (cf. Dana and Onnes, A., 1927, 101) to 4·1° abs., the limit of the range examined. Measurements of sp. heat at const. vol. have also been made between 2·96° and 4·007° abs. M. S. B.

Specific heat of silver from 1·35° to 20·3° abs. W. H. Keesom and J. A. Kok (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 301—306).—The at. heat of Ag increases from 0·000254 g.-cal. at 1·35° abs. to 0·3995 g.-cal. at 20° abs. The val. of θ for Ag is almost const. in the liquid–solid H range; it reaches a max. at 5·4° abs. (θ=226) and decreases below this temp. to θ 165 at 1·35° abs. The at. heat curves of Zn and Ag intersect so that below 14° abs. Ag has a larger at. heat than Zn. M. S. B.

Exact measurement of the specific heat of solid substances at high temperatures. V. Cooling correction of the metal calorimeter in exact high-temperature calorimetry. F. M. Jaeger, E. Rosenbohm, and J. A. Bottema (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 347—352).—The conditions have been determined for making the leakage modulus of a metal calorimeter as small and const. as possible. M. S. B.

Exact measurements of the specific heats of solid substances between 0° and 1625°. VI. Neumann–Joule–Kopp–Regnault law concerning the molecular heat of chemical compounds as a function of the atomic heats. F. M. Jaeger and J. A. Bottema (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 352—362).—The mol. heat of PtSn is less than the sum of the at. heats of Pt and Sn at the same temp. and the difference increases approx. linearly with rise of temp. At 20° it is 4·54% and at 200° 8·70%. This contradicts the law of the additive character of at. heats. The sp. heat of white Sn at 0° is 0·05393 and of PtSn 0·03836. *X*-Ray data for PtSn are given: a_0 4·103, c_0 5·428 Å. The compound is hexagonal and the cell contains 2 mols. M. S. B.

Vapour pressure of liquid water that has recently been frozen. A. W. C. Menzies (Proc. Nat. Acad. Sci., 1932, **18**, 567—568).—The v.p. of H_2O which has reached equilibrium temp. of 25° and 3·5° 10 min. after having been frozen does not differ by more than 0·05 mm. from that of H_2O cooled directly from 100°. O. J. W.

Vapour pressure of sodium. E. Thiele (Ann. Physik, 1932, [v], **14**, 937—970).—The v.p. of Na was determined between 614° and 771° abs., using an improved streaming method and employing vac.-distilled Na. The partial pressures of the Na atoms and the Na mols. were calculated; the heat of dissociation is 16,800 g.-cal. The heat of vaporisation of Na atoms at 0° abs. is 26,200±130 g.-cal., and the chemical const. of Na is 0·85±0·10. W. R. A.

Vapour pressures and vapour densities of beryllium and zirconium halides. W. Fischer and O. Rahlfs (Z. Elektrochem., 1932, **38**, 592).—The following m.p., sublimation temp., and heats of sublimation in kg.-cal. are recorded: $BeCl_2$ 405°, —, 29; $BeBr_2$ 487°, 470°, 31; BeI_2 480°, 480°, 28; $ZrCl_4$ 436°, 332°, 26; $ZrBr_4$ 449°, 356°, 27; ZrI_4 499°, 430°, 30. For the Zr halides the v.d. accord with the unimol. formula; $BeBr_2$ exists as Be_2Br_4 at low temp. (20% in saturated vapour at the b.p.). The Be halides react with SiO_2; $ZrCl_4$ and $AlCl_3$ react slightly, and TiF_4 reacts very rapidly; Zr and Al bromides and iodides do not react. H. F. G.

Behaviour of certain organic materials when heated to 650° at an initial pressure of 1000 kg. per sq. cm. G. Tammann and A. Rühenbeck (Z. anorg. Chem., 1932, **207**, 368—370).—Pressure–temp. curves have been determined for various hydrocarbons, alcohols, and ethers. In all cases the pressure shows at first a linear increase with rise of temp.; at higher temp. the pressure either (*a*) rises more rapidly (EtOH, Et_2O, $C_6H_3Me_3$, etc.); (*b*) rises more slowly (PhMe, Ph_2, stilbene, etc.); or (*c*) passes through a max. and then rises rapidly (C_6H_6, $C_{10}H_8$, anthracene, etc.). H. F. G.

Relation between [specific] volume of saturated vapour and capillary properties of liquids. N. A. Kolosovski and B. N. Grebenschtschikov (J. Gen. Chem. Russ., 1932, **2**, 189—192).—It is shown theoretically that $\sigma d_1/d_2$=const.=0·0688; σ is the surface tension of a liquid at the b.p., and d_1 and d_2 are respectively the relative densities of the liquid and of its saturated vapour. This equation is verified for a no. of non-associated liquids, but does not hold for associated liquids. R. T.

Compressibility of liquid helium at 2·7° abs. W. H. Keesom and K. Clusius (Proc. K. Akad. Wetensch. Amsterdam, 1932, **35**, 320—322).—A preliminary determination at 2·71° abs. and a pressure of 5—10 kg. per sq. cm. gave vals. of the order of $7—8\times10^{-8}$ sq. cm. per kg., which is greater than the compressibility of any other liquid hitherto measured. The val. for lower pressures obtained by extrapolation is in satisfactory agreement with the val. calc. from the expansion coeff. and the difference between the sp. heats at const. pressure and const. vol. M. S. B.

Viscosity of a fluid containing small drops of another fluid. G. I. Taylor (Proc. Roy. Soc., 1932, **A**, **138**, 41—48).—Mathematical. Einstein's expression for the viscosity of a fluid containing small solid spheres in suspension is extended to liquids containing small drops of another liquid in suspension. An expression is derived for the size of the largest drop that can exist in a fluid undergoing distortion at a given rate. L. L. B.

Diffusion of metals in solid lead. W. Seith and J. G. Laird (Z. Metallk., 1932, **24**, 193—196).—The rate of diffusion (*D*) of Ag, Bi, Tl, and Sn in Pb is given by the expression $D=Ae^{-Q/RT}$. At 285° the diffusion consts. are Ag $0{\cdot}79\times10^{-2}$, Bi $3{\cdot}8\times10^{-5}$, Tl $2{\cdot}7\times10^{-5}$, Sn $1{\cdot}4\times10^{-5}$, and Pb 6×10^{-6} (sq. cm., day). Hence the rate of diffusion decreases with increasing similarity between the metal and Pb. A spectrographic method of measuring the rate of diffusion of one metal into another is described. A. R. P.

Diffusion of metals in the solid state. V. Diffusion and corrosion of Cu–Ni alloys. G. Grube and A. Jedele (Z. Elektrochem., 1932, **38**, 799—807).—A rod of Ni electrolytically plated with Cu and a rod of Cu plated with Ni were heated in an atm. of H_2 at 1000° and 1025° and the amount of diffusion was determined. Ni diffuses into Cu more rapidly than Cu into Ni. The diffusion coeff. of Ni into Cu increases with increasing depth of penetration or with increasing concn. of Cu in the mixed crystals. The opposite is the case for the diffusion coeff. of Cu into Ni. The diffusion coeff. of Cu into Ni is reduced to about one third by the presence in the latter of 0·5% Mn. In a solution of 0·146*M*-$(NH_4)_2CO_3$ and 0·148*M*-H_2O_2 at 20° Ni–Cu alloys containing $<$ 30 at.-% of Ni are attacked. Alloys of higher Ni concn. are completely resistant. In $4N$-H_2SO_4 containing $0·5M$-$KClO_3$ at 25° both components dissolve at all concns. and between 75 and 80 at.-% Ni corrosion increases very rapidly with increasing Ni concn. This is apparently due to the fact that the magnetic α-mixed crystals are more readily attacked than the non-magnetic β-mixed crystals. M. S. B.

Liquid sodium amalgams. G. R. Paranjpe and R. M. Joshi (J. Physical Chem., 1932, **36**, 2474—2482).—The literature indicates that these amalgams are sols of Na in Hg with micelles of the composition $(Na_x)Hg_y$. To define an amalgam, the method of prep., age, and previous history are necessary. C. T. S. (*c*)

***X*-Ray study of electrolytic Fe–Ni alloys.** K. Iwase and N. Nasu (Bull. Chem. Soc. Japan, 1932, **7**, 305—314).—*X*-Ray diagrams for mixtures of Fe and Ni deposited from sulphate solutions show that both α and γ solid solutions are present at concns. of 14—58% Ni. The *X*-ray lines are diffuse and the lattice consts. of both α and γ solutions pass through a max. with increasing Ni concn. It is suggested that each metal generally forms its own crystal lattice during deposition and that solid solutions are subsequently formed by diffusion. A. G.

Structure and chemical composition of some metallic alloys. N. Parravano and V. Caglioti (Mem. R. Accad. Italia, 1932, **3**, [Chim.], 5—21).—*X*-Ray data for the system Zn–Mn up to 33 at.-% Mn show that the hexagonal ε phase, like the ε phases of brasses, is stable from 24 to 33% Mn at room temp. and from 24 to 12·5% Mn at higher temp. It contains 2 atoms in the unit cell: *a* varies from 2·754 (33% Mn) to 2·764 Å. (12·5% Mn). The γ phase has a body-centred cubic structure, with 52 atoms per unit cell, and is analogous to the γ phases of brasses: *a* 9·11 Å. It exists in the region 22·21—8·09% Mn at room temp. only. The alloys with 11·07—8·094% Mn also show lines of a γ′ or β′ phase, which has not been completely identified. The η phase consists of a 1—2% solution of Mn in Zn and is unstable. Formulæ for the various intermetallic compounds are proposed. O. J. W.

General laws governing the changes in the structure and properties [of metals] during transformation processes. G. Sachs (Z. Metallk., 1932, **24**, 241—247).—A review of recent work and theories on the mechanism of the breakdown of solid solutions with the formation or separation of intermetallic compounds. A. R. P.

Transformations in the gold–copper system and their theoretical importance in the study of transformations in solid metals. L. Graf (Z. Metallk., 1932, **24**, 248—253).—The AuCu and $AuCu_3$ transformations in Au–Cu alloys take place slowly in polycryst. aggregates and are two-phase reactions, whereas in single crystals they take place rapidly as single-phase reactions. The AuCu transformation takes place in two stages, in the first of which the lattice symmetry changes from cubic to tetragonal, and in the second the atoms regroup themselves from random orientation into a regularly oriented lattice; the first change occurs rapidly and completely, whereas the second is much slower, so that it is possible to arrest the transformation in an intermediate stage characterised by a tetragonal lattice with heterogeneously distributed regularly oriented fields. In this state the alloy AuCu has an electrical resistance 25% greater than, and a tensile strength about double that of, the fully-transformed alloy. The first stage in the transformation is attributed to changes in the state of the free valency electrons in the lattice, and the second stage to thermodynamic conditions. The fact that larger crystals undergo transformation more readily than smaller crystals indicates a definite connexion between the mechanism of the two stages; a theoretical explanation of this is given. A. R. P.

Cause of the austenite–martensite transition at room temperature. E. Scheil (Z. Elektrochem., 1932, **38**, 554—557).—The γ–α-Fe transition at low temp. is not due to thermal displacement of atoms, and cannot be induced by the operation of shear stresses set up, *e.g.*, during quenching, since the initial temp. is not altered on stressing a fine-cryst. specimen. It is probably due to the existence of a mechanically unstable condition, this view being supported by the diminution of elasticity at the transition temp. H. F. G.

Ternary system silver–copper–phosphorus. H. Moser, K. W. Fröhlich, and E. Raub (Z. anorg. Chem., 1932, **208**, 225—237).—The binary systems Cu–P and Ag–P and the ternary system have been investigated by micrographic and thermal methods. There is no indication of the reported existence of Cu_5P_2. Cu_3P and Cu are not miscible in the solid state, but systems containing 14—26% P are homogeneous. When Ag–P mixtures containing >2% P are melted in a closed tube two liquid layers are formed. Under normal atm. pressure not more than 1·45% of P can be retained as phosphide. Ag and AgP_2 form a eutectic, whereas AgP_2 and AgP_3 give mixed crystals over a wide range. Ternary systems with varying ratios of Cu : P are described. F. L. U.

Relation between magnetic properties, especially coercive force, and structure of alloys, and the development of new types of magnetic alloys. W. Köster (Z. Elektrochem., 1932, **38**, 549—553).—The finer is the structure, the greater is the coercive force. Measurements with various C and alloy steels, and the influence of tempering on the hysteresis loop, are described; the systematic development of new alloys is also discussed. H. F. G.

Determination of the shape and arrangement of ferromagnetic precipitations by means of the magnetic balance. E. Gerold (Z. Metallk., 1932, **24**, 255—257).—If the curves for longitudinal and transverse magnetisation of a non-magnetic metal containing segregations of a magnetic constituent coincide, it follows that the latter exists in separate particles completely surrounded by the non-metallic ground mass; this occurs, *e.g.*, in Cu with 2% Fe. If the curves do not coincide, then the magnetic phase exists as tenuous films, forming a network throughout

the ground mass. After rolling alloys of the first type the magnetic inclusions are elongated and the magnetic properties are no longer isotropic.
A. R. P.

Van der Waals forces between tetrahalide molecules. J. H. Hildebrand and J. M. Carter (J. Amer. Chem. Soc., 1932, 54, 3592—3603).—The expansion on mixing has been measured for various binary mixtures of tetrahalides. $(\partial P/\partial T)_V$ has been measured for the pure liquids and mixtures and $(\partial E/\partial V)_T$ calc. The latter is very nearly a pure vol. function.
J. V. V. (*c*)

Refractive index of liquid mixtures with acetic acid as a component. N. A. Pushin and P. G. Matavulj (Z. physikal. Chem., 1932, 161, 341—345).—Binary systems of AcOH with various amines have been examined. In all cases n exceeds the val. calc. by the mixture rule, the excess being a max. at a composition which corresponds with a simple mol. ratio and often represents a known solid compound.
R. C.

Specific heat of aqueous sulphuric acid. A. Sokolik (J. Gen. Chem. Russ., 1932, 2, 311—316).—The sp. heat (C) of the system H_2SO_4–H_2O has been measured at 60° and 80°. The results obtained, together with those of other authors, indicate that C for H_2SO_4,H_2O obeys the simple mixture rule; for all other mixtures C is higher, due to formation of other hydrates.
R. T.

Thermochemical examination of solutions. II. Specific heat of aqueous ethylene glycol at various temperatures. M. B. Neuman and I. A. Kurliankin (J. Gen. Chem. Russ., 1932, 2, 317—321).—The sp. heat (C) of aq. $(CH_2{\cdot}OH)_2$ is a linear function of temp.; that of $(CH_2{\cdot}OH)_2$ is given by $C=0{\cdot}5388+0{\cdot}00112T$.
R. T.

Vapour pressures of the system ethyl alcohol–ethyl acetate. W. Mund and G. Heim (Bull. Soc. chim. Belg., 1932, 41, 349—376).—An apparatus fitted with a glass spring manometer for the determination of the v.p. of mixtures is described, the vol. of the vapour phase being very small in order to avoid change in the composition of the liquid. The v.p. of EtOH, EtOAc, and binary mixtures of these have been determined over the range 0—100°. The results agree well with those of previous investigators.
D. R. D.

Partial pressures and refractivities of binary mixtures of benzene and some of its polar derivatives. A. R. Martin and B. Collie (J.C.S., 1932, 2658—2665).—Data are given for mixtures of C_6H_6 with PhCl, PhBr, NH_2Ph, PhOMe, PhCN, and PhOH (refractivities only), and correlated with the dipole moment and mol. radius of the polar mol.
D. R. D.

Fractionation of liquid binary mixtures. II. I. Rabcewicz-Zubkowski (Rocz. Chem., 1932, 12, 655—661).—When both components of a mixture are unassociated or are associated to the same degree, the quotient p_A/p_B, where p_A and p_B are the v.p. of the more (A) and the less volatile component (B), respectively, rises with fall in temp.; this increase in p_A/p_B is usually more marked when A is unassociated and B is associated. In the latter case p_A/p_B may increase, remain const., or diminish with fall in temp.
R. T.

Striæ in chemical processes. V. System methyl alcohol–acetone; employment of the "visual method." H. Alber (Z. anal. Chem., 1932, 90, 87—99).—The "visual method" (cf. A., 1931, 1263) has been employed successfully in obtaining pure samples of MeOH and $COMe_2$, and in determining the n and distillation curves for mixtures. The latter agree well with previous results and indicate the existence of a const.-boiling mixture at 87% and probably at 95% $COMe_2$.
M. S. B.

Equilibria between three and four liquids at room temperature. E. Jänecke (Z. Elektrochem., 1932, 38, 583—588).—The miscibilities of H_2O and 18 org. liquids, taken in pairs, and of the various binary and ternary mixtures with pure H_2O and with aq. solutions of K_2CO_3, K_3PO_4, NH_3, etc., have been determined qualitatively. Seven groups of liquids, forming in all 54 three-layer mixtures, and two groups forming 24 four-layer mixtures are described. All these mixtures contain aq. NH_3, an inorg. salt, and two org. liquids. The theory of miscibility is discussed.
H. F. G.

Mixed crystals of Ca_2SiO_4 and Mn_2SiO_4. W. L. C. Greer (Amer. Min., 1932, 17, 135—142).—The compounds form mixed crystals in all proportions; n decreases regularly with decrease in the latter. Ca may replace Mn at least up to 50% in the orthosilicates.
Ch. Abs.

Solubility of hydrogen and helium in liquid ammonia. V. V. Ipatiev and V. P. Theodorovitsch (J. Gen. Chem. Russ., 1932, 2, 305—310).—The solubility (S)–temp. curve of H_2 in liquid NH_3 is a straight line, whilst that of He is convex to the temp. axis; in both cases S increases with rise of temp. The S–pressure curves are in both cases rectilinear. H_2 is about three times as sol. as He.
R. T.

Liquid ammonia as a solvent. I. Solubility of inorganic salts at 25°. H. Hunt (J. Amer. Chem. Soc., 1932, 54, 3509—3512).—The data for a no. of salts are recorded.
E. R. S. (*c*)

Solubility of alkali halides in acetone. A. Lannung (Z. physikal. Chem., 1932, 161, 255—268).—The solubilities have been determined at 18° and 37°. The conductivity of F' in $COMe_2$ at infinite dilution at 18° is 96. The H_2O or MeOH content of $COMe_2$ may be determined from the conductivity of a saturated solution of NaCl.
R. C.

Effect of water and alcohols on solubility of salts in acetone. A. Lannung (Z. physikal. Chem., 1932, 161, 269—278).—The influence of H_2O and alcohols on the solubility of NaCl, and of H_2O on the solubility of various alkali salts, has been determined at 18°. The results for salts which form hydrates are interpreted, and a method of determining the activity coeff. of H_2O in $COMe_2$ from v.-p. and solubility data is described.
R. C.

Different solubilities of optical antipodes in active solvents. E. Schröer (Z. Elektrochem., 1932, 38, 595—596).—The aq. extract of a solution of *r*-mandelic acid in *d*-carvone is dextrorotatory, the acid recovered from the carvone being lævorotatory. The reverse effect is observed when *l*-carvone is used as the solvent. The approx. partition coeffs. K_d and K_l are 4·991 and 5·007, respectively. H. F. G.

Solubility of barium hydroxide in dilute solutions of sodium hydroxide. S. M. Neale and W. A. Stringfellow (Trans. Faraday Soc., 1932, 28, 765—766).—Data for 0—1·84*N*-NaOH are recorded. J. G. A. G.

Influence of valency on activity. Solubility of cerium iodate in aqueous solutions of certain electrolytes. J. Chloupek, V. Daneš, and B. A. Danešova (Chem. Listy, 1932, 26, 531—533).—The solubility of $Ce(IO_3)_3$ is increased by the presence of KNO_3, K_2SO_4, $MgSO_4$, or $MgCl_2$. R. T.

Isodimorphism of formates. F. Lewinterówna (Arch. Min. Soc. Sci. Varsovie, 1931, 7, 21—48).—The solubility of mixed crystals of Cu and Mn, Cu and Zn, and Cu and Cd formates ($2H_2O$) differs from that calc. from Retger's rule, and the three systems correspond with Roozeboom's 4th type. The partition coeff. is not in general const. R. T.

Equilibrium between mixed crystals of nickelous and manganous nitrate, and of nickelous and zinc nitrate hexahydrates and their saturated solutions. T. Koepplówna (Arch. Min. Soc. Sci. Varsovie, 1931, 7, 8—20).—The solubility data for mixed crystals of $Ni(NO_3)_2,6H_2O$ and $Mn(NO_3)_2,6H_2O$ correspond with Roozeboom's 5th type; those for $Ni(NO_3)_2,6H_2O$ and $Zn(NO_3)_2,6H_2O$ correspond with the 1st type. The solubility of the mixed crystals is not the arithmetic mean of that of the constituent salts. Nernst's distribution law is followed when one of the constituents is present in low concn. The results indicate that the mixed crystals are solid solutions. R. T.

Equilibrium of mixed crystals of ferrous and cupric sulphates and of cupric and cobaltous nitrates with their saturated solutions. W. Schrenzlowa (Arch. Min. Soc. Sci. Varsovie, 1931, 7, 131—146).—Solubility measurements indicate that the pairs $FeSO_4,7H_2O$–$CuSO_4,5H_2O$ and $Cu(NO_3)_2,6H_2O$–$Co(NO_3)_2,6H_2O$ are isodimorphous; these pairs are of Roozeboom's 5th and 4th types, respectively. The partition coeff. is in both cases variable. The solubility of the mixed crystals is not the arithmetic mean of that of their constituent salts. R. T.

Crystallisation of ammonium chloride with cadmium chloride. A. Swaryczewski (Bull. Acad. Polonaise, 1932, A, 128—144).—The crystallisation of solutions of NH_4Cl alone and with the addition of 0·05, 0·2, and 1·0 wt.-% $CdCl_2$ has been followed by analysing the solution (kept at const. temp.) at regular time intervals. Periodic curves were obtained, indicating alternate dissolution and crystallisation processes. Photomicrographs of the mixed crystals reveal a zonal structure, which probably corresponds with the periodicity of crystallisation. The solubility of NH_4Cl is not markedly influenced by the presence of $CdCl_2$, but the rates of crystallisation and of dissolution are thereby reduced. The distribution of $Cd^{\cdot\cdot}$ between the crystals and the solution depends both on the composition of the solution and on the conditions of crystallisation; with increasing rate of crystallisation the crystals become richer in $Cd^{\cdot\cdot}$. The existence of the compound $4NH_4Cl,CdCl_2$ in the mixed crystals is not supported by determinations of *n*, and *X*-ray evidence fails to establish a new compound. E. S. H.

Periodic precipitation of silver salts. (Mlle.) S. Veil (Compt. rend., 1932, 195, 606—608).—Liesegang rings formed by drops of aq. $AgNO_3$ on gelatin impregnated with K chromate, phosphate, or arsenate are described. Rings obtained by reversal of the electrolytes do not show the secondary microscopic stratification (cf. A., 1920, ii, 26). C. A. S.

Partition of saturated fatty acids between water and toluene. N. A. Kolosovski and I. Megénine (Meshenin) (Bull. Soc. chim., 1932, [iv], 51, 1000—1004, and J. Gen. Chem. Russ., 1932, 2, 197—201).—Data are given for HCO_2H, AcOH, and $EtCO_2H$, at 25°. D. R. D.

Capillary chemistry. R. Dubrisay and R. Arditti (Bull. Soc. chim., 1932, [iv], 51, 1199—1202).—Certain substances in solution may be separated by taking advantage of their unequal distribution between the liquid and a foam formed on the surface by bubbling CO_2 or N_2 through the solution. In this way mixtures of Na laurate with Na oleate, stearate, or arachidate, and of night-blue with basic fuchsin, have been separated into their constituents, and commercial oleic acid has been purified. D. R. D.

Distribution of radioactive substances between solid crystalline and liquid phases. VIII. Distribution of radium-*D* (lead) and a mixture of radium-*D* and radium between crystalline barium nitrate or chloride and its saturated aqueous solution at 0° and 25°. A. Polessitski (Z. physikal. Chem., 1932, 161, 325—335; cf. this vol., 14).—The distribution of $Ra\text{-}D(NO_3)_2$ between $Ba(NO_3)_2$ and its solution follows Nernst's distribution law, the distribution ratio changing in favour of the liquid phase as the temp. rises. The same is true of the distribution of $Ra\text{-}DCl_2$ between $BaCl_2,2H_2O$ and solution if the Ra-*D* concn. lies within the miscibility limits of $BaCl_2$ and $PbCl_2$. If $Ra\text{-}D(NO_3)_2$ and $Ra(NO_3)_2$ are simultaneously distributed between $Ba(NO_3)_2$ and its solution or $RaCl_2$ and $Ra\text{-}DCl_2$ between $BaCl_2,2H_2O$ and its solution each salt distributes itself as if the other were absent. R. C.

Laws governing isomorphous separation of small amounts of substances with crystallising salts. H. Käding, R. Mumbrauer, and N. Riehl (Z. physikal. Chem., 1932, 161, 362—372).—By steady evaporation of a saturated solution or rapid crystallisation of a supersaturated solution the distribution of the substance present in small amount between the solution and crystals may be represented by a logarithmic formula (cf. A., 1925, ii, 381), but the crystals are not homogeneous. By the slow crystallisation of supersaturated solutions, which gives homogeneous crystals, and by prolonged stirring after rapid crystallisation of a supersaturated solution systems are obtained for which the Nernst distribution law is valid; the concns. should preferably be expressed in wt.-% (cf. A., 1931, 1225). R. C.

Adsorption of carbon dioxide, ethylene, and hydrogen on pyrophoric iron and gold powder. A. Magnus and R. Klar (Z. physikal. Chem., 1932, 161, 241—254).—At 0°, 20°, and 40° the isotherms for CO_2 and C_2H_4 on Au deviate slightly and that for C_2H_4 on Fe deviates considerably from the isotherms for the same gases on C (this vol., 223); this is ascribed to the presence on Au and Fe of active centres. Au and Fe continue to sorb H_2 slowly for a long time, and no reproducible adsorption isotherms have been obtained. R. C.

Adsorption of ionium by manganese [dioxide]. A. Pylkoff (J. Chim. phys., 1932, 29, 430—435).—Io and its isotope U-X_1 are pptd. simultaneously with MnO_2, which is a better adsorbent than CeO_2. E. S. H.

Adsorption of sugars by charcoal. F. Hayashi (J. Biochem. Japan, 1932, 16, 1—16).—Mineral acids do not increase the adsorption of glucose by blood C (cf. A., 1929, 133). With increasing mol. wt. of the sugar there is increased adsorption. Surface-active substances (MeOH, EtOH, PrOH, $Bu^{\alpha}OH$, $COMe_2$, AcOH, PhOH) produce an inhibiting effect which is inversely proportional to the normal adsorption. Conditions for the separation of glucose and sucrose by adsorption are given. F. O. H.

Effect of chemical and physical factors on activity of charcoal. III, IV. E. V. Alexeevski and J. S. Pikazin (J. Gen. Chem. Russ., 1932, 2, 327—334, 335—340).—III. The adsorptive properties of birch C saturated with 0·1*N* and *N* alkalis (Na, K, Li, NH_4, Ba, Ca, and Sr hydroxides) and then heated at 450° under reduced pressure are practically the same as those of the original C for C_6H_6 vapour, for C_2H_2, and for aq. *iso*-C_5H_{11}·OH and PhOH. The adsorptive capacity of the C is augmented for CCl_3·NO_2 vapour, as a result of catalytic decomp. of the adsorbate, with liberation of fresh active surfaces.

IV. Treatment of C with NH_4X (X=Cl, CO_3, C_2O_4, OAc, SO_4, MoO_4, tartrate, S_2O_8, NO_3, H_2PO_4, and ClO_4) leads to only insignificant changes in its adsorptive properties; in the case of salts of NH_4 with non-volatile acids the product binds more alkali from solutions than does the original C. C treated with NH_4CNS is largely inactivated. R. T.

Swelling of charcoal. II. Factors controlling the expansion caused by water, benzene, and pyridine vapours. D. H. Bangham, N. Fakhoury, and A. F. Mohamed (Proc. Roy. Soc., 1932, A, 138, 162—183; cf. A., 1931, 160).—Details are given of an apparatus for measuring the expansion of a pinewood charcoal rod in contact with the vapours of C_6H_6, C_5H_5N, and H_2O. It is assumed that the expansion is a measure of the pressure in the surface phase and from this it is shown that the Gibbs equation is approx. valid over a wide pressure range for C_6H_6 and C_5H_5N, but not for H_2O. At low pressures the adsorption of C_6H_6 and C_5H_5N is a complex phenomenon involving two distinct processes: the first causes a large expansion of the charcoal and consists in the formation of a two-dimensional film, the second is accompanied by a contraction and is accelerated by heat. In the case of H_2O vapour, the " mol. expansion " curves between 0 and 23·5° are similar in form to the *p*–*v* graph of a gas undergoing condensation by isothermal compression, but the surface phase is the less condensible the higher is the temp. At −30° the surface vapour phase condenses to form a solid film. L. L. B.

Adsorption. Methods of obtaining saturated vapours. L. J. Burrage (Chem. News, 1932, 145, 206—211).—Methods and apparatus whereby a stream of air can be saturated with the vapour of H_2O or org. liquids at definite pressures are described. E. S. H.

Heats of adsorption of hydrogen and carbon monoxide on copper. R. A. Beebe (Trans. Faraday Soc., 1932, 28, 761—765).—By using a single-junction thermocouple in direct contact with the reduced Cu granules it is found that adsorption of the initial portions of CO does not occur uniformly throughout the catalyst, but in successive layers. The adsorption of H_2 for the entire range and that of CO for the later portions is approx. uniform and the heats of adsorption are independent of the quantity of gas already adsorbed. Non-uniform adsorption may account for discrepancies between recorded heats of adsorption. J. G. A. G.

Remarkable reaction of nitrous oxide adsorbed on charcoal. L. Meyer (Naturwiss., 1932, 43, 791).—Below 0° the adsorption of N_2O by activated C is a reversible physical change, but at higher temp. decomp. occurs. N_2 is liberated and the O remains adsorbed, being held probably by the free valencies of the C atoms. The velocity of decomp. is almost independent of the temp. The reaction may be used to measure the active surface of the C, since it ceases when the surface has become covered with a monat. layer of O. D. R. D.

Increase in hygroscopicity of potassium chlorate in presence of traces of potassium chloride. O. J. Druetzka (Bull. Soc. Chim. Yougoslav., 1932, 3, 105—107).—$KClO_3$ containing 3% KCl is as hygroscopic as pure KCl. R. T.

Kinetics of adsorption by porous powders from solutions of substances of high mol. wt. V. B. Iljin and N. N. Shelechovtzeva (J. Gen. Chem. Russ., 1932, 2, 436—441).—The velocity of adsorption of Me-violet (*A*) from aq. solution by blood C is greater for 0·1% than for 0·04% solutions, and is greater when *A* is added to suspensions of C than when dry C is added to solutions of *A*. The adsorption coeff. diminishes with increasing concn. of *A* and with time. R. T.

Adsorption of paraffin vapours by water. Significance of Traube's rule. H. Cassel and M. Formstecher (Kolloid-Z., 1932, 61, 18—26).—The surface tension, π, of H_2O against the vapours of *n*-C_4H_{10}, -C_6H_{14}, and -C_7H_{16} has been measured at 0° and 12°. The curves relating π to v.p., *p*, are convex towards the *p* axis and can be expressed by $\log p = A + \log \pi + \beta\pi/2{\cdot}3RT - \log(1+\alpha\pi)$, where *A*, α, and β are consts. This form indicates a mol. attractive force. The paraffins have a limited solubility in the adsorption layer. The heats of

adsorption, calc. from the temp. coeffs., are of the order of magnitude of heats of condensation. The data show that Traube's rule is valid for paraffins, supporting the view that the mols. lie with their flat surfaces against the H_2O. The behaviour of the corresponding fatty acids and alcohols is discussed.
E. S. H.

Adsorption and complex compounds of sucrose with surface-active substances; their destruction and displacement of equilibrium by micro-flotation. D. Talmud and P. Pochil (Kolloid-Z., 1932, **61**, 101—111).—The existence of adsorption compounds of sucrose with colloidally disperse, surface-active substances, and of complex compounds of sucrose with mol. disperse, surface-active substances, and semi-colloids has been established by comparing the velocity of dialysis of the mixtures with that of the components. The compounds are readily destroyed by acids or alkalis, and also by dialysis, when the surface-active substance is not dialysable. A micro-flotation method is also described for the separation of the sucrose, whatever the nature of the surface-active substance. This process has been applied to the purification of molasses and increases the yield of sucrose obtained therefrom by crystallisation. E. S. H.

Thermodynamics of surface phenomena. N. Barbulescu (J. Chim. phys., 1932, **29**, 418—429).—Theoretical. E. S. H.

Wetting experiments with hydrophilic and hydrophobic powders in a system of two immiscible liquids. I. E. Berl and B. Schmitt (Kolloid-Z., 1932, **61**, 80—90).—The conditions for the wetting and flotation of powders in a system of H_2O and C_6H_6 in presence of a flotation agent are examined theoretically. With Pb glance and Zn blende the amount of the agent (K Et xanthate or Na oleate) required to cause phase reversal is directly proportional to the surface of the powder. Pb glance readily oxidises to $PbSO_4$ at corners and edges of the finely-divided material, thus producing a more hydrophilic powder. The effect of addition agents, such as K_2CrO_4, Na_2CO_3, or KCN, has been investigated and is interpreted in terms of the change in the direction of hydrophobic or hydrophilic properties due to adsorption. E. S. H.

Surface tension of the surface of contact of benzene solution of palmitic acid and aqueous solution of sodium hydroxide or barium hydroxide. L. Gay and M. Donnet (J. Chim. phys., 1932, **29**, 385—402).—The interfacial tension has been examined with reference to the concn. of both solutions. All the curves show a sharp break, named the "Adam point," which represents the formation of an "epiphase" or two-dimensional phase of the corresponding soap at the surface of separation. In the case of $Ba(OH)_2$ solutions, the curves show two more breaks. The first of these, the "Marcelin point," corresponds with the initial formation of a three-dimensional soap phase from the epiphase, and the second point indicates the completion of this phase. E. S. H.

Effect of neutral salts on properties of solutions of non-electrolytes. III. Surface tension of solutions of salts in mixtures of organic liquids and water. P. P. Kozakievitsch and M. M. Lomikovskaya (J. Gen. Chem. Russ., 1932, **2**, 238—248).—The surface tension (σ)–EtOH concn. curves of the systems aq. EtOH–MX (M=Li or Na, X=Cl, Br, or I) pass through a max.; this effect is ascribed to combination of salt with EtOH. The influence of the halides increases in the order Cl, Br, I. $NaHSO_3$ increases the σ of aq. $COMe_2$, owing to combination with $COMe_2$, and $AgNO_3$ has a similar action in aq. NH_2Ph. R. T.

Present status of theories of solution with special reference to the problem of the solubility of non-electrolytes. H. L. Ward (Washington Univ. Stud. Sci. Tech., 1932, [ii], No. 6, 61—79).—A discussion. Ch. Abs.

Molecular size of dissolved silicic acids. E. Gruner and J. Elöd (Z. anorg. Chem., 1932, **208**, 317—320; cf. A., 1931, 1021).—The f.-p. depression of solutions of silicic acid prepared by Willstätter's method has been determined. When the results are corrected for the potentiometrically determined activity of the accompanying HCl, instead of for its amount as found by analysis, it is found that the solutions contain pure monosilicic acid. F. L. U.

Density of solutions of sodium, potassium, and sodium bromide in liquid ammonia. W. C. Johnson and A. W. Meyer (J. Amer. Chem. Soc., 1932, **54**, 3621—3628).—Vals. of *d* for solutions of various concns. are recorded. E. R. S. (*c*)

Viscosity of strong electrolyte solutions according to electrostatic theory. H. Falkenhagen and E. L. Vernon (Phil. Mag., 1932, [vii], **14**, 537—565).—Theoretical. The original central-symmetric electric density of the ionic atm. is deformed when a velocity gradient exists in a solution. The related shearing force has been calc. to give a term proportional to the sq. root of the concn. γ, which is additive to the viscosity, $\eta_\gamma=\eta_0(1+A\sqrt{\gamma})$. A has been calc. as a function of T, of the dielectric const., of the viscosity η_0 of the pure solvent, and of the nos., valencies, and mobilities of the ions, together with certain general consts. H. J. E.

Distribution of suspended particles under gravity. C. M. McDowell and F. L. Usher (Proc. Roy. Soc., 1932, **A**, **138**, 133—146).—Recent observations on the distribution of the particles of colloidal systems under the influence of gravity have led to results greatly at variance with earlier work. The work of Porter and Hedges (A., 1923, ii, 743) and of Barkas (A., 1925, ii, 289) is criticised on the ground of inadequate temp. control and failure to reach a state of equilibrium. A method of measuring the distribution of particles of colloidal Au over a range of 1 cm., the suspension being maintained at a temp. varying by ≯0·001° per hr., is described. Perrin's law is found to hold over a range of 0·9 cm. from the surface and up to a concn. of 10^{12} particles per c.c. L. L. B.

Sedimentation of clays. E. W. Kanning, R. J. Hartman, and F. Childs (J. Physical Chem., 1932, **36**, 2369—2382).—The size of the particles of various Indiana clays has been calc. from the velocity of fall of particles, indicated by the sedimentation in definite time intervals. C. T. S. (c)

Orientation and deformation of disperse particles in streaming liquids. W. Haller (Kolloid-Z., 1932, 61, 26—41).—A mathematical treatment of the orientation of anisodimensional particles and of the deformation of non-solid particles under the influence of streaming. Two opposing factors are considered in orientation, viz., the streaming of the liquid and the Brownian movement of the particles. Deformation is considered in relation to the form, elasticity, and internal friction of the particles. Published data indicate that the streaming double refraction of sols such as V_2O_5 is in accordance with the theory developed for the orientation of anisodimensional particles, whilst the behaviour of lyophilic colloids (myosin) is in agreement with the deformation theory. E. S. H.

Determination of size, form, and solvation of macro-molecules. G. V. Schulz (Z. physikal. Chem., 1932, **161**, 441—462; cf. this vol., 993).—Theoretical. The relative viscosity of fresh rubber solutions agrees with the val. calc. by Eisenschitz' equation, using the osmotic sp. solvation vol. and assuming that the dissolved mols. are thread mols. stretched out to their full length. These latter are highly solvated. In hemicolloidal solutions for which Staudinger's relation is valid (this vol., 121) there is only slight solvation, owing to the high osmotic pressure. In the ageing of rubber or gelatin solutions the long mols. disintegrate; this is followed by changes in the solvation, and finally the fragments come to lie side by side in bundles, apparently held together by principal valencies. In general, the osmotically measured solvation vol. is equal to the true solvation vol. R. C.

Structure of colloidal particles. II. Kinetics of formation of atakamite sols. S. M. Liepatov, E. J. Vinietzkaya, and A. A. Morozov (J. Gen. Chem. Russ., 1932, 2, 260—270).—The duration of the induction period preceding the formation of sols of $[Cu(OH)_2Cu](OH)Cl$ from aq. $Cu(OAc)_2$ and NaCl varies inversely with the relative concn. of NaCl. The process consists of three stages: chemical reaction between $Cu(OAc)_2$ and NaCl, formation of nuclei, and aggregation of nuclei, with consequent flocculation. The conductivity of the systems falls continuously; this is ascribed to the low velocity of the chemical reaction, and not to adsorption of ions on the coagulate. R. T.

Extension double refraction of colloids in solution. W. Kuhn (Z. physikal. Chem., 1932, **161**, 427—440; cf. this vol., 993).—A suspension of optically isotropic elongated particles which become doubly refracting as a result of extension or compression exhibits double refraction when a flow gradient is set up in it. The flow double refraction of rubber, gelatin, and polystyrene solutions is accounted for in this way, which shows that the dispersed particles are not linear, but are coiled up in such a way as to be effectively isotropic. The ratio of length to thickness of the particles deduced from the streaming double refraction agrees with the val. deduced from the viscosity by means of an equation which takes into account a pronounced Brownian motion. R. C.

Calculation of the mol. wt. of a polar colloid from the data for the dispersion of its aqueous solution. B. M. Bloch and J. Errera (Physikal. Z., 1932, 33, 767—769).—Theoretical. W. R. A.

Fowweather's gold sol. W. Herrmann (Klin. Woch., 1932, 11, 902—903; Chem. Zentr., 1932, ii, 187).—In the photo-reduction of $KAuCl_4$ by $K_2C_2O_4$ in the cold, freshly distilled H_2O and freshly prepared $K_2C_2O_4$ solution must be used. A. A. E.

So-called colloidal carbon from carbohydrates and sulphuric acid. B. L. Vanzetti (Rend. Sem. Fac. Sci. Univ. Cagliari, 1931, 1, 49—50; Chem. Zentr., 1932, i, 3393).—When sucrose, glucose, fructose, and cellulose in H_2O are slowly treated with H_2SO_4, a brown or black coagulum separates after some days from the dark, apparently colloidal, solution, the supernatant liquid becoming first light yellow and then colourless. Later the supernatant liquid shows no Tyndall effect, but a blue fluorescence. Small quantities of H_2S are produced. After 2—3 months the solution is converted into a black gelatinous mass, which after washing with H_2O and drying forms a hard mass. The aq. extracts afford oxidation products. A. A. E.

Exchange reactions and structure of the micelles of stannic acid sols. R. Wintgen (Kolloid-Z., 1932, 61, 1—18; cf. A., 1931, 909).—When SnO_2 sols, peptised by NaOH, are treated with electrolytes which form insol. or sparingly sol. stannates, an irreversible coagulum is formed. Turbidity is first produced when the amount of added electrolyte is equiv. to the amount of NaOH in the micelles; complete flocculation occurs when the amount of electrolyte is equiv. to the total NaOH in both the micelles and the dispersion medium. Electrolytes which form sol. stannates produce a reversible coagulum and in this case the points of incipient turbidity and of complete coagulation depend, not on the amount added, but on the concn. A quant. investigation of the ion exchanges involved in the formation of the irreversible coagula shows that the equivalence noted does not indicate that discharge of the particles begins when the exchange of $Na^{\cdot}$ for other cations is complete. Exchange reactions occur even when the electrolyte causes no visible change in the colloid. Assuming the sol. particles to be approx. spherical, secondary aggregates, it is inferred that the average micelle has 14,850 charges and consists of 370 primary particles, each containing 2800 mols. of SnO_2 and 100 atoms of Na. E. S. H.

Does cellulose acetate dissolve molecularly in organic liquids? I. Sakurada and S. Lee (Kolloid-Z., 1932, 61, 50—54).—Measurements of the viscosity of different preps. of cellulose acetate in a mixture of $CHCl_3$ and C_6H_6 are not in agreement with the view (A., 1930, 1414) that the substance is mol. dispersed. E. S. H.

Starches and the colloidal state. M. Catoire (Ann. Inst. Pasteur, 1932, 49, 500—537).—A detailed discussion of the colloidal state with special reference to micellar complexes and the chemical composition of starch in particular. Natural starch is to be considered as consisting of biological micelles, which in turn consist of chemical micelles; the latter are polymerides of organo-mineral complexes. P. G. M.

Coagulation of casein and albumin sols by alcohols at different p_H. B. Jirgensons (Kolloid-Z., 1932, 61, 41—46; cf. A., 1931, 1368).—In the coagulation of casein sols by MeOH, EtOH, and Bu^aOH, with increasing concn. of alcohol the turbidity increases to a max. and then decreases to a sharp min., after which it increases again. The positions of the max. and min. vary with the particular alcohol, but in general the max. lies at 12—35 vol.-% and the min. at 40—60 vol.-%. The max. bears a linear relation to the dielectric const. of the alcohol and varies with p_H. The behaviour of the alcohols towards albumin sols is similar. With Bu^aOH the max. is displaced in the direction of higher concn. of alcohol when the p_H is lowered, but less change is produced in the other alcohols. The existence of labile, strongly polar, alcohol–H_2O complexes is inferred. E. S. H.

Application of physico-chemical analysis to the study of peptisation. I. Peptisation of pea proteins. A. Dumanski, E. G. Antonovitsch, and A. B. Silaev (J. Gen. Chem. Russ., 1932, 2, 297—304).—Less protein is extracted from pea meal when the vol. of H_2O is increased; this is attributed to dilution of peptising electrolytes. Max. peptisation of pea globulin is obtained with 10% NaCl, which yields solutions containing 2·42% of globulin; the max. globulin concn. does not exceed 0·3% with KCl, 0·93% with $BaCl_2$, 0·5% with NaOH, and 0·2% with HCl. R. T.

Silicic acid gels. II. Time of setting as a function of temperature. C. B. Hurd and P. S. Miller (J. Physical Chem., 1932, 36, 2194—2204; cf. this vol., 464).—Solutions of water-glass with the ratio $SiO_2 : Na_2O$ varying from 1·58 to 3·86 were treated with AcOH at 273—328·8° abs. The graph of log. setting time against 1/temp. (abs.) is a straight line for all the water-glasses except the one containing the most alkali. From the graphs the average " heat of activation " for the reaction leading to the setting of silicic acid gel is 16,640 g.-cal. Gel formation probably occurs by elimination of H_2O from two OH groups of neighbouring silicic acid mols. J. W. P. (*c*)

Variations in extinction coefficients during course of jelly formation. S. Prakash (J. Physical Chem., 1932, 36, 2483—2496; cf. A., 1930, 1369).—Variations in the extinction coeff., k, during jelly formation were studied with Fe^{III}, Cr^{III}, Al, and Zr hydroxides, Th, Sn^{IV}, and Ce^{IV} arsenates, $Sn_3(PO_4)_4$, Th, Fe^{III}, and Zr molybdates, Zr borate, and mercurithiosalicylic acid. The jellies may be perfectly transparent, with no change in K, or opalescent at the point of setting, but finally become opaque before or at the point of setting. C. T. S. (*c*)

Gelation of sucrose with metal hydroxides. W. Coltof (Kolloid-Z., 1932, 61, 54—68).—Gels are formed by the interaction of KOH with $CaCl_2$, $SrCl_2$, or $BaCl_2$ in presence of sucrose. Gelation does not occur until the mol. ratio $Ca(OH)_2$: sucrose exceeds 3 : 2, but with $Sr(OH)_2$ the mass gelates when the ratio is 1 : 1. With $Ba(OH)_2$ the mol. ratio must exceed 1 : 1. In general, excess of KOH aids gelation and excess of the chloride has the reverse effect. Gelation is more difficult with increasing dilution of the components. The presence of increasing quantities of sucrose causes pptd. alkali hydroxides to assume a more transparent, soft, and sol. form, until gels are produced at the ratios given. The microscopical and ultramicroscopical appearance of these gels, prepared in different ways, is described. E. S. H.

Kinetics of the sol–gel transformation. I. Relation between concentration of coagulating electrolyte and setting period of jellies. S. Prakash and H. L. Dube (Z. anorg. Chem., 1932, 208, 163—168).—Times of setting of sols of $FeAsO_4$, ZrO_2, CeO_2, and Cr arsenate (negative or positive) are related to the concn. of electrolyte by the expression $t=ac^{-b}$, in which a and b are const. in any given experiment. F. L. U.

Isoelectric point of serum-globulin as determined by cataphoresis. F. O. Howitt and E. B. R. Prideaux.—See this vol., 1271.

Isoelectric point of collagen. M. Shimidzu (Collegium, 1932, 794—798).—The isoelectric point of hide collagen as determined by means of Fe and Au sols is p_H 4·69. D. W.

Isoelectric point of silk. M. Harris (Bur. Stand. J. Res., 1932, 9, 557—560).—Colloidal solutions prepared by dissolving silk fibroin in 50% aq. LiBr and dialysing were mixed with buffers and a small amount of quartz powder was added. Electrophoretic measurements with these systems indicate an isoelectric point at p_H 2·5. E. S. H.

Colloid chemistry of gluten. H. L. B. de Jong (Trans. Faraday Soc., 1932, 28, 798—812).—The isoelectric point of gliadin is p_H 6·5—6·6 and that of glutenin is 5·4—5·3. The deviations from the additive law on mixing gliadin and glutenin indicate complex formation, in which the gliadin part is always positively charged and the glutenin part negatively charged. The components appear to retain their charges in the complex, whilst their degree of solvation is changed. Complex formation is limited to the region between the isoelectric points and is a max. at a definite p_H, which depends on the ratio of the two proteins and on the electrolytes present. The complex is comparable with natural gluten. E. S. H.

Effect of ammonia and amines on viscosity of collodions. P. Pascal and J. Grévy (Compt. rend., 1932, 195, 726—729).—Addition of increasing amounts (10—200 mg. per 100 g. of solution) of NH_3 to a 4% (by wt.) solution of unstabilised industrial cellulose nitrate in 65 : 35 Et_2O–EtOH (99·3%) gives rise at first to a large increase in the viscosity, followed by a decrease to vals. much below the viscosity of the original solution. Equiv. amounts of NH_2Me, $NHMe_2$, and NH_2Et have similar but more marked effect, whilst that of NMe_3 is still greater, causing pptn. of part of the cellulose nitrate. Aromatic bases have little effect. C. A. S.

Solvation of rubber sols. J. Lens (Rec. trav. chim., 1932, 51, 971—980).—V.-p. lowering has been measured in sols of pure and crude rubber in CCl_4, $CHCl_3$, C_6H_6, MeOH, EtOH, and $COMe_2$. The results are discussed from the point of view of solvation. Solvation of particles in one of the first three solvents is greatly reduced by addition of one of the last three. In the case of octyl alcohol a sudden decrease of solvation occurs at about 42° when the sol is cooled. The system rubber–solvent is considered to have more than two components. F. L. U.

Complex coacervation. XII. Coacervation of hydrophilic sols with dyes. H. G. B. de Jong and J. Lens. **XIII. Auto-complex coacervation of trypaflavine.** H. G. B. de Jong and F. A. Menalda (Biochem. Z., 1932, 254, 15—34, 35—46; cf. this vol., 807).—XII. Coacervation occurs either when a basic dye acts on a negative hydrophilic sol or when an acid dye acts on a positive hydrophilic sol. The combination gum arabic–trypaflavine exhibits complex coacervation probably of the mixed type III—IV (complex and auto-complex coacervation). Gelatin–Na picrate exhibits auto-complex coacervation, the picrate ion being adsorbed between the positive ionogenic positions on the surface of the particles. The behaviour of the combination positive gelatin–tropæolin-*O* is more complicated.

XIII. In its behaviour towards solutions of neutral salts containing multivalent anions [$K_4Fe(CN)_6$, $Na_4P_2O_7$, $CH(SO_3K)_3$, Na citrate] and in the formation of films at the interface when $CHCl_3$ is added, trypaflavine acts to some extent as a hydrophilic colloid. The droplets which separate from solution on addition of $Na_4P_2O_7$ indicate auto-complex coacervation, but when $CH(SO_3K)_3$ is added the material which separates is solid and it is not certain that such coacervates are produced. The auto-complex coacervation in trypaflavine solutions does not occur unless a certain concn. of the dye is attained and is almost or completely prevented by suitable non-electrolytes (carbamide, urethane, chloral hydrate, NH_2Ac, resorcinol, pyrogallol, glucose) or by rise in temp. W. McC.

Applications of cryoscopic measurements to biological problems. F. F. Nord, O. M. von Ranke-Abonyi, and G. Weiss (Z. Elektrochem., 1932, 38, 632).—The freezing of a complex lyophilic colloidal solution may cause both aggregation and breaking down of the particles, with resulting changes, possibly in different directions, of the viscosity and surface tension of the solution. The influence of freezing on solutions of colloids capable of acting as emulsifying agents has been studied; the viscosity of gelatin and albumin emulsions is reduced, and that of Na oleate, gum arabic, and saponin emulsions is increased, after freezing. The stability of emulsions prepared with emulsifiers which have been frozen is somewhat higher than the normal. H. F. G.

Insulin. I. Cataphoresis of insulin alone and in presence of glucose: the question of an insulin–glucose reaction *in vitro*. F. O. Howitt and E. B. R. Prideaux.—See this vol., 1292.

Organic phosphorus compounds in plants and animals. III. Exosmosis of phosphorus from plant cells. IV. Effect of animal and vegetable lecithin on diffusion of acids and alkalis in gels. H. Magistris (Biochem. Z., 1932, 253, 64—80, 81—96).—III. See this vol., 1181.

IV. The diffusion of acids and of alkalis in gelatin and agar gels is accelerated by low concns. of cholesterol, but retarded by low concns. of various kinds of lecithin. With suitable proportions of the two substances the diffusion is unaffected. High concns. of cholesterol and of the lecithins retard the diffusion, the influence of the cholesterol, however, being less pronounced than that of the lecithins. The effects produced by the latter vary with their origin and methods of prep. Org. acids diffuse more rapidly than inorg. and alkali hydroxides more rapidly than alkaline-earth hydroxides. HBO_3 and NH_3 diffuse very readily; $Sr(OH)_2$ more rapidly than $Ca(OH)_2$ or $Ba(OH)_2$. The rate of diffusion of acids and alkalis is also affected by their concn. Within certain limits increase in concn. of mineral acid increases their rate of diffusion; at higher concns. the rate decreases. With org. acids the effect of concn. is less pronounced. In some cases the addition of lecithin (>2%) produces visible alteration in the degree of dispersion of the gel. W. McC.

Chemical equilibria of reactions between hydrocarbons. I. V. P. Sharkova and A. V. Frost. **II.** A. A. Vedenski and A. V. Frost (J. Gen. Chem. Russ., 1932, 2, 534—541, 542—552).—I. The equilibrium const. for $C_6H_6+3H_2\rightleftharpoons C_6H_{12}$ is given by $\log K=9590/T-9{\cdot}9194\log T+0{\cdot}002285T+8{\cdot}566\pm0{\cdot}084$.

II. The val. of $\log K$ for $2C_6H_6\rightleftharpoons Ph_2+H_2$ (I) is $-0{\cdot}83\pm0{\cdot}14$ at 845° and $-0{\cdot}69\pm0{\cdot}11$ at 920°; for $Ph_2+C_6H_6\rightleftharpoons C_6H_4Ph_2+H_2$ $\log K$ is $-0{\cdot}58$ at 845°. Nernst's approx. formula for K is not applicable to reaction (I). R. T.

Methane equilibria from absolute entropies, and use of Ehrenfest symmetry number. A. R. Gordon and C. Barnes (J. Physical Chem., 1932, 36, 2601—2609).—The abs. entropy, S, and the heat capacity at const. pressure have been calc. for gaseous CH_4 at 300—1200° abs. The calc. vals. of $R\log_e K$ for $CH_4+2H_2O=CO_2+4H_2$ at 600—700° abs. agree with experiment, and $\Delta S°$ and $\Delta F°$ have been derived for 298·1° abs. The vals. of $R\log_e K$ have been calc. for C (graphite)$+CO_2=2CO$ at 1123—1223° abs. The calc. vals. of $R\log_e K$ for C (graphite)$+2H_2=CH_4$ at 700—1200° abs. agree with experiment only at the lower temp. For CH_4 $\Delta F°_{298\cdot1}$ is $-12{,}490$. Geometrical symmetry is a sufficient, but not a necessary, condition for the existence of a symmetry no. If the use of a symmetry no. leads to a val. for the entropy in approx. agreement with the observed val. this affords no evidence for the shape of the mol. F. D. R. (*c*)

Free energy of enolisation in gaseous phase of substituted acetoacetic esters. J. B. Conant and A. F. Thompson, jun. (J. Amer. Chem. Soc., 1932, 54, 4039—4047).—Measurements of the equilibrium const. of enolisation in the gaseous state show that there is a connexion between the structure of the

compound and the free energy of enolisation in the gaseous state. Comparison of the results with ΔF referred to the liquid equilibrium mixture or a dil. solution shows that the parallelism between structure and free energy is often obscured by solvent effects, which may be as large as 1 kg.-cal. A dil. hexane solution seems to approximate to the gaseous state in most instances, as far as free energy vals. are concerned, but the regularity is less marked; for ketonic esters and diketones a dil. hexane solution will probably yield results significant to $\pm 0{\cdot}3$ kg.-cal.
C. J. W. (*c*)

Equilibria in boric acid–diol–water system. II. N. Vermaas (Rec. trav. chim., 1932, **51**, 955—963; cf. this vol., 228).—In continuation of previous work, potentiometric titrations of OH-acids (HZ) with KBO_2 have been carried out. Vals. of K_1 $(=[H^{\cdot}][BZ'\,]/[HB][HZ])$, $K_2(=[H^{\cdot}][BZ_2']/[HB][HZ]^2)$, and $K_3(=[H^{\cdot}][Z']/[HZ])$ have been calc. for α-hydroxy*iso*butyric, *cyclo*pentanol- and *cyclo*hexanol-2-carboxylic, methylethyl- and ethylpropyl-glycollic acids.
F. L. U.

Amphoteric hydrated oxides, their aqueous solutions and crystalline compounds. XV. Conversion of ions of monotungstic acid into those of hexatungstic acid with increase in hydrogen-ion concentration of solutions of alkali tungstate. K. F. Jahr and H. Witzmann (Z. anorg. Chem., 1932, **208**, 145—156; cf. this vol., 809).—Measurements of diffusion coeffs. of Na tungstate in solutions of different acidity show that transformation of mono- into hexa-tungstate ions occurs within the range p_H 6—8. No definite intermediate stage was recognised. F. L. U.

Szyszkovski's neutral salt effect coefficient in the light of modern theories of electrolytes. A. Skapski (Bull. Acad. Polonaise, 1932, **A**, 46—49).—Theoretical. E. S. H.

Application of the differential tensimeter to the measurement of dissociation tensions. Dissociation of ammonium salts. M. Centnerszwer and S. Kowalski (Bull. Acad. Polonaise, 1932, **A**, 50—64).—An apparatus for measuring the v.p. or dissociation pressure of solid substances in a given atm. is described. The v.p. and dissociation of NH_4Cl and NH_4Br in air have been measured over a range of temp.; the influence of excess of the dissociation products is in accordance with mass action. The heats of dissociation calc. with the aid of Nernst's equation are in approx. agreement with experimental vals. E. S. H.

Redetermination of thermal dissociation equilibria of inorganic compounds. III. Determination of dissociation equilibrium of calcium hydroxide by means of high-temperature vacuum balance. S. Tamaru and K. Siomi (Z. physikal. Chem., 1932, **161**, 421—426; cf. this vol., 468).—The dissociation pressure has been determined at 405—500°. R. C.

Water vapour equilibrium over tungsten and its oxides. L. Wöhler, Z. Shibata, and R. Kunst (Z. Elektrochem., 1932, **38**, 808—812).—The coeff. $K_1=[H_2O]/[H_2]$ for the system W_2O_5–WO_3 varies with the proportions of the two oxides present, indicating that they form a solid solution. This explains the fact that W_2O_5 is never obtained pure by the reduction of WO_3, 2—3% of WO_3 always remaining. The corresponding vals. K_2 and K_3 for the systems W_2O_5–WO_2 and WO_2–W, respectively, were found to be const. as previously observed (A., 1923, ii, 471), and thus WO_2 is easily obtained pure by reduction. Neither W_4O_{11} (cf. A., 1931, 447, 583), nor any oxide other than W_2O_5, was found between WO_2 and WO_3.
M. S. B.

Dissociation of synthetic crystalline manganese oxides. F. Krüll (Z. anorg. Chem., 1932, **208**, 134—144).—The dissociation of cryst. MnO_2 in O_2 at 1 atm. begins at 500—550°. Mn_2O_3 decomposes at 900—950° into Mn_3O_4, which is stable at 1000°. Mn_3O_4 thus prepared absorbs O_2 at 900° to form Mn_2O_3, which in turn is slowly converted into MnO_2 at 500°. In all cases the partial pressure of O_2 was maintained const. at 1 atm. Rates of decomp. and of recombination were measured.
F. L. U.

Dissociation of manganese spar and manganese carbonate. J. Krustinsons (Z. Elektrochem., 1932, **38**, 780—783).—Dissociation of Mn spar at 1 atm. is observable at 407·5°, but can be completed only at approx. 700° when the CO_2 pressure is 485 mm. By heating the product to a still higher temp. practically no further dissociation is obtained. The results can be explained by the formation of a solid solution of MnO and $MnCO_3$. The heat of dissociation calc. from Nernst's formula is 25·39 g.-cal. Some CO_2 is given up by artificial $MnCO_3$ between 30° and 130°, but is re-absorbed on cooling. Actual dissociation begins only at 270°/1 atm. and is not complete until a temp. of 480° is reached, when the CO_2 pressure is 680 mm. The form of the dissociation curve is best explained by the formation of intermediate products. No CO due to reduction of CO_2 by MnO has been observed.
M. S. B.

System calcium oxide–phosphorus pentoxide. G. Trömel [with H. Schneiderhöhn] (Mitt. Kaiser Wilh.-Inst. Eisenforsch., 1932, **14**, 25—36; Chem. Zentr., 1932, i, 3025—3026).—In addition to the meta-, pyro-, and ortho-phosphates, $4CaO,P_2O_5$ is formed; oxyapatite, $10CaO,3P_2O_5$, was not observed.
A. A. E.

Equilibrium diagrams of binary systems with acetic acid and amines as components. N. A. Pushin and I. I. Rikovski (Z. physikal. Chem., 1932, **161**, 336—340).—F.-p. diagrams show that AcOH combines only in equimol. proportions with C_5H_5N, piperidine, quinoline, and $NHPh{\cdot}NH_2$, but with NH_2Ph forms only a diacetate. R. C.

Binary systems. I. System *as*-*o*-xylidine–carbonic acid. F. E. C. Scheffer and J. Smittenberg (Rec. trav. chim., 1932, **51**, 1008—1011; cf. A., 1931, 310).—Phase equilibria for the system *o*-4-xylidine–CO_2 are shown in a *p*–*t* diagram. Metastable unmixing occurs over a considerable range. The system belongs to the type H_2S–NH_3. F. L. U.

Freezing of solutions as a method of investigation in pure chemistry. IX. Mixtures con-

taining phenylglycollic and phenylaminoacetic acids. J. Timmermans and K. Motiuk (Bull. Soc. chim. Belg., 1932, **41**, 399—411).—The methods previously described (A., 1931, 676) show that no compounds are formed in the systems: *d*- or *l*-phenylglycollic acid–*l*-malic acid; *d*- or *l*-phenylglycollic acid–*l*-chlorosuccinic acid; *d*- or *l*-phenylglycollic acid–*l*-asparagine; *d*-phenylglycollic acid–*d*- or *l*-tartaric acid; *l*-phenylglycollic acid–*l*-phenylglycine. *d*-Phenylglycollic acid, however, forms an equimol. compound with *l*-phenylglycine. D. R. D.

Ternary system composed of the nitrates of potassium, sodium, and lead. K. Laybourn and W. M. Madgin (J.C.S., 1932, 2582—2589).—KNO_3 and $NaNO_3$ form a continuous series of solid solutions. KNO_3–$Pb(NO_3)_2$ and $NaNO_3$–$Pb(NO_3)_2$ form simple eutectic systems, whilst the complete system KNO_3–$NaNO_3$–$Pb(NO_3)_2$ has one ternary eutectic, no compounds being formed. D. R. D.

Polytherms of ternary systems containing water, an alkali sulphate, and a sulphate of the vitriol type. VI. A. Benrath. **VII.** A. Benrath and W. Thiemann (Z. anorg. Chem., 1932, **208**, 169—176, 177—193; cf. this vol., 229).—VI. Solid phases have been characterised and their solubilities determined between 0° and 100° for systems containing sulphates of K+Co, NH_4+Co, Rb+Co, K+Ni, NH_4+Ni, Tl^I+Ni, and Rb+Ni.

VII. Similar data have been obtained for sulphates of Tl^I+Co, NH_4+Mg, NH_4+Cd, and Na+Cd. Formation of the double *salts* $CdSO_4,(NH_4)_2SO_4,2H_2O$ and $3CdSO_4,(NH_4)_2SO_4,5H_2O$ was observed. F. L. U.

Equilibria $Pb+SnCl_2 \rightleftharpoons PbCl_2+Sn$ and $Cd+PbCl_2 \rightleftharpoons CdCl_2+Pb$ in melts. Applicability of the ideal mass-action law. F. Körber and W. Oelsen (Z. Elektrochem., 1932, **38**, 557—563).—Contrary to the report of Lorenz, the equilibria at 500—600° conform to the ideal law of mass action, but if the mixtures are not cooled with sufficient rapidity, *e.g.*, by pouring on to a Cu block, large deviations are observed. The equilibrium const. for the system $Pb+SnCl_2$ is 3·45±0·45 at 600° and 5·6±0·7 at 500°; the calc. heat of reaction is 5·6—7 kg.-cal. per mol. as compared with 3·7—4·9 calc. from the heats of formation of the chlorides. No evidence could be obtained of a transition in the Sn-rich mixtures, as reported by Lorenz. For the system $Cd+PbCl_2$ the equilibrium const. at 600° is 37·5±5·5; the temp. coeff. is very large, the calc. heat of reaction being 7·85 kg.-cal. per mol. The heat of reaction between Cd and $SnCl_2$ is 11·7 kg.-cal. per mol. The apparent applicability of the mass-action law to heterogeneous systems of this type is discussed. H. F. G.

Thermal decomposition of zinc and cadmium carbonates in an atmosphere of water vapour. A. Lehrman and N. Spear (J. Physical Chem., 1932, **36**, 2664—2669).—No equilibrium is reached with $CdCO_3$, but with $ZnCO_3$ and H_2O vapour at 1 atm., equilibrium is rapidly attained. F. D. R. (*c*)

Thermodynamics of lead bromide. J. Y. Cann and R. A. Sumner (J. Physical Chem., 1932, **36**, 2615—2620).—For the reaction $Pb(s)+2AgBr(s)=PbBr_2(s)+2Ag(s)$ e.m.f. measurements give $\Delta F^\circ_{298\cdot1}$, −16258; $\Delta S^\circ_{298\cdot1}$, −12·599; $\Delta H^\circ_{298\cdot1}$, −20014. From these vals. other data are calc. F. D. R. (*c*)

Nitrogen compounds of germanium. II. Equilibrium in system Ge–NH_3–Ge_3N_4–H_2. Dissociation of germanic nitride. G. H. Morey and W. C. Johnson (J. Amer. Chem. Soc., 1932, **54**, 3603—3610).—Equilibrium data for the reaction $3Ge+4NH_3=Ge_3N_4+6N_2$ are recorded. ΔH at 883—937° abs. is 155,600 g.-cal. According to NH_3 equilibrium data, the equilibrium const. of the reaction $Ge_3N_4=3Ge+2N_2$ varies from 19·63 at 883° to 0·650 at 937°. ΔH for 883—937° is −102,000 g.-cal. J. V. V. (*c*)

Polyiodides in benzonitrile. J. H. Martin (J.C.S., 1932, 2640—2643).—The *compounds* $KI_3,2PhCN$, m.p. 53°, $NaI_3,2PhCN$, m.p. 67°, $LiI_3,4PhCN$, m.p. 92·5°, $HI_3,4PhCN$, m.p. 97°, and $LiI_3,4o\text{-}C_6H_4Me\cdot CN$ have been obtained by crystallisation from solutions of the corresponding monoiodides and I in the appropriate nitrile. The dissociation pressure increases with the at. wt. of the metal, and RbI_3 and CsI_3 do not combine with PhCN. No similar compounds could be prepared using MeCN or $CH_2Ph\cdot CN$. PhCN extracts KI and I_2 in equimol. proportions from a solution of I in aq. KI. D. R. D.

Equilibria in reduction [oxidation, and carburisation] processes in iron [XI]. R. Schenck (Z. anorg. Chem., 1932, **208**, 255—256; cf. this vol., 811).—A correction. F. L. U.

Study of aqueous solutions at high temperatures. I, II. E. I. Achumov and B. B. Vassiliev (J. Gen. Chem. Russ., 1932, **2**, 271—281, 282—289).—I. Methods and apparatus for the determination of solubility of salts at high temp. are described.

II. Equilibrium diagrams for KCl–NaCl–$MgCl_2$–H_2O at 125°, 150°, 200°, and 265° are given. R. T.

Solvent properties of soap solutions. III. System sodium oleate–sodium chloride–water–ethyl acetate. E. L. Smith (J. Physical Chem., 1932, **36**, 2455—2473; cf. this vol., 802).—At 25° the system Na oleate–NaCl–H_2O has one more degree of freedom than is allowed by the phase rule, since the solubility of Na oleate curd fibres is a function of their diameter. Na oleate, EtOAc, and H_2O yield six phases: isotropic Na oleate solution, middle soap, neat soap, curd soap, wet EtOAc, and vapour. Na oleate, NaCl, and EtOAc are almost immiscible. The quaternary system yields six phases: neat soap, curd soap, NaCl, brine, EtOAc, and vapour. The proportion of soap in the colloidal state can be calc. approx. from the data. C. T. S. (*c*)

Entropies of some simple polyatomic gases calculated from spectral data. R. M. Badger and S. Woo (J. Amer. Chem. Soc., 1932, **54**, 3523).—The entropies of CO_2, N_2O, HCN, and C_2H_2 at 298·2° abs. have been calc. The "virtual" entropies (those to be compared with calorimetric data) are 51·07, 52·58, 48·23, and 48·00 E.U., respectively. The corresponding abs. entropies are 51·07, 56·94, 51·79, and 50·75. J. B. A. (*c*)

Internal effect in thermodynamic transformations. V. Njegovan (Arh. Hemiju, 1932, 6, 154—161).—Mathematical. R. T.

Heat of formation of hydrogen chloride. H. von Wartenberg and K. Hanisch (Z. physikal. Chem., 1932, 161, 463—469).—The val. 21·89±0·01 kg.-cal. at 24° has been obtained by direct synthesis. R. C.

Calorimetric method for determining the intrinsic energy of a gas as a function of the pressure. E. W. Washburn (Bur. Stand. J. Res., 1932, 9, 521—528).—A method for determining the change in internal energy of a gas ($\pm < 1$ g.-cal. for a litre bomb) under pressure is suggested. A known mass of gas is compressed in a bomb at a known pressure and allowed to expand slowly to atm. pressure; the bomb is immersed in a calorimeter and the cooling effect is compensated by electrical heating. E. S. H.

Free energy, entropy, and heat of formation of iron carbide (Fe_3C). C. P. Yap and C. L. Liu (Trans. Faraday Soc., 1932, 28, 788—797).—The following data are obtained for the reaction 3α-Fe+C=Fe_3C at 25°: free energy 9300, heat of formation 12,300, entropy of formation 9·9, abs. entropy 31·8 g.-cal. per mol. Fe_3C is stable above 750°. E. S. H.

Heats of combustion of the chloroacetic acids and their esters. E. Schjånberg (Svensk Kem. Tidskr., 1932, 44, 227—231).—Data are recorded for acetic, mono-, di-, and tri-chloroacetic acids, their Pr^{α}, Pr^{β}, Bu^{α}, Bu^{β}, and *iso*amyl esters, and for the Me, Et, and allyl chloroacetates. The difference in the series mono-, di-, and tri-chloroacetic esters, and in the series Et, Pr, etc., is not const. Calculation of the energy of decomp. of the C·Cl linking gives vals. which also show no constancy; in some series, *e.g.*, the Bu and allyl esters, the vals. increase with the Cl content, but diminish in others, *e.g.*, the Et and Pr^{β} esters. H. F. H.

Concentration at which heats of dilution are measured in the calorimetric method. V. K. La Mer and I. A. Cowperthwaite (J. Amer. Chem. Soc., 1932, 54, 4114—4115).—The vals. recorded by Lange and Robinson (Chemical Reviews, 1931, 9, 89) for heats of dilution, whilst probably correct for the final concns., do not constitute measured vals., but depend on the validity of the Debye–Hückel theory. C. J. W. (*c*)

Electric conductivity of solutions of alkali metals in liquid ammonia. L. Farkas (Z. physikal. Chem., 1932, 161, 355—361).—The variation with concn. of the electron conductivity may be explained by supposing that the electrons undergo "non-mechanical" transitions from one alkali metal atom to another in the direction of the field, and that the alkali metal atoms in the solution are arrayed in a regular manner as in a crystal lattice, the interat. distance varying with the concn. This theory leads to results in agreement with published data for solutions of Na in NH_3. R. C.

Conductivity of salts and alkalis in sucrose solutions. E. Landt [with C. Bodea and Saalman] (Z. Elektrochem., 1932, 38, 630—631).—The vals. of the product of λ_{∞} and the viscosity for solutions of NaCl, KCl, and $BaCl_2$ in saturated sucrose solution are 618·7, 727·7, and 508·1, respectively, at 20°. Decrease of hydration of the ions does not alone suffice to explain the abnormal conductivity. Walden's rule is increasingly valid for solutions of NEt_4 picrate as the temp. is raised from 35° to 50°. It is probable that in sucrose solutions there exist large aggregates of solvent and solute mols. which are responsible for the high viscosity and act as obstacles to the movements of ions. The mobility of an ion is depressed the more, the larger is the ion. Kohlrausch's law is valid for all the solutions studied, but the Debye–Hückel–Onsager theory is only qualitatively applicable to sucrose solutions. Sucrose behaves as a dibasic acid in solutions containing $Ca(OH)_2$ etc.; it is not correct to assume that in such solutions the conductivities of the "sucrate" and of the alkali are independent of the sucrose concn. H. F. G.

Conductivity data of aqueous mixtures of hydrogen peroxide and organic acids. II. W. H. Hatcher and E. C. Powell (Canad. J. Res., 1932, 7, 270—282).—On adding H_2O_2 to aq. org. acids (HCO_2H, AcOH, $EtCO_2H$, succinic and monopersuccinic acids), there is a fall in conductivity due to formation of non-ionised complexes of the type RCO_2H,H_2O_2. These eliminate H_2O slowly, forming the ordinary peracids, $RCOO_2H$, the H of which is not ionisable. It is shown conductometrically and by titration with alkali and phenolphthalein that monopersuccinic acid is monobasic. D. R. D.

Electrochemistry of ethereal solutions. VI. Conductivity of ethereal solutions in connexion with complex formation. M. Ussanovitsch. **VII. System antimony trichloride–ethyl ether.** M. Ussanovitsch and F. Terpugov (J. Gen. Chem. Russ., 1932, 2, 443—446, 447—454).—VI. Halides of As or Sb which give non-conducting solutions in org. solvents form compounds with the latter of a different type from the oxonium compounds present in conducting solutions.

VII. Conductivity curves for the system $SbCl_3$–Et_2O are given for 0—100°. The max. sp. conductivity is 2·6 for 95% $SbCl_3$. The decomp. potential is 0·97 volt. The electrolyte is $Et_2O,2SbCl_3$. R. T.

Explanation of certain secondary phenomena in the determination of hydration of ions. J. Baborovský (Chem. Listy, 1932, 26, 474—476).—The discrepancies between the vals. for electrolytic transport of H_2O and the transport nos. of ions found for aq. H, alkali, and alkaline-earth halides are due not to electro-osmotic factors, but to reduction of the mobility of the anion by the parchment membrane used, and to dehydration of the latter by the electrolytes at higher concn. R. T.

Theory of surface conductivity. J. J. Bikerman (Z. Elektrochem., 1932, 38, 763—764).—McBain and Dubois' objection to Smoluchowski's expression for surface conductivity (A., 1931, 1121), on the ground that the double layer would be too thin to exist, is based on an error in the val. taken for the dielectric const. The surface conductivity measurements of White, Urban, and van Atta (this vol., 699) give a much larger val. for the double layer. M. S. B.

Similar electrical conductivity of moving and stationary surfaces: the Laing paradox. R. Dubois (Z. Elektrochem., 1932, **38**, 764—769).—Surface conductivity is to be ascribed to (1) the conductivity of the solid walls and (2) the conductivity due to the mobile ions of the electrical double layer. (1) depends on the excess free charge of the solid walls and (2) is the numerical sum of the ionic charges in the double layer, independent of sign. At the isoelectric point the part due to (1) is zero, but that due to (2) has a finite val., which explains the surface conductivity observed by Briggs at the isoelectric point (A., 1928, 713). Calculations from available data indicate that the conductivity of the solid walls forms 13—46% of the total surface conductivity. The effective mobility of the ions attached to the walls is as great as, or even considerably greater than, that of ordinary dissolved ions. Smoluchowski's equation for surface conductivity is incorrect, since it leads to a val. for the thickness of the double layer of < at. dimensions (cf. preceding abstract). M. S. B.

Thermo-electric behaviour of tungsten, molybdenum, and tantalum. A. Schulze (Z. Metallk., 1932, **24**, 206).—The e.m.f. of the Pt–Mo couple rises from 1·22 mv. at 100° to 10·6 at 500°, 29·40 at 1000°, and 42·73 mv. at 1300°. The corresponding figures for the Pt–W couple are 0·77, 8·89, 28·28, and 43·04 mv., and for the Pt–Ta couple 0·42, 4·41, 15·42, and 25·40 mv. Below 0° the e.m.f. is of opposite sign and passes through a min. at about —150°. The e.m.f. of the W–Mo couple rises to a max. of 2 mv. at 600° and then falls smoothly to zero at 1200°, whilst that of the Ta–W couple is 0·35 at 100°, 4·75 at 500°, 12·86 at 1000°, and 17·64 mv. at 1300°. A. R. P.

Calomel electrode. I. Dependence of electrode potential on lapse of days and on temperature. II. Junction potential between a concentrated and a dilute potassium chloride solution. M. Hiraki (Acta Schol. Med. Kioto, 1922, **14**, 300—316, 288—299).—I. The potential of a freshly-prepared HgCl electrode is stabilised in about 2 weeks, independently of the concn. of the KCl or of the purity of the materials used. Between 5° and 40° equilibrium is attained in 30—40 min. Temp. coeffs. of 0·1*N*-, 3·5*N*-, and saturated HgCl electrodes are recorded.

II. When dil. and conc. KCl solutions are brought into contact in an agar medium, the equilibrium diffusion potential is attained in 30—40 min.; the variation is <0·1 mv. Ch. Abs.

Standard electrode potentials of Ag–AgCl and calomel electrodes and single potentials of calomel electrodes. H. M. Spencer (J. Amer. Chem. Soc., 1932, **54**, 3647—3648).—From Randall and Young's data $E^0_{298\cdot1}$ for Ag–AgCl is —0·2222$_1$ volt, compared with —0·2223 volt by Carmody's extrapolation. If Gerke's val. of 0·0455 volt is taken for the difference between the HgCl and Ag–AgCl electrodes, $E^0_{298\cdot1}$ for the HgCl electrode is 0·2677 volt. On this basis the single potentials for calomel electrodes with various concns. of KCl are calc. Correcting for liquid junction potential, the "normal HgCl electrode" val. is —0·2800 volt. R. H. C. (*c*)

Causes of the hydrogen effect. IV. L. Wolf [with L. Penjkova-Uspenskaja] (Z. Elektrochem., 1932, **38**, 622—627; cf. this vol., 586).—The fall of p_H during use of the H electrode is due to replacement of the $H^{\cdot}$ in the outer surface of the electrical double layer on the Pt by cations from the electrolyte. The magnitude of the H effect varies with the area of the Pt electrode; an electrode transferred from one solution to another does not show the effect a second time, unless washed. No effect is observed unless Pt-black and H are present simultaneously. H. F. G.

Electrochemical behaviour of aluminium. III. R. Müller (Z. anorg. Chem., 1932, **208**, 304—312; cf. A., 1926, 1105).—When $AlBr_3$ is dissolved in a large amount of C_5H_5N 220·9 kg.-cal. are evolved, of which about 99·9% is heat of formation of $AlBr_3,3C_5H_5N$, the remainder being heat of dissolution of the solvate. With PhCN 44 kg.-cal. are evolved, due to formation of $AlBr_3,4PhCN$, which dissolves in excess of PhCN without measurable thermal effect. Electrode potentials of (amalgamated) Al in a saturated solution of $AlBr_3$ in C_5H_5N, in the eutectic mixture (13·15% C_5H_5N), and in PhCN saturated with $AlBr_3$ are, respectively, 0·87, 0·33, and 0·52 volt negative to H. All these vals. are much lower than those calc. on the assumption that the potential is determined by the process $Al \longrightarrow Al^{\cdot\cdot\cdot}$. F. L. U.

Electrometric studies of the precipitation of hydroxides. VII. Glass-electrode titrations of mercuric salt solutions. H. T. S. Britton and (Miss) B. M. Wilson (J.C.S., 1932, 2550—2557).—The p_H at which HgO is pptd. on running aq. NaOH into aq. $Hg^{\cdot\cdot}$ salts varies from salt to salt, owing to the varying degrees of ionisation and complex ion formation. $Hg(ClO_4)_2$ is considerably ionised, but not appreciably hydrolysed, $HgSO_4$ and $Hg(NO_3)_2$ suffer considerable ionisation and appreciable hydrolysis, whereas $HgCl_2$, $HgBr_2$, $Hg(CN)_2$, $Hg(NO_2)_2$, and $Hg(OAc)_2$ are weak electrolytes. Pptn. occurs when the solubility product $[Hg^{\cdot\cdot}][OH']^2=10^{-26}$ is reached. Addition of KX (X=halogen) to aq. HgX_2 raises the p_H at which pptn. occurs, owing to formation of HgX_4''. HgI_4'' is not affected by NaOH. D. R. D.

Theory of glass electrode. II. Glass as a water electrode. M. Dole (J. Amer. Chem. Soc., 1932, **54**, 3095—3105; cf. this vol., 700).—The failure of the glass electrode to act as a perfect H electrode in strongly acid solutions is explained on the assumption that $H^{\cdot}$ migrates through the glass with 1 mol. of H_2O of hydration. This theory indicates that the glass electrode will not act like a H electrode in non-aq. solutions. M. D. (*c*)

Influence of formation of complexes on attainment of equilibrium in certain oxidation–reduction systems. W. F. Jakób and M. R. Reznar (Chem. Listy, 1932, **26**, 461—466).—E_H for mixtures of aq. $[H_2(MoO)_6]H_5(NH_4)_5$ and $NH_4[Mo_2O\cdot MoO_4(OH)_7]$ has been measured at p_H 3·4—5·2. The E_H–p_H curve is not rectilinear, pointing to possible reaction between oxidation–reduction complexes and $H^{\cdot}$, with consequent activity changes. R. T.

Potentiometric study of Scholl's anthroxyl radicals. L. F. Fieser and W. Y. Young (J. Amer. Chem. Soc., 1932, 54, 4095—4100).—These radicals (A., 1931, 846) form, with their reductants, fairly stable oxidation–reduction systems, the potentials of which have been measured. In dil. acid solution the reductant of the radical is formed by the intramol. condensation of the corresponding α-aroylanthrahydroquinone. C. J. W. (c)

Electrokinetic potential of porcelain diaphragms. A. Vašíček (Chem. Listy, 1932, 26, 503—507).—Electro-osmotic measurements of the electrokinetic potential (P_κ) of an unglazed porcelain diaphragm in aq. KCl are not in agreement with those obtained by the filtration potential method, owing to electrolytic transport, which becomes considerable in conc. solutions. The P_κ–dilution curve rises linearly from 0·02*N*- to a max. at 0·002*N*-KCl, below which it gradually falls. R. T.

Electro-osmosis at porcelain diaphragms in aqueous potassium chloride. J. Velíšek and A. Vašíček (Chem. Listy, 1932, 26, 507—512).—The electro-osmotic potential of a porcelain diaphragm has a max. val. of 42 mv. in 0·002*N*-KCl. The diaphragm used has much larger pores than kaolin diaphragms. R. T.

Electro-osmosis with a ceramic diaphragm in aqueous solutions of some alkali halides. J. Velíšek and A. Vašíček (Coll. Czech. Chem. Comm., 1932, 4, 428—443; cf. A., 1931, 434).—Electro-osmotic measurements have been made for aq. solutions of LiCl, NaCl, KCl, KBr, and KI at concns. of 0·00005—1·0*N*, using a porcelain diaphragm. The electro-kinetic potential curve shows a max. for LiCl, NaCl, and KCl, but not for KBr and KI. At medium concns. electro-osmotic transport is nearly the same for all electrolytes investigated. J. W. S.

Variation of the electrokinetic potential with the chemical composition of the diaphragm. N. Schönfeldt (Z. Elektrochem., 1932, 38, 628—630).—The electrokinetic potential ζ of sintered Al_2O_3 diaphragms containing up to 95% of SiO_2, BeO, or $AlPO_4$ in 0·05% KCl solutions has been measured. ζ varies, differently in each case, with the percentage composition of the diaphragm, and similar variations are observed with diaphragms consisting of a mixture of coarse and fine Al_2O_3. There is apparently no relation between ζ and the composition of the diaphragm. H. F. G.

Electrokinetic phenomena. IX. Electrophoresis and electro-osmosis. H. A. Abramson (J. Gen. Physiol., 1932, 16, 1—3).—For surfaces coated with purified cryst. horse serum-albumin, the ratio of the electro-osmotic mobility to the electrophoretic mobility is approx. unity. This result confirms the theory of Henry (A., 1931, 1232). W. O. K.

Technique of electro-osmotic measurements. P. I. Andrianov (Kolloid-Z., 1932, 61, 46—47).—A modified form of the apparatus of Harkevitsch (A., 1929, 265) is described. E. S. H.

Overvoltage. V. Moving-coil oscillograph system for study of overvoltage and transfer resistance. A. L. Ferguson and G. M. Chen (J. Physical Chem., 1932, 36, 2437—2445; cf. this vol., 701).—An oscillograph–commutator system is described for use in the study of transient electrode phenomena. Oscillograms for charging and discharging intervals are given and a direct comparison of the polarisation potentials as determined simultaneously by the commutator and direct methods is obtained. Previous results with the commutator–potentiometer system are confirmed. R. H. C. (c)

Effect of applied voltage on electrolysis in residual current range. G. H. Damon (J. Physical Chem., 1932, 36, 2497—2503).—Below 0·5 volt the residual current is practically independent of voltage, but above 0·5 volt increases rapidly with the voltage. For the higher voltages it is greater in air than in vac. R. H. C. (c)

Electrochemical periodicities. M. Lignana (Nature, 1932, 130, 474).—A cell with a Cu anode and 25% H_2SO_4 as electrolyte in which the ratio of e.m.f. to circuit resistance has a certain crit. val. shows periodic variations of the current which flows through it. The effect is due to the alternate formation and destruction of a thin anodic layer, analogous to that responsible for the passivity of metal electrodes. L. S. T.

Depth distribution of current in electrolytic cells. O. Busse (Z. Elektrochem., 1932, 38, 783—793).—Measurements of the thickness of the electrolytically deposited layer of metal on the cathode, and direct measurement of c.d. at a divided cathode, do not give satisfactory results. Concordant results are obtained by the following methods: (1) fall in c.d., measured by changes in wt., along a divided bent cathode; (2) potential fall at different parts of the surface of a bent cathode by means of a test electrode; (3) tracing of equipotential lines through the electrolyte by a test electrode. Vals. of $\gamma=E_b/\alpha$ are recorded, where E_b is the e.m.f. of the bath and α is obtained from $z=u^\alpha$, z being the potential at a point in the bath at a distance u from the anode. A bath with a high γ val. gives the most favourable results. It is obtained at low temp., high c.d., and low electrical conductivity. M. S. B.

Theory of passivity phenomena. XVI. Properties of natural coating of iron after various kinds of mechanical treatment. W. J. Müller and W. Machu (Z. physikal. Chem., 1932, 161, 411—420).—The pore area in the coating is greater if the metal has been rubbed only with coarse emery paper or has received the highest polish than if it has been treated only with moderately fine emery paper. The thickness of the film, judged by its resistance, is independent of such mechanical treatment. R. C.

Topochemistry of corrosion and passivity. III. E. Pietsch [with E. Josephy, B. Grosse-Eggebrecht, and W. Roman] (Korrosion u. Metallschutz, 1932, **8**, 57—66; Chem. Zentr., 1932, ii, 117—118; cf. this vol., 128).—It is probable that the processes involved in the dissolution of the material, following adsorption, are associated with an exchange of electric charge. This is significant for the chemical, but not for the adsorption, process. In the case of Pt–Zn in dil. H_2SO_4, SO_4'' is adsorbed on the Zn and H on the Pt at the Pt–Zn phase boundary; the two negative charges liberated by the formation of the $[Zn^{\cdot\cdot}SO_4'']$ complex in the Zn lattice pass by way of the Pt to $2H^{\cdot}$ and discharge these to H_2. This, having relatively to H a small adsorption potential, leaves the surface, whilst the $[Zn^{\cdot\cdot}SO_4'']$ complex, being unstable in the lattice, passes into solution. A. A. E.

Passivity of gold. W. J. Shutt and A. Walton (Trans. Faraday Soc., 1932, **28**, 740—752; cf. A., 1930, 1527).—The potential changes accompanying the spontaneous reactivation of a passivated Au anode in 0·125—4*N*-HCl have been investigated by an improved method at temp. between 15° and 65·5°. The interruption of the passivating current is followed instantaneously by an abrupt fall of potential to an almost const. val. A subsequent small inflexion is followed by a slow voltage drop which terminates in a sudden fall to the normal potential of active Au. The "total time of recovery," θ, varies considerably with c.d. at high rates of stirring, and the temp. coeff. of θ is of the order of that required by a chemical reaction rather than of physical processes. θ is increased by dissolved Cl_2 and by decreasing [HCl]. For HCl–KCl mixtures, $\theta=k/[H^{\cdot}]+\theta_{Cl}$, where θ_{Cl} decreases rapidly with [Cl′], with passivating c.d., and with increased stirring, and *k* is approx. const. The time required for cathodic reduction increases with passivating current, duration of passivity, and less efficient stirring. Passivation of Au in H_2SO_4 was investigated, and the thickness of the oxide film in HCl and H_2SO_4 is shown to be only uni- or bi-mol. A mechanism consistent with the results is developed. The first stage in the reactivation is independent of acid content, but proceeds at a rate approx. proportional to $[Cl']^2$ and involves the interaction of a peroxide with Cl′ to produce Cl_2 and Au_2O_3, which subsequently dissolves at a velocity governed by $[H^{\cdot}]$. J. G. A. G.

Passivation of tantalum in non-aqueous solvents. A. Methyl, ethyl, propyl, butyl, and *iso*-amyl alcohols. P. Schupp (Z. Elektrochem., 1932, **38**, 774—777).—The valve action of Ta in alcohols is similar to that in H_2O. The max. e.m.f. is very low in MeOH and increases with the mol. wt. of the alcohol. The low vals. do not, however, represent true max., but are due to oxidation of the alcohol by anodic O instead of formation of Ta_2O_5. The thickness of the oxide layer depends only on the voltage employed and is proportional to it. Its val. is the same in alcohols as found by Günther-Schulze in H_2O (A., 1931, 546, 1130). $Ca(NO_3)_2$ was used as electrolyte. M. S. B.

Brönsted's kinetic equation and Debye's theory. A. Musil (Monatsh., 1932, **61**, 229—273).—A theoretical interpretation of the divergences from the classical laws of chemical kinetics in the alkaline hydrolysis of esters is based on Brönsted's kinetic equation and Debye's theory. J. W. S.

General considerations in connexion with the chain-reaction theory. N. N. Semenov (Trans. Faraday Soc., 1932, **28**, 818—822).—A theoretical discussion, emphasising the rôle of free energy in chemical kinetics and ascribing secondary importance to temp., concn., catalysts, etc. E. S. H.

Inert gas effects in chain reactions. H. W. Melville (Trans. Faraday Soc., 1932, **28**, 814—818).—A discussion of the effects of foreign gases on chain reactions between O_2 and H_2, CH_4, PH_3, H_2S, CS_2, and P_4, respectively, reveals regularities, which are in accordance with the theory developed. The inert gas has a greater accelerating influence on reactions which involve the oxidation of light mols. The mass of the chain carrier mols. appears to increase with increasing mass of the mol. of combustible substance. E. S. H.

Function of the solvent in unimolecular reactions. M. Magat (Z. Elektrochem., 1932, **38**, 619).—The influence of the solvent may be due to the formation of swarms containing solute and solvent mols. H. F. G.

Thermal dissociation. I, II. M. F. Strunnikov (J. Gen. Chem. Russ., 1932, **2**, 140—153, 154—165).—I. Theoretical. Reactions are preceded by dissociation with formation of free valencies, or by the production of additional valencies, this applying to all substrates present.

II. Examples of the above processes are given, and catalysis is considered from this point of view. R. T.

Rate of dissociation of nitrogen tetroxide. C. E. Teeter, jun. (J. Amer. Chem. Soc., 1932, **54**, 4111).—Richards and Reid's results for the velocity coeff. (this vol., 916) could not be confirmed. Velocity coeffs. calc. from Einstein's original equations may be 20% too low. C. J. W. (*c*)

Thermal decomposition of methane. L. S. Kassel (J. Amer. Chem. Soc., 1932, **54**, 3949—3961).—The decomp. in quartz bulbs at 700—850° is initially unimol. and homogeneous. Under some conditions there is an induction period. The primary process is probably the formation of CH_2 and H_2 with a rate coeff. of $5\times10^{11}e^{-79385/RT}$ and the next step the combination of CH_2 and CH_4 to give C_2H_6. H_2 greatly retards the decomp., which is accounted for by supposing C_2H_6 to lose H in successive steps to C_2H_4, C_2H_2, and C, all the steps being reversible. L. P. H. (*c*)

Energy exchanges between unlike molecules. Decomposition of methyl ether, ethyl ether, acetone, and their binary mixtures. L. S. Kassel (J. Amer. Chem. Soc., 1932, **54**, 3641—3647).—Contrary to Steacie's observation (this vol., 576, 701), mixtures of Et_2O with Me_2O or $COMe_2$ decompose at a rate which indicates that the transfer of internal energy occurs about as readily between unlike as between like mols. H. A. B. (*c*)

Homogeneous thermal polymerisation of $\Delta^{\alpha\gamma}$-butadiene. W. E. Vaughan (J. Amer. Chem. Soc., 1932, **54**, 3863—3876).—The reaction at 720—

1·5 mm. and 326—436° follows the second-order equation over the greater portion of the association. The rate is expressible by log $k = -568_0(1/T)+7{\cdot}67_3$.
W. E. V. (*c*)

Kinetics of the oxidation of gaseous acetaldehyde. W. H. Hatcher, E. W. R. Steacie, and F. Howland (Canad. J. Res., 1932, 7, 149—161).—The velocity of reaction in $MeCHO$–O_2 mixtures at 60—120° has been studied by observing the pressure change at const. vol. During the somewhat lengthy induction period, CO_2, H_2O, and HCO_2H are the main products, whilst in later stages of the reaction peroxides and their oxidation products are formed. An increase of the surface in contact with the reacting mixture increases the induction period. The main reaction is of the chain type, the chains commencing, and to some extent ending, at the walls of the vessel; its order varies from about 1·7 at 60—100° to 1·47 at 120°. The heat of activation is 8·7±0·7 kg.-cal. Bodenstein's views on the reaction, and particularly his opinion that the induction period is due to the effect of inhibitors derived from stop-cock grease, do not accord with the results obtained. H. F. G.

Mechanism of the initiation and propagation of detonation in solid explosives. W. Taylor and A. Weale (Proc. Roy. Soc., 1932, A, 138, 92—116).—An investigation has been made of the conditions whereby a thin layer of explosive can be initiated to explosive decomp. by percussive forces of the same order of magnitude as those present in the shock waves associated with detonations. Ignitions may be caused by impacts with insufficient energy to raise the sample of explosive to the ignition temp. The temp. variation of the ignition process has been studied and an exponential relation found, suggestive of a surface activation mechanism.
L. L. B.

Photographic studies of detonation of explosives. T. Urbański (Rocz. Chem., 1932, 12, 715—769).—Photographs of detonation of picric acid (I) and of cellulose nitrate (II), taken at intervals of 0·0001 sec., indicate that the primary flame consists of blue, green, red, and infra-red rays, whilst blue rays are absent from the secondary flame, representing reaction between the products of explosion. In both flames the intensity of the rays increases in the order blue, green, red. The primary flame consists of a central core, with a rosette of rays around it; with time, these rays form a series of rings, of the shape of truncated cones. The non-luminous products of detonation of (II), but not of (I), re-emit light on contact with Cu. The duration of the primary flame is 0·0004—0·0005 sec., respectively, for (I) and (II); the duration of emission of green and red light by the secondary flame is, respectively, 0·0008 and 0·001 sec. for (I). R. T.

Kinetics of reaction of potassium permanganate with hydrogen peroxide in acid solutions. II. W. Limanowski (Rocz. Chem., 1932, 12, 638—650).—The velocity of reduction of $KMnO_4$ by excess of H_2O_2 in presence of H_2SO_4, HNO_3, or H_3PO_4 is given by $dx/dt = k_1b(1-x)+k_2ax(1-x)$, where x is the relative fall in concn. of $KMnO_4$, a its initial concn., and b that of H_2O_2. $KMnO_4$ is simultaneously reduced by H_2O_2 and by $Mn^{\cdot\cdot}$; alkali metal phosphates and fluorides catalyse the latter but not the former reaction. $H^{\cdot}$ in low concn. retard, and in higher concn. accelerate, reaction. The process of reduction of Mn^{VII} to Mn^{II} is practically instantaneous. The temp. coeff. of the reaction between $KMnO_4$ and H_2O_2 is 2·06, and of that between $KMnO_4$ and $Mn^{\cdot\cdot}$ 1·52, over the range 0—20°. In low concn. of H_2O_2 and acids, glass and SiO_2 catalyse the reaction. R. T.

Kinetics of the [thermal] iodine–oxalate reaction. R. O. Griffith and A. McKeown (Trans. Faraday Soc., 1932, 28, 752—760; cf. this vol., 702; A., 1924, ii, 327; 1925, ii, 141).—The data obtained at temp. between 40° and 60° with $M/100$—$M/1500$ I and $M/6$—$M/12$ Na and K oxalate in $M/5$—$M/1000$ KI are consistent with the reaction $Na_2C_2O_4+I_2 \longrightarrow 2NaI+2CO_2$, proceeding by way of two simultaneous and independent processes. The velocity coeff. of the process unimol. with respect to I_2 has the temp coeff. 9·4 and the crit. increment of the rate-determining step $HOI+HC_2O_4' \longrightarrow H_2O+2CO_2+I'$ is 18,550 g.-cal. The following is suggested for the process semi-mol. with respect to I_2: (*a*) $I_2 \rightleftharpoons 2I$, (*b*) $I_2+I' \rightleftharpoons I_3'$, (*c*) $I+C_2O_4'' \longrightarrow I'+C_2O_4'$, and (*d*) $C_2O_4'+I_2 \longrightarrow 2CO_2+I+I'$; the crit. increment of (*c*) is computed to be 17,800 g.-cal. approx. There is no evidence for a reaction between HC_2O_4' and I atoms. J. G. A. G.

Velocity of esterification of alcohols in acetic acid. A. Kailan and R. Raff (Monatsh., 1932, 61, 116—142).—The velocities of esterification at 25° of $Pr^{\alpha}OH$, $Pr^{\beta}OH$, $Bu^{\alpha}OH$, $Bu^{\beta}OH$, *sec.*- and *tert.*-butyl, *n*-amyl, and *n*-octyl alcohols, pentan-β- and -γ-ol, γ-methylbutan-α-ol (containing 20·8% of *l*-β-methylbutan-α-ol), and octan-β-ol in AcOH containing "0·112 mol." and "1·1 mol." H_2O per kg. of 100% acid, have been determined (cf. A., 1929, 655). In presence of HCl as catalyst the velocity is increased by a higher initial H_2O content, but in its absence the reverse is the case; in the former case it is approx. proportional to the HCl content. The influence of the catalyst is the more marked the higher is the velocity coeff. In the drier AcOH in presence of HCl, where the steric effect is most marked, the velocity coeff. of the *n*-primary alcohols is approx. 10 times that of the corresponding *n*-β-OH-compounds, and decreases steadily to C_4, further elongation of the chain being without effect. In branched-chain alcohols the vals. are the lower the nearer is the OH group to the position of branching.
H. A. P.

Velocity and mechanism of racemisation. I. Rochelle salt. A. N. Campbell and A. J. R. Campbell (J. Amer. Chem. Soc., 1932, 54, 3834—3841).—The rate of inactivation of Na K tartrate when heated with NaOH has been measured. The interpretation of the experimental results is rendered difficult by the formation of a lævorotatory complex. The evidence for the existence of this complex depends on the sign of rotation, [OH′], and a phase theory study of the system Na K tartrate–H_2O–NaOH. S. L. (*c*)

Ester formation in glycerol and ethyl alcohol. A. Kailan and P. Ulicny (Monatsh., 1932, 61, 169—

188).—The velocities of esterification of *n*- and *iso*-valeric, *n*-hexoic, *n*-octoic, and benzoic acids in glycerol, and of *o*-, *m*-, and *p*-toluic acids in EtOH, under the influence of HCl, and of *n*-valeric acid in glycerol with H_2SO_4 as catalyst, have been measured at 25° (cf. A., 1930, 710). With carefully dried starting materials the velocity coeffs. for a unimol. reaction are in all cases proportional to the HCl concn., but in the initial presence of H_2O this is so only in the case of the aliphatic acids in glycerol. The vals. for *o*-, *m*-, and *p*-toluic acids are in the ratio 1 : 3·28 : 3·02.

H. A. P.

Kinetics of reaction between bromoacetate and thiosulphate ions at great dilutions. A. N. Kappanna and H. W. Patwardhan (Rec. trav. chim., 1932, 51, 379—382; cf. A., 1929, 516).—Repetition of previous work over a wider range of temp. (30—90°) confirms the validity of the Brönsted–Debye theory as applied to this reaction, contrary to the results obtained by La Mer (A., 1930, 168). The energy of activation of the reacting ions is calc. to be 15,680 g.-cal.

F. L. U.

Rates of hydrolysis to betaines of some quaternary bases of α-aminonitriles. Quaternary ammonium bases. T. D. Stewart and K. Korpi (J. Amer. Chem. Soc., 1932, 54, 3977—3988).—The alkaline hydrolysis of quaternary ammonium substituted MeCN to the betaine cannot be represented as a simple second-order reaction between positive and negative ions. In presence of excess of OH′ the rate is proportional to $[NH_4^{\bullet}]^{1\cdot3}$ and to $[OH']^{1\cdot6-1\cdot8}$. When the concns. are equal the sum of the indices is about 2·4. These relations are unchanged by changes in salt concn., temp., and the homologue.

C. J. W. (*c*)

Study of kinetic processes on metal surfaces by radioactive methods. O. Erbacher (Z. Elektrochem., 1932, 38, 532—535).—The deposition of radioactive elements on "noble" metals, either by forming a H_2 film on the latter or by using a solution in which the metal dissolves with formation of a complex ion, is described. Interchange of ions between a metal and an equilibrium solution of its ions is reduced by pretreatment of the electrode, but the effect always extends below the surface layer of atoms. Interchange between an electrode and ions of another metal, such as occurs with Ni in a solution containing $Ni^{\bullet\bullet}$ and $Bi^{\bullet\bullet\bullet}$, may be reduced by pretreatment to such an extent that only the surface layer is involved. If a single layer of a radioactive element be deposited in this manner on a surface of a metal, the abs. extent of the surface may be determined. With polished, roughened, and platinised Pt the active surfaces are in the ratio 1 : 10 : 100. H. F. G.

Velocity of dissolution of marble in acids. II. W. Jacek (Bull. Acad. Polonaise, 1932, A, 65—73; cf. A., 1931, 1242).—The velocity of dissolution of a marble sphere in HCl increases proportionally to the concn. at low concns. only. A max. velocity is reached as the concn. of HCl is increased, after which the velocity falls greatly. This behaviour is considered to be due to the covering of the marble surface by bubbles of CO_2. E. S. H.

Inflammation temperature of activated carbons. E. Berl and E. Weingärtner (Z. physikal. Chem., 1932, 161, 315—324).—The inflammation temp., *T*, is generally the lower the more highly developed is the surface. *T* rises with increase in the degree of graphitisation, measured by decrease in the sp. resistance of the C. Some CO_2 appears at temp. a little below *T*, which suggests that *T* is the min. temp. at which corrosion of the surface is sufficiently great to start combustion. R. C.

Velocity and equilibrium constants of the reaction between carbon and ferrous oxide in the production of steel. H. Schenk, W. Riess, and E. O. Brüggemann (Z. Elektrochem., 1932, 38, 562—568).—The reaction $FeO+C\longrightarrow CO+Fe$ has been studied by determining by Herty's method of adding Al to the melt the FeO content of steel produced in commercial furnaces (15,000—60,000 kg.). The $d[C]/dt$–[FeO][C] curves for 0·14—0·5% C steels are linear, but the apparent velocity coeffs. vary with [C]. If, however, the concn. of free C, and not that of total C, be considered, it may be assumed that k_1 is independent of [C], and the calc. val. of k_1 is then 0·418. The combined C is probably present as $(Fe_3C)_6$. The velocity coeff. $k_2'=0\cdot458\times10^4[Fe]_{free}$, where Fe_{free} is the percentage of uncombined Fe calc. by taking log $D=7\cdot43$, *D* being the dissociation const. of $(Fe_3C)_n$. H. F. G.

Temperature increment of the velocity of heterogeneous reactions. V. Reactions of salts rich in oxygen. K. Fischbeck and K. Schnaidt (Z. Elektrochem., 1932, 38, 769—773).—The temp. increment of the reaction velocity of $KMnO_4$ with H_2 is 11·5—13·8 kg.-cal. and with CO 11·5—14·4 kg.-cal., the val. increasing with the proportion of $KMnO_4$ decomp. The corresponding vals. for KIO_3 are 20·4—22·0 and 36·3 kg.-cal., respectively. M. S. B.

Active oxides. LIV. Rate of decomposition of zinc carbonate into zinc oxide and carbon dioxide. G. F. Hüttig, A. Meller, and E. Lehmann (Z. physikal. Chem., 1932, B, 19, 1—21).—At 415—460° the velocity passes through a max., attained when the ZnO–$ZnCO_3$ interface has reached a max., and after this point is equal to $kn^{2/3}$, *n* being the proportion of undecomposed $ZnCO_3$, from which it is concluded that decomp. begins at the surface of the crystals and progresses inwards at a uniform rate, and that the $ZnCO_3$ mols. at the interface have a much greater rate of decomp. than the others. *k* varies with the temp., *T*, according to the equation $\log_e k=A/T+B$. The rate of the reaction $ZnO+CO_2\longrightarrow ZnCO_3$ is proportional to the CO_2 pressure and to $n^{2/3}$. The reaction velocities are also affected by the total activity of the solid phase, which depends on the age of the ZnO, and is a max. when *n* is about 0·6. To secure ZnO of max. activity the CO_2 pressure in the gas phase should be high, the reaction temp. low, and the rate of reaction as great as possible.

R. C.

Oxidation of substances in colloidal solution. S. A. Vosnessenski and I. M. Tzinn (J. Gen. Chem. Russ., 1932, 2, 491—501).—Aq. suspensions of S are rapidly oxidised by Cl_2 and Br, but not by I. The velocity of oxidation is diminished in the presence of Na_2SO_4 or $NaHSO_3$; kaolin and $Fe(OH)_3$ have no action, $Al(OH)_3$ reduces only the initial velocity of reaction, whilst powdered alabaster and protective colloids (humins) considerably retard reaction. R. T.

Influence of high concentrations of salts on velocity of oxidation of suspensions of sulphur by bromine. S. A. Vosnessenski and I. M. Tzinn (J. Gen. Chem. Russ., 1932, 2, 502—503).—NaCl (1—4*N*) inhibits oxidation of S by Br to a greater extent than do equiv. concns. of LiCl; this is ascribed to the greater hydration of $Li^{\cdot}$ and to its capacity for giving rise to aquo-acids. R. T.

Velocity of dissolution of oxygen in water and in solutions of substances reacting with it. Influence of liquid surface films on velocity. S. A. Vosnessenski and L. A. Klutschaev (J. Gen. Chem. Russ., 1932, 2, 506—514).—The initial velocity of dissolution (v_0) of O_2 in aq. Na_2SO_3 is const., and is unaffected by stirring. In pure H_2O v_0 is the same as for aq. Na_2SO_3; with time, the velocity increases, and has a max. final val. in 0·3—0·8*N*-Na_2SO_3. The val. of v_0 is unaffected by surface films of liquid paraffin, paraffin oil, or kerosene $\ngtr 5\ \mu$ thick, but after 1 hr. such films cause retardation of reaction. Films $\nless 10\ \mu$ thick retard reaction from the beginning. R. T.

Open-air corrosion of copper. III. W. H. J. Vernon.—See B., 1932, 940.

Catalytic action of water vapour in combustion of carbon monoxide. H. Passauer (Z. physikal. Chem., 1932, 161, 299—304).—The rate of combustion of a moist CO–air mixture is the same as that of a dry CO–air mixture containing CO_2 and H_2 in amounts such as would furnish the same amount of H_2O by the water-gas reaction. It thus appears that the catalysis of the combustion of CO by H_2O depends on the water-gas reaction. The decomp. of the H_2O probably occurs in the preheating zone, but is incomplete if the air–CO mixture contains $>$ about 3% H_2O. R. C.

Use of an electrode to study irreversible reactions: the polymerisation of acetaldehyde. V. Hnizda and D. J. Brown (J. Physical Chem., 1932, 36, 2842—2843).—The polymerisation of MeCHO can be followed by observing the change of p.d. of solutions of MeCHO against a standard electrode. The results indicate that $H^{\cdot}$ has a preserving effect, which is proportional to its concn., whilst Cl' appears to catalyse the polymerisation proportionally to its concn. E. S. H.

Catalytic decomposition of hydrogen peroxide by iodine–iodide couple. II, III. Rate of oxidation in neutral and in acid solution of hydrogen peroxide by iodine. H. A. Liebhafsky (J. Amer. Chem. Soc., 1932, 54, 3499—3508; cf. this vol., 818).—One of the steps in the oxidation of H_2O_2 by I_2 which determines the rate has been isolated by measuring the rate of O_2 evolution from approx. neutral solutions, saturated with I_2, the most probable mechanism being $IO'+H_2O_2 \longrightarrow H_2O+I'+O_2$. At 25° the sp. reaction const., k, is in such agreement with the val. deduced from the steady state measurements as to show that the hydrolysis equilibrium of I_2 is always established in the I_2–I'–H_2O_2 reaction system. By measuring the O_2 evolution from acid solutions in the presence of $Tl^{\cdot}$ a second rate-determining step has been isolated, probably $HIO+H_2O_2 \longrightarrow H_2O+H^{\cdot}+I'+O_2$. At 25° k agrees with the val. deduced from steady state measurements. It is concluded that the reaction system can be interpreted in terms of the three compensating reactions within the wide range of experimental conditions over which the corresponding rate laws have been definitely established. H. F. J. (*c*)

Rôle of ozone as an oxidation catalyst. III. Chemical reactivity of ozone in the absence of oxygen in the ozonolysis of benzaldehyde and sodium sulphite. E. Briner and H. Biedermann (Helv. Chim. Acta, 1932, 15, 1227—1234; cf. this vol., 235).—When PhCHO and Na_2SO_3 are oxidised by O_3–O_2–N_2 mixtures of different proportions, (*a*) the total oxidation taking place falls from 300 and 112% to 44 and 40%, respectively (with regard to the amount of O_3 decomposed), and (*b*) the amount of BzO_2H formed falls to nearly 0, as the amount of O_2 is decreased from 99 to 0·5%. In absence of O_2, O_3 reacts by decomp. to O_2+O; therefore, efficiencies above 33% [not 100% (*loc. cit.*)] indicate that the O_3 has catalysed oxidation by O_2. (*b*) proves that per-acids are formed by O_2 and not by O_3. The catalytic action of O_3 is shown only in oxidations which occur spontaneously even in absence of O_3. Possible mechanisms of the catalysis are discussed. R. S. C.

Crystal structure and catalytic activity of carbon. U. Hofmann and W. Lemcke (Z. anorg. Chem., 1932, 208, 194—212; cf. this vol., 16).—The adsorptive capacities of technical active charcoals, of soots, and of graphites, and their catalytic activity in promoting the combination of H_2 and Br, are closely parallel and depend on the total accessible surface of graphite crystals. "Activation" by heating in CO_2 at 950° increases the adsorptive power and catalytic activity of prepared charcoals and soots by enlarging the pores and thus making a larger surface accessible, whereas it diminishes the catalytic efficiency of retort C or Ceylon graphite by preferentially destroying the smallest crystals. The heat of activation of the HBr synthesis is the same whether catalysed by Ceylon graphite or by "supranorit." F. L. U.

Catalysis of reaction between solids. IV. Decomposition of stannic oxide by radiation from radium. S. Tamaru and K. Otiai (Z. physikal. Chem., 1932, 161, 346—354; cf. this vol., 705).—As a result of exposure to the radiation from Ra, SnO_2 becomes able to catalyse the formation of stannate from SnO_2 and CaO in the same way as SnO. SnO can be isolated from it by vac.-sublimation, but no metallic Sn is present. Ultra-violet light has no action on SnO_2. R. C.

Catalytic hydrogenation and polymerisation. C. Schuster (Z. Elektrochem., 1932, 38, 614—618).—Various kinds of active C serve as catalysts for the hydrogenation of adsorbed olefines (C_2H_4—

C_5H_{10}). Traces of Ni on the C produce proportionate increases of the velocity coeff. of the reaction. The velocity decreases rapidly with increase of mol. wt. of the hydrocarbon. For Δ^{α}-butylene the rate is proportional to $p^{1 \cdot 5}$, p being the C_4H_8 pressure, whereas for C_2H_4 it is independent of the concn. The heat of activation ranges between 3600 and 6800 g.-cal. During hydrogenation of C_2H_4, Δ^{β}-butylene is formed; the velocity of polymerisation is proportional to the C_2H_4 concn., and the heat of activation is about 5000 g.-cal. H. F. G.

Nickel [prepared] by the Raney process as a catalyst of hydrogenation. L. W. COVERT and H. ADKINS (J. Amer. Chem. Soc., 1932, 54, 4116—4117).—By a modification of this process (B., 1927, 606), a Ni catalyst active at low temp. and pressures is obtained. $COMe_2$ is completely hydrogenated after 11·2 hr. at 23° and 2—3 atm. pressure, and mesityl oxide and $CH_2Ac\cdot CO_2Et$ behave similarly. Complete hydrogenation occurs at room temp. and 110 atm. with PhCHO, MeCHO, CHPh:CH·CHO, $(NPh:)_2$, and $CH_2Ph\cdot CN$. C. J. W. (*c*)

Reaction between nitrous oxide and hydrogen on platinum. H. CASSEL and E. GLÜCKAUF (Z. physikal. Chem., 1932, B, 19, 47—62).—The reaction has been investigated at 600—1400° abs. in presence of an excess of H_2 and under 10^{-3} mm. pressure. Up to 775° the only reaction is $N_2O_{ads.}+(H_{2\,gas} \rightleftharpoons H_{ads.}) \longrightarrow N_{2\,gas}+H_2O_{ads.}$, and the relative reaction velocity, *G*, remains const. during the reaction. When the temp., *T*, rises above about 775° *G* falls abruptly, and in the course of reaction passes through a min. At this temp. the partial pressure of O_2 formed by the thermal decomp. of the N_2O has become sufficient to form on the Pt surface an oxide film on which the catalysed reactions occur with diminished velocity, being also retarded by adsorbed O (cf. this vol., 1073). As *T* rises, the min. in *G* during the reaction becomes less and less pronounced, and disappears at about 1250°, the dominant reaction now being $H_{2\,gas}+O_{ads.} \longrightarrow H_2O_{ads.}$. R. C.

Vapour-phase catalytic oxidation of hydrocarbons. T. J. WILKEN-JORDEN.—See B., 1932, 927.

Catalytic decomposition of germane. T. R. HOGNESS and W. C. JOHNSON (J. Amer. Chem. Soc., 1932, 54, 3583—3592).—The rate of decomp. on a Ge surface at 283—374° is proportional to $p^{1/3}$, where p is the pressure of the undissociated GeH_4. H_2 inhibits the decomp. at lower temp. The heat of activation is 39·7±2 kg.-cal. per mol. The results are discussed in terms of Langmuir's adsorption theory. J. V. V. (*c*)

Reactions between gas and solid. VI. Azotation of calcium carbide and the effect of catalysts on its velocity. T. AONO (Bull. Chem. Soc. Japan, 1932, 7, 287—297).—The optimal quantity of CaF_2 necessary to produce the max. velocity of azotation is a function of the temp. as well as of the quantity of carbide. The reaction between CaC_2 and N_2 is also accelerated by active C and hence probably by C formed in the reaction. A. G.

Dissociation of gypsum in presence of catalysts. I. E. ADADUROV and V. P. PLIGUNOV (J. Appl. Chem., Russia, 1932, 5, 149—156).—Displacement of SO_3 by SiO_2 is not a chemical, but a catalytic, reaction; the action of Al_2O_3, Fe_2O_3, and Cr_2O_3 is similar to that of SiO_2, the quantity having little effect on the yield of SO_3. CH. ABS.

Heat of activation of thermal dissociation of gypsum in presence of catalysts. I. E. ADADUROV (J. Appl. Chem., Russia, 1932, 5, 157—162).—Since the heat of activation at 700—900° is only 9500 g.-cal. per mol., the decomp. must depend on intramol. rearrangements. At 900—1100° the process is catalytic. CH. ABS.

Catalytic decomposition of carbon disulphide by steam and hydrogen. K. BUNTE and F. LORENZ (Gas- u. Wasserfach, 1932, 75, 765—771, 787—791).—MoS_3 and a mixture of U sulphides are efficient catalysts for the reactions $CS_2+2H_2O \longrightarrow CO_2+2H_2S$ and $CS_2+4H_2 \longrightarrow 2H_2S+CH_4$. The corresponding oxides may be used, but they are converted into sulphides during the reaction; there is thus no poisoning of the catalyst, and C is not deposited, as the working temp. can be kept low. The influence of temp., concn., and streaming velocity has been examined; at 400° the U sulphide catalyst gives 100% efficiency. N_2, NH_3, and heavy hydrocarbons found in coal gas have practically no influence on the reactions, but the presence of CO has a slight, favourable influence. The addition of alkali to the catalyst is feebly activating at high temp., but has the reverse effect at low temp. E. S. H.

Influence of catalyst of a primary reaction on the velocity of a secondary one. S. A. IVLEV (J. Gen. Chem. Russ., 1932, 2, 504—505).—The oxidation of peat humins by HOCl is accelerated by addition of $CoCl_2$, which catalyses the decomp. of HOCl. R. T.

Anodes for zinc plating. G. B. HOGABOOM and A. K. GRAHAM.—See B., 1932, 986.

Deposition of bright zinc–cadmium alloys from cyanide baths. C. J. WERNLUND.—See B., 1932, 987.

Cadmium plating. C. M. HOFF.—See B., 1932, 986.

Electrolytic cadmium plating. F. PIETRAFESA and C. LUCIANI.—See B., 1932, 942.

Electrolytic manganese dioxide. G. W. NICHOLS.—See B., 1932, 991.

Preparation of manganese dioxide by electrolysis. V. P. ILINSKI and N. P. LAPIN.—See B., 1932, 979.

Preparation of manganese dioxide by electrolysis with alternating current. N. KAMEYAMA and H. IIDA.—See B., 1932, 1028.

Electrolysis of fused acetates and propionates. G. B. MOORHOUSE (Trans. Faraday Soc., 1932, 28, 766—776).—A fused mixture of Li, Na, and K acetates was electrolysed at 200° between a bright Pt anode and a Pb cathode in the apparatus described. The main products were CO_2 and C_2H_6, with small quantities of CO, CH_4, H_2, C_2H_4, and MeOAc. The yield of CH_4 and CO was increased and that of C_2H_6 decreased by adding H_2O to the electrolyte. The chief products of the electrolysis of a fused mixture of Li and Na propionates at 230° were CO_2, C_4H_{10}, C_2H_4, C_2H_6, with some CO, H_2, and $EtCO_2Et$. The most probable mechanism of the Kolbe synthesis is the interaction of discharged ions. Mechanisms for the formation of the by-products are suggested. The Kolbe synthesis is fairly good with C anodes, but with Pt-black and Au the yields are poor with acetate and moderate with propionate. J. G. A. G.

Relation between Kolbe's reaction and hydrogen-ion concentration. VII. Mechanism of Kolbe's reaction. H. R. Matsuda (Bull. Chem. Soc. Japan, 1932, 7, 297—305).—$EtCO_3H$ is formed during the electrolysis of $EtCO_2H$. A. G.

Decomposition and synthesis of ammonia under the action of alpha rays. J. C. Jungers (Bull. Soc. chim. Belg., 1932, 41, 377—398; cf. A., 1931, 580).—When pure NH_3 at 25° is irradiated with α-rays from Rn, $M/I=1{\cdot}16(1-0{\cdot}157\sqrt{q})$, where M=no. of mols. decomposed, I=no. of pairs of ions formed, and q=no. of millicuries÷vol. of reaction chamber. The addition of N_2 to the NH_3 does not alter the val. of M/I until the mixture contains $<1\%$ of NH_3, but the addition of H_2 causes a rapid fall in M/I. D. R. D.

Photochemical studies. XIV. Decomposition of nitrous oxide sensitised by mercury vapour. W. M. Manning and W. A. Noyes, jun. (J. Amer. Chem. Soc., 1932, 54, 3907—3917).—The total reaction between excited Hg and N_2O may be represented $Hg+N_2O \longrightarrow HgO+N_2$. Two possible primary steps are the production of an excited O atom and a N_2 mol., or a normal N atom and a NO mol. Velocity measurements indicate that the N_2O mol. has a very large effective cross-section in its interaction with excited Hg. W. E. V. (c)

Quantum efficiency of photochemical decomposition of potassium persulphate. R. H. Crist (J. Amer. Chem. Soc., 1932, 54, 3939—3942; cf. A., 1927, 323, 428).—The quantum efficiency is unity for neutral and alkaline solutions. The effect of KCl, HCl, $KCl+H_2SO_4$, and $HgCl_2+H_2SO_4$ has been investigated. A capillary Hg arc may be improved by deflexion with a magnet. G. M. M. (c)

Photolysis of octacyanides of quadrivalent molybdenum. G. A. Barbieri (Rend. Accad. Sci. Ist. Bologna, 1931, 35, 93—97; cf. A., 1931, 1255).—Exposure to sunlight for several hr. of a conc. solution of the yellow *salt* $Na_4Mo^{IV}(CN)_8,C_6H_{12}N_4,8H_2O$ containing excess of hexamethylenetetramine gave blue *crystals* of $Na_3[Mo^{IV}(H_2O)(OH)_2(CN)_5],2C_6H_{12}N_4,3H_2O$, showing that the substitution of CN by OH in the photolysis of the complex $[Mo^{IV}(CN)_8]$ is preceded by the replacement of 1 mol. KCN by 1 mol. H_2O, as in the photolysis of ferrocyanides. The blue compound, in conc. solution with a large excess of NaOH, gave reddish-violet *crystals* of $Na_4[Mo^{IV}(OH)_4(CN)_4],6H_2O$, whereas the unsubstituted $[Mo(CN)_8]$ is stable to alkalis. A conc. solution of this compound, treated with a large excess of NaOAc and $C_6H_{12}N_4$, gave violet *crystals* of $2Na_3[Mo^{IV}(H_2O)(OH)_3(CN)_4],3C_6H_{12}N_4,8H_2O$ (cf. A., 1928, 159). O. J. W.

Action of heat and of ultra-violet rays on mercury fulminate. M. Patry and P. Laffitte (Bull. Soc. chim., 1932, [iv], 51, 1205—1212).—Below 139·5° $HgC_2N_2O_2$ decomposes slowly, evolving CO_2 and becoming successively brown, yellow, and white. Above 172° it explodes. Between these temp. the results depend on the pressure, explosion occurring more readily with higher pressure. $PbEt_4$ facilitates explosion. Under the action of light from a Hg-vapour lamp, $HgC_2N_2O_2$ is converted into a black isomeride or polymeride, which is not so readily detonated as the ordinary form, although more inflammable and more easily decomposed by heat. D. R. D.

Concentration at emulsification and grain size [in photographic emulsions]. Lüppo-Cramer (Z. wiss. Phot., 1932, 31, 179—181).—Photomicrographs show that the size of the grains in a AgBr–AgI emulsion increases as the H_2O content at emulsification is decreased. The effect is less marked in emulsions containing only AgBr. J. L.

Photoanisotropic effect (Weigert effect) with dyes. I. T. Kondo (Z. wiss. Phot., 1932, 31, 153—167).—1700 dyes have been tested, both in gelatin and in collodion emulsions; in 450 cases the Weigert effect has been detected (cf. A., 1929, 871). Nearly all the dyes giving the effect are brown, red, yellow, or intermediate between these in colour. The amount of the effect varies greatly with the method of prep. of the sensitive layers. A trace of moisture destroys the dichroism. The dyes are not always sensitive in both gelatin and collodion emulsions. The majority of the dyes show no certain double refraction; a few dyes (all yellow), showing dichroism in both emulsions, also show strong double refraction in one emulsion only. The effect is reversible by exposure to light polarised in the plane at right angles to that of the initial exposure. J. L.

Effect of intensity and underlying fogs on the latent image. F. E. Poindexter and L. E. James (J. Opt. Soc. Amer., 1932, 22, 525—536).—Using fast plates, reciprocity failure is greatest for low intensities of illumination. Exposure to low-intensity white light after exposure to a stronger white light, or exposure to white light after red light, is more efficient than the reverse order of exposures. This effect is not found when using two intensities of the same coloured light, in the case of certain narrow bands of green and red light. These results are discussed in support of the photomechanical (crystal shattering) hypothesis of the formation of the latent image. No change in the latent image with the time between exposure and development has been found. J. L.

Photographic emulsion; variables in sensitisation by dyes. B. H. Carroll and D. Hubbard (Bur. Stand. J. Res., 1932, 9, 529—545).—The relative spectral sensitisation of photographic emulsions by dyes (erythrosin, pinacyanol, pinaverdol, and pinaflavol) increases slowly with the concn. of the dye and is affected only slightly by the formation of sensitivity nuclei (*e.g.*, from allylthiocarbamide), which increase greatly the abs. sensitivity to any wave-length. The effect of $[H^{\cdot}]$ is sp. for the dye and is $<$ that of $[Ag^{\cdot}]$. In general, sensitisation increases with increasing $[Ag^{\cdot}]$; sp. effects are explained by supposing that spectral sensitisation depends on adsorption of the ion of the dye by the oppositely-charged ion of the AgCl lattice. Changes in adsorption of basic dyes may be sufficient to counteract the general trend when a certain excess of $Ag^{\cdot}$ is reached. E. S. H.

Action of ultra-violet light on ethane. W. KEMULA, S. MRAZEK, and S. TOŁŁOCZKO (Chem. Listy, 1932, **26**, 466—473).—C_2H_6 yields C_4H_{10}, C_6H_{14}, and C_8H_{18}, together with traces of CH_4, on irradiation with ultra-violet light in presence of Hg vapour. The proportion of C_4H_{10} in the product varies directly with the rate of flow and the pressure, and inversely with the temp. of the receiver. Both the linkings C·C and C·H undergo activation; the rate of activation is independent of the pressure and of the rate of flow, but depends exclusively on the intensity of irradiation. R. T.

Oxidation of solutions of iodoform. R. DUBRISAY and G. EMSCHWILLER (Compt. rend., 1932, **195**, 660—662).—A C_6H_6 solution of CHI_3 exposed to light is oxidised with formation of a little I and HI. Addition of small amounts of these substances to a solution kept in the dark produces the same result, thus explaining the photochemical after-effect. HI may be replaced by other mineral acids, but not by AcOH. In such solution with addition of HCl and I there is a varying period of induction, due probably to impurities in the solvent. Once started the reaction proceeds at a rate varying directly with $[CHI_3]$ and [HCl], inversely with [I]. The nature of the solvent has much effect on the rate; oxidation occurs in C_6H_6, C_6H_{14}, CCl_4, and $COMe_2$, but not in Et_2O, CS_2, or PhMe. Addition of certain substances, *e.g.*, PhOH or quinol, checks or inhibits oxidation (cf. A., 1925, ii, 595). C. A. S.

Chlorine-sensitised photo-oxidation of tetrachloroethylene in carbon tetrachloride solution. R. G. DICKINSON and J. A. LEERMAKERS (J. Amer. Chem. Soc., 1932, **54**, 3852—3862).—The photochemical chlorination of C_2Cl_4 in CCl_4 is strongly inhibited by O_2. In presence of both O_2 and Cl_2 photosensitised oxidation to $CCl_3{\cdot}COCl$ (87%) and $COCl_2$ occurs. With radiation of wave-length 4358 Å. the rate of oxidation in a uniformly illuminated layer is proportional to the first power of the intensity of the incident radiation and to the first power of $[Cl_2]$, is independent of $[O_2]$, and varies only slightly with $[C_2Cl_4]$, unless this is very high. The rate of oxidation has been measured at 3°, 20°, and 36°; the temp. coeff. of the yield is 1·20. The quantum yields have been determined. L. K. (*c*)

Hydrolysis of acetone in ultra-violet light. M. QURESHI and N. A. TAHIR (J. Physical Chem., 1932, **36**, 2670—2673).—The quantum efficiency varies from 0·13 to 0·14, for concns. of 0·05—0·5M. The ratio of the efficiencies at 30° and 40° is 1·41. The temp. coeff. is 1·52. The rate of hydrolysis is directly proportional to the intensity. I. J. P. (*c*)

Photolysis of chloropicrin in aqueous solution. E. V. ALEXEEVSKI (J. Gen. Chem. Russ., 1932, **2**, 341—344).—Aq. $CCl_3{\cdot}NO_2$ is decomposed by X-rays, and by voltaic arc and quartz–Hg vapour lamp illumination. R. T.

Sensitised photolysis of azo-compounds by zinc oxide. I. FUKUSHIMA, M. HORIO, and M. OHMORI (J. Soc. Chem. Ind. Japan, 1932, **35**, 398—399B).—In EtOH–H_2O solution azobenzene in presence of ZnO is reduced photochemically almost quantitatively to hydrazobenzene in the absence of O_2, but no detectable change occurs in presence of O_2. Crystal-scarlet and *pp'*-hydroxyazobenzene, however, show simultaneous oxidation and reduction in light, the reaction being more rapid in presence of O_2. J. W. S.

Testing materials with γ-rays. N. RIEHL (Z. Elektrochem., 1932, **38**, 548—549).—With 30 mg. of Ra or meso-Th and a distance of 30 cm. between the prep. and the plate an exposure of 2 (16) hr. is sufficient with a thickness of 10 (80) mm. of Fe; air inclusions totalling 1·5 (3) mm. may be detected in a thickness of 10 (80) mm. The method will not detect hair cracks etc. It does not require complicated apparatus, and has other advantages over the X-ray method when dealing with thick castings or dense materials (Pb). H. F. G.

Effect of supersonic radiation on bromothymol-blue. A. R. OLSON and N. B. GARDEN (J. Amer. Chem. Soc., 1932, **54**, 3617—3620; cf. A., 1929, 523; this vol., 480).—The inhomogeneity of commercial bromothymol-blue is responsible for conflicting reports on the effect of supersonic radiations. Proof is given that $[H^{\cdot}]$ changes on destruction of the indicator. H. F. J. (*c*)

Behaviour of a grainless emulsion towards α-particles. M. BLAU and H. WAMBACHER (Monatsh., 1932, **61**, 99—106).—The sensitivity of a "grainless" (Lüppo-Cramer) AgBr emulsion to α-particles, as measured by the rate of darkening on exposure, is much less than is expected from its sensitivity to visible light and is not proportional to the intensity of radiation. Contrary to expectation, the emulsion is desensitised by $NaNO_2$ and, to a smaller extent, by $NaHSO_3$, but is sensitised normally by NaN_3. It is suggested that the strong ionising action of the α-particles may lead not only to a photochemical decomp. of the $NaNO_2$, but also to formation of Ag^+ from the Ag set free and combination of this with NO_2' or O ions. H. A. P.

Preparation of atomic hydrogen for organic preparative purposes. H. KROEPELIN and E. VOGEL (Naturwiss., 1932, **45**, 821).—4 litres per hr. of strongly activated H_2 may be obtained with the apparatus described. Activation is effected by means of a heated W spiral. D. R. D.

Iodochlorides of the alkali and alkaline-earth metals; structure and constitution. M. G. DE CELIS and E. MOLES (Anal. Fís. Quím., 1932, **30**, 540—551).—KCl_4I may be obtained in good yield by passing Cl_2 through a slightly acidified mixture of KCl (9 g.), H_2O (5 g.), and I (10 g.) at 60° until all the I has dissolved; the solution is then heated at 70°, when crystals separate on continuing the passage of Cl_2. $NaCl_4I,2H_2O$ and $LiCl_4I,4H_2O$, and the Ca, Sr, and Mg salts (all $+8H_2O$) may be prepared by the same procedure. The *d* of these compounds have been determined; the mol. vols. conform to the additive law ($MCl_x+ICl_3+yH_2O$). H. F. G.

Oxidation of aqueous alkali sulphite solution by cupric salt in presence of pyridine. P. Baumgarten (Ber., 1932, **65**, [*B*], 1637—1645).—Oxidation of alkali sulphite solution by $CuSO_4$ in presence of C_5H_5N affords a 60% yield of *N*-pyridiniumsulphonic acid (I), $2Cu^{\cdot\cdot}+SO_3''+C_6H_5N=2Cu^{\cdot}+C_5H_5N^{+}—\cdot SO_2O$. About 30% of sulphite is converted into sulphate, $2Cu^{\cdot\cdot}+SO_3''+H_2O=2Cu^{\cdot}+H_2SO_4$, and the remaining 10% into dithionate, $2SO_3''+2Cu^{\cdot\cdot}=S_2O_6''+2Cu^{\cdot}$. Reaction is quant. with $CuSO_4$ and Na_2SO_3 in the ratio 2 : 1. (I) is determined by transformation by NaOH into the Na salt of glutaconaldehyde (converted into the corresponding dianil hydrochloride) and $NH_2\cdot SO_3H$ (determined as H_2SO_4 after treatment with HNO_2) or by decomp. with NH_3 into C_5H_5N and $NH_2\cdot SO_3NH_4$ (determined as $BaSO_4$). The formation of SO_3 as a step in the oxidation is postulated. H. W.

Polyiodides of rubidium. I. Iodine and rubidium iodide. T. R. Briggs and E. S. Patterson (J. Physical Chem., 1932, **36**, 2621—2624; cf. A., 1930, 1521, 1522).—In the system $RbI–I_2$ from 60° to the b.p. of the saturated liquid phase (238°) the only solid phases are I_2, RbI, and RbI_3 (m.p., incongruent, 188°); there is no indication of the existence of higher polyiodides. L. F. A. (*c*)

Possibility of following recrystallisation of silver by colour reaction with ferric chloride. Properties of silver chloride layer formed by superficial action of ferric chloride on silver. E. Beutel and A. Kutzelnigg (Monatsh., 1932, **61**, 189—198, 199—205).—Immersion of Ag sheet in aq. $FeCl_3$ (20%) results in the formation of a coloured film of AgCl (identified by m.p., solubility in $Na_2S_2O_3$, NH_3, etc.), accompanied by an increase in wt. which reaches a max. in a few sec. The film, which can be removed by HNO_3, is stable in diffused daylight, but is darkened by direct sunlight or ultra-violet light to a brownish-grey independent of its original colour; this change is due to decomp. into Ag and Cl_2. It is also reduced to Ag by base metals. The colour and wt. of the film are influenced markedly by pre-treatment (heat or cold-working) of the metal. Min. brightness occurs with previous heating at 100° or 600—650°, and the wt. of AgCl film formed under comparable conditions falls rapidly as the temp. of pre-treatment is raised from 500° to the m.p. Etching with HNO_3 (*d* 1·33) before immersion into $FeCl_3$ gives a brighter shade if treatment has been carried out below 660°, and otherwise a duller shade. Cryst. Ag, like cold-worked, gives deeper shades. It is suggested that the variations in colour are a function of size of grain and, to some extent, of orientation of the crystallites. H. A. P.

Ammonium, potassium, and sodium silver thiosulphates. III. Sodium silver thiosulphate. G. Spacu and J. G. Murgulescu (Z. anorg. Chem., 1932, **208**, 157—162; cf. this vol., 1007).—The existence of the following *compounds* has been established by potentiometric titration of $Na_2S_2O_3$ with $AgNO_3$, supplemented by analyses: $[Ag_4(S_2O_3)_3]Na_2,4H_2O$; $[AgS_2O_3]Na$; $[AgS_2O_3]Na,H_2O$; $[Ag_2(S_2O_3)_3]Na_4,2H_2O$; $[Ag(S_2O_3)_2]Na_3,2H_2O$. The second and fourth are not new. F. L. U.

Silver ferrites. VI. Mechanism of formation of Böhm's goethite and influence of hydrogen-ion concentration on the ageing of orthoferric hydroxide at high temperatures. A. Krause, H. Lakościukówna, and J. Cichowski (Z. anorg. Chem., 1932, **208**, 282—292; cf. this vol., 805).—$Fe(OH)_3$ is insol. in 2*N*-NaOH or -KOH at temp. up to 150°, but > 0·2 g. of orthoferric hydroxide, α- or γ-FeOOH is dissolved by 100 c.c. of 18*N*-NaOH at its b.p. On cooling, a white cryst. Na ferrite separates. Hydrolysis occurs on dilution and $Fe(OH)_3$ is pptd. Conc. solutions of KOH dissolve only traces of the hydroxide, and the solutions are unstable. Products of hydrolysis of Na ferrite were proved by the Ag ferrite method to be polyorthohydroxides. Dehydration is greatly influenced by $[H^{\cdot}]$, and is most marked in presence of 0·01*N*-NaOH. The mechanism of ageing of the orthohydroxide is discussed. F. L. U.

New hydrates of magnesium perchlorate. Their structural relation to known forms of hydrated perchloric acids and properties as intensive dehydrating agents. G. F. Smith, O. W. Rees, and V. R. Hardy (J. Amer. Chem. Soc., 1932, **54**, 3513—3523).—*Di-* and *tetra-aquo-perchlorates* of Mg are described. The heats of hydration of the Mg perchlorates have been measured. That of the anhyd. salt is 33,000 g.-cal. per mol. *X*-Ray powder diagrams are different for each hydrate. H. F. J. (*c*)

Preparation of phosphorescent substances. V. Calcium, strontium, and barium sulphides. N. F. Zhirov (J. Appl. Chem., Russia, 1932, **5**, 177—192).—The use of the following secondary solvents has been investigated: $SrWO_4$ shifts the spectrum towards the red (CaS>SrS>BaS), the intensity being max. at 25% $SrWO_4$; $BaWO_4$ is less satisfactory (Ba>Sr>Ca); $MgWO_4$ shifts it towards the violet and increases the intensity (Sr>Ba>Ca); $BeWO_4$ shifts slightly towards the violet (Sr>Ba>Ca) and increases the intensity (Sr>Ca>Ba); $Al_2(WO_4)_3$ is valueless; $Ca_3(PO_4)_2$ shifts towards the violet (Ba>Sr>Ca), and $Sr_3(PO_4)_2$ (Ca>Ba>Sr) and $Ba_3(PO_4)_2$ (Sr>Ba=Ca) towards the red. The optimal concn. of phosphates is 20—50%. Ch. Abs.

Molecular transformations of calcium sulphate at high temperatures. P. N. Laschtschenko and A. I. Morozova (J. Appl. Chem., Russia, 1932, **5**, 15—24).—At 450° $CaSO_4$ loses its ability to combine with H_2O, and at >650° it is converted into a form different from anhydrite. Dissociation commences at 1020—1080°. Ch. Abs.

Reaction of the alkaline-earth metals with nitrogen. A. von Antropoff [with H. Klingebiel and K. H. Krüger] (Z. Elektrochem., 1932, **38**, 588—589).—Na, and probably also NaOH, in Ca accelerates the reaction with N_2, not catalytically, but by its action in converting the Ca_3N_2 film into a porous form. Microscopical observations show the Na droplets to be absorbed by the Ca_3N_2 film, with the production of yellowish-brown rings and cracks in the film. Traces of A retard the reaction, as the A becomes conc. in the pores of the Ca_3N_2, but after evacuating the vessel the initial velocity is readily reattained; Na vapour produces a similar effect. Ba and Sr exhibit no reduction of reactivity towards N_2 at high temp., and the same is true of the reactivity of Ca towards H_2. H. F. G.

Calcium phosphates and silicophosphates. F. Körber and G. Trömel (Z. Elektrochem., 1932, 38, 578—582).—Largely a review of published work. Pure $Ca_3P_2O_8$ and $Ca_4P_2O_9$ have been prepared. Hydroxyapatite, $Ca_{10}(PO_4)_6(OH)_2$, is extremely stable, being formed in moist air at 1100°, and by pptn. from aq. solution. In Ca-rich mixtures containing CaO, P_2O_5, and SiO_2, the compounds $9CaO,P_2O_5,3SiO_2$ and $5CaO,P_2O_5,SiO_2$ exist at high temp.; α-$3CaO,P_2O_5$ exhibits an extended miscibility region in the ternary diagram. H. F. G.

Calcium phosphates and apatite. A. Schleede, W. Schmidt, and H. Kindt (Z. Elektrochem., 1932, 38, 633—641).—On prolonged treatment with H_2O, di-, tri-, and tetra-calcium phosphates yield hydroxyapatite, $3Ca_3(PO_4)_2,Ca(OH)_2$. $5CaO,P_2O_5,SiO_2$, Thomas meal, and Rhenania phosphate, on the other hand, hydrolyse only very slowly. Practically all natural Ca phosphates are of the apatite structure. The *X*-ray diagram of $Ca_3(PO_4)_2$ prepared by pptn. exhibits the lines of apatite, and, less strongly, those of $CaHPO_4$, but after heating the material to 600—800° a characteristic diagram is obtained. Tetracalcium phosphate of definite structure is obtainable only by rapid crystallisation from the fused state; slow cooling, in presence of H_2O vapour, results in the formation of hydroxyapatite and CaO; $3Ca_3(PO_4)_2,CaO$ is not formed. Pure $3Ca_3(PO_4)_2,Ca(OH)_2$ may be prepared by boiling $Ca_3(PO_4)_2$ with $0{\cdot}5N$-KOH for many hr. and heating the washed product at 900°; the temp. of decomp. into tri- and tetra-phosphate is $>1500°$. H. F. G.

Hydrothermal synthesis of calcium aluminates and silicates from lime and alumina or kaolin. III. S. Nagai (J. Soc. Chem. Ind. Japan, 1932, 35, 394—398B).—The hydrothermal reactions between CaO and raw or calcined kaolin in different proportions have been investigated comparatively under various conditions of pressure, temp., and time. J. W. S.

Effect of alkaline media on crystallisation of calcium aluminates and on the setting of aluminous cements. Seailles (Compt. rend., 1932, 195, 662—664).—Al_2O_3 and CaO in solution form $3CaO,Al_2O_3,nH_2O$ or $4CaO,Al_2O_3,12H_2O$ according as the p_H is $>$ or $<$ 12, irrespective of the nature of the base present, the action of CaO not being sp. (cf. B., 1929, 173; A., 1930, 872). The detrimental effect of the presence of a small amount of CaO in aluminous cements is due to rapid conversion, when p_H is $>$ 12, of the anhyd. CaO,Al_2O_3 into $4CaO,Al_2O_3,12H_2O$ with pptn. of Al_2O_3, a reaction occurring much more rapidly than the re-formation of CaO,Al_2O_3. C. A. S.

Double salts of cadmium ferricyanide. F. Čuta (Coll. Czech. Chem. Comm., 1932, 4, 400—411; cf. A., 1929, 1407).—The solubility of $Zn_3[Fe(CN)_6]_2$ and $Cd_3[Fe(CN)_6]_2$ in solutions of alkali chlorides is explained by supposing that the less dissociated $ZnCl_2$ and $CdCl_2$ liberated by double decomp. are held as complexes by the Cl'. The following *compounds* are described: $CdKFe(CN)_6$; $CdKFe(CN)_6,2KCl,5H_2O$; $CdNH_4Fe(CN)_6,2NH_4Cl,1{\cdot}5H_2O$; $LiCd_4[Fe(CN)_6]_3,16H_2O$; $Na_2Cd_5[Fe(CN)_6]_4,20H_2O$; $NH_4Cd_4[Fe(CN)_6]_3,NH_4Cl,13H_2O$. J. W. S.

Action of carbon dioxide on barium at the ordinary temperature. P. Remy-Gennete (Bull. Soc. chim., 1932, [iv], 51, 1029—1035).—When kept in an atm. of dry CO_2, Ba is attacked superficially, owing to the reaction $5Ba+2CO_2=BaC_2+4BaO$. Ba may be preserved in vac. or in an atm. of A. D. R. D.

Barium radium salts of high emanation. F. Strassmann (Z. Elektrochem., 1932, 38, 544).—The evolution of emanation from Ba salts containing Ra is not governed solely by the sp. surface, but varies also with the structure of the salt; thus for insol. fatty acid salts of large surface it increases with increase of the chain length. Widely differing results are obtained with substituted fatty acid salts, especially with cyclic compounds. For homologous and isomeric compounds the effect increases with decrease of *d*, whilst the hardness of the crystals also plays a part. Structure is, nevertheless, the most important factor. H. F. G.

Radiochemical methods in chemistry, physics, and biology. G. von Hevesy (Z. Elektrochem., 1932, 38, 504—511).—A review, dealing particularly with applications of radioactive indicators. From measurements of the conductivity of PbI_2, in conjunction with diffusion experiments, it is shown that at low temp. ($< 270°$) the current is carried primarily by the I', but at higher temp. by the $Pb^{\cdot\cdot}$. The heat of activation of the movement of the Pb ions in the lattice, calc. from measurements of the rate of diffusion, is 27 kg.-cal. per mol. H. F. G.

Action of ammonia and certain organic bases on calomel. R. Voynnet (J. Pharm. Chim., 1932, [viii], 16, 344—350).—Hg_2Cl_2 is decomposed by NH_3 and most amines or their hydrochlorides with the formation of Hg and $HgCl_2$. The latter salt then combines with the reagent. *Compounds* with the bases indicated or their hydrochlorides have been obtained: $2CH_2Ph{\cdot}NH_2,HCl,HgCl_2$; novocaine, $2C_{13}H_{20}O_2N_2,HCl,HgCl_2$; $NPhMe_2,HCl,HgCl_2$; cocaine, $C_{17}H_{21}O_4N,HCl,HgCl_2$; $3NH_2Ph,2HgCl_2$ and $2NH_2Ph,HCl,HgCl_2$; $3C_5H_5N,2HgCl_2$. The same compound is not obtained in all cases by the direct action of $HgCl_2$ on the base. NH_3 gives the known compound NH_2HgCl, whilst NH_4Cl gives a complex compound of Hg, Cl, and NH_3, and not $HgCl_2$ as generally stated. The compound is sol. and gives the reactions of $Hg^{\cdot\cdot}$ salts. The readiness with which the reaction takes place is less the less is the alkalinity of the base. The bearing of these reactions on the medicinal use of Hg_2Cl_2 is discussed. M. S. B.

Additive compounds of boron trichloride. A. Stieber (Compt. rend., 1932, **195**, 610—611).—On mixing BCl_3 and AsH_3 at $-80°$, or by passing H_2 through AsH_3 into BCl_3 at that temp., prisms of BCl_3,AsH_3 are obtained; this dissociates at $-40°$, or if kept in a sealed tube at room temp. decomposes into BCl_3, As, and H_2. BCl_3,PCl_3 is similarly obtained by the first method as a white solid which can be sublimed in needles, and reacts with $COMe_2$ to form a solid or a viscous liquid, according to temp. C. A. S.

Formation of the spinel Al_2ZnO_4 by reaction in the solid state. K. Hild (Z. physikal. Chem., 1932, **161**, 305—314).—In the formation of the spinel by reaction of ZnO with Al_2O_3 reaction sets in at the interface at about 975°. Above about 1100° the magnitude and variation with temp. of the reaction velocity depend on the rate of diffusion of ZnO through the spinel. R. C.

Nitrogen compounds of gallium. I. Ammonates of gallium tribromide and gallium tri-iodide. II. Gallium trifluoride trihydrate and its reaction with ammonia. W. C. Johnson and J. B. Parsons. **III. Gallic nitride.** W. C. Johnson, J. B. Parsons, and M. C. Crew (J. Amer. Chem. Soc., 1932, **54**, 2588—2595, 2651—2654).—I, II. Interaction of the anhyd. halides with liquid NH_3 gives the *hexammonates*, $GaBr_3,6NH_3$ and $GaI_3,6NH_3$, in which the NH_3 is replaceable by H_2O. $GaF_3,3H_2O$, a white powder, forms GaF_3,H_2O,NH_3 with liquid NH_3.

III. *Gallic nitride*, GaN, obtained by interaction of NH_3 with Ga at 900°, sublimes above 800° and reacts with O_2 above 900°, forming Ga_2O_3. L. F. A. (*c*)

Purification of carbon for spectroscopic purposes. G. Heyne (Angew. Chem., 1932, **45**, 612).—Very pure C is obtained by heating the material at 2000° in Cl_2 or in a N_2–CCl_4 mixture; the ultimate lines of B, and occasionally of Cu, alone are obtained in the spark spectrum. If heating at 2800—3000° in N_2+H_2 is employed, lines of numerous other elements are observed. H. F. G.

Silicon hydride, monatomic or triatomic hydrogen. A. B. Van Cleave and A. C. Grubb (J. Physical Chem., 1932, **36**, 2817—2818).—Polemical (cf. Schultze, this vol., 107). E. S. H.

Silicon fluorochlorides. W. C. Schumb and E. L. Gamble (J. Amer. Chem. Soc., 1932, **54**, 3943—3949; cf. this vol., 482).—The *compounds* SiF_3Cl, b.p. $-70·0°$, m.p. $-138°$, and SiF_2Cl_2, b.p. $-31·7°$, m.p. $-144°$, have been prepared by interaction of Si_2F_6 and Cl_2, and the v.p. at $-86°$ to $-58°$ and at $-78°$ to 16°, respectively, measured. They are readily hydrolysed to HCl, HF, H_4SiO_4, and H_2SiF_6. Indications of the existence of $SiFCl_3$ have been obtained. L. K. (*c*)

Modifications of lead chromate. H. Wagner, R. Haug, and M. Zipfel (Z. anorg. Chem., 1932, **208**, 249—254; cf. this vol., 351).—Monoclinic $PbCrO_4$ free from the rhombic modification can be prepared by pptg. an inorg. Pb salt with a large excess of CrO_4'' at 60—100°. The tetragonal variety, obtainable pure only by pyrogenic methods, can be prepared in the form of mixed crystals containing $PbSO_4$ and $PbMoO_4$ by pptn. A no. of mixed crystals with $PbCrO_4$ are described. *X*-Ray diagrams are given. F. L. U.

Preparation of active thorium precipitates. P. M. Wolf and N. Riehl (Z. Elektrochem., 1932, **38**, 543—544).—By employing a specially prepared ash-free C to adsorb the emanation, and depositing the active ppt. electrochemically on Pt by a method devised by Erbacher (unpublished) very pure Th-*B* preps. may be obtained in 75% yield. H. F. G.

Rediscovery of nitryl chloride. W. A. Noyes (J. Amer. Chem. Soc., 1932, **54**, 3615—3617).—Schumacher and Sprenger's method of prep. (A., 1929, 1155) is the best. H. F. J. (*c*)

Reactions of compounds with even numbers of electrons. Nitrogen trichloride and nitrogen tetroxide. W. A. Noyes (J. Amer. Chem. Soc., 1932, **54**, 3612—3614; cf. A., 1931, 52).—The interaction of NCl_3 dissolved in $CHCl_3$ and N_2O_4 at 0° to $-35°$ gives N_2, O_2, N_2O, Cl_2, NO_2Cl, and NOCl. The formation of NO is explained by supposing an initial covalency reaction in which the positive nitric oxide ion combines with the negative dichloride ion to form the same dichlorodinitrogen oxide which is formed by the interaction of NO and NCl_3. N_2O is formed from this by the loss of Cl_2. H. F. J. (*c*)

Phosphorus bromochlorides. T. Miłobędzki (Chem. Listy, 1932, **26**, 458—461).—A *résumé* of the work of the author and his collaborators on this subject. R. T.

Oxidation of phosphine by atmospheric oxygen in presence of hydrogen. I. N. Buschmakin, A. A. Vedenski, and A. V. Frost (J. Gen. Chem. Russ., 1932, **2**, 415—420).—PH_3 is quantitatively converted at 300° into H_3PO_3 and H_3PO_4 by O_2 in presence of H_2. Explosion does not take place if the proportion of PH_3 to H_2 is $\nless 1:11$ and if the PH_3 is free from traces of P or P_2H_4. At 20° the reaction takes several days for completion, the velocity being proportional to the partial O_2 pressure, but independent of the partial PH_3, H_2, or N_2 pressures. R. T.

Reactions of vanadium carbide. S. E. Oldham and W. P. Fishel (J. Amer. Chem. Soc., 1932, **54**, 3610—3612).—With gaseous HCl at 750° it forms CH_4, H_2, VCl_2, and VCl_3. It is insol. in aq. HCl, but sol. in hot oxidising acids, forming hydrated V_2O_5. H. F. J. (*c*)

Preparation of pure hydrogen sulphide; system hydrogen sulphide–carbon dioxide in the interval 153—213° abs. A. Klemenc (Z. Elektrochem., 1932, **38**, 592—595).—The only trustworthy method for the prep. of pure H_2S is that of direct synthesis; 100% yield may be obtained at a pumice surface at 600°. H_2S has m.p. $-85·6°$ (lit. $-82·9°$), b.p. $-60·7°$, d^{190} 0·9883, d^{210} 0·9539; the v.p. has been determined between $-66°$ and 120°. Calculation from the *d* of the synthetic H_2S yields 32·065 for the at. wt. of S, thus demonstrating the purity of the material. Liquid H_2S and CO_2 are only partly miscible under 1 atm. total pressure; on cooling, the pure components separate. No compound is formed. The quadruple point is at $-95·2°$, 253·2 mm., and 9·79% CO_2. H. F. G.

Preparation of dithionates by sulphonation of sulphites. P. Baumgarten (Ber., 1932, **65**, [*B*], 1645—1646).—Approx. 60% $K_2S_2O_7$ (17 g.) is added to $K_2S_2O_5$ (6·6 g.) and $KHCO_3$ (18 g.) in H_2O (75 c.c.) at 10°. After 0·5 hr. at 10° and 5 hr. at 20° the solution is heated, treated with excess of $Ba(OH)_2$, and filtered. The filtrate when treated with CO_2, filtered, and conc. yields $K_2S_2O_6$ in about 12% yield. Replacement of $K_2S_2O_7$ by *N*-pyridiniumsulphonic acid or trimethylsulphamic acid raises the yield to 80% or 92%, respectively. H. W.

Lead chamber process. II. Violet acid [SO_5NH_2]. (A). E. Berl and H. H. Saenger. **III. Violet acid. (B).** E. Berl and K. Winnacker (Z. anorg. Chem., 1932, **208**, 113—123, 124—133; cf. B., 1931, 585).—II. Cathodic reduction of $OH·SO_2·NO_2$ dissolved in 98% H_2SO_4 gives rise to "violet acid" (SO_5NH_2), which is rapidly oxidised when the current is interrupted. It has also been made by allowing N_2O_4 and H_2O vapour to impinge on liquid SO_2 at —70°. When 100% H_2SO_4 or 15% oleum is in contact with NO at high pressure, violet acid is formed immediately. With 97% acid the action is slow, and with 85% undetectable.

III. A method of analysing violet acid has been devised and its formation from H_2SO_4 and NO studied. The proportion of H_2SO_4 transformed varies from 4% at 8 atm. to 59% at 190 atm. The reaction is reversible. The chemical behaviour of violet acid, which is regarded as an important intermediate product in the chamber process, is discussed. F. L. U.

Fluorine polyhalides. H. S. Booth, C. F. Swinehart, and W. C. Morris (J. Physical Chem., 1932, **36**, 2779—2788; cf. this vol., 823).—Structural formulæ are suggested for compounds of the type M^IFICl_3. E. S. H.

Dilute perchloric acid as oxidising agent. A. Travers and Silice (Compt. rend., 1932, **195**, 709—710).—Dil. aq. $HClO_4$ oxidises under pressure at 260°. Thus whilst to oxidise Cr^{III} at the ordinary pressure $\nless$ 65% acid is required, 20% acid acts rapidly at 260° in a sealed tube, and 5% acid effects partial oxidation. 65% aq. $HClO_4$ oxidises Cr^{III} but not Mn^{II}. C. A. S.

Transformation from rose to green manganous sulphide. G. Landesen (J. Physical Chem., 1932, 36, 2521—2522; cf. A., 1931, 1140).—Polemical. I. J. P. (*c*)

Transformation from rose to green manganous sulphide. H. B. Weiser and W. O. Milligan (J. Physical Chem., 1932, **36**, 2840—2841).—Polemical (cf. preceding abstract). E. S. H.

Reactions between hydriodic acid and highly insoluble compounds. E. R. Caley (J. Amer. Chem. Soc., 1932, **54**, 4112—4113; cf. this vol., 1100).—A note on the action of HI on the alkaline-earth sulphates, $Cr_2(SO_4)_3$, $CrCl_3$, $CrBr_3$, $PbSO_4$, $PbCrO_4$, Ag halides, and other complex insol. compounds. C. J. W. (*c*)

Metal carbonyls. W. Hieber and co-workers. XVII. Volatile iron nitrosocarbonyl, $Fe(CO)_2(NO)_2$. J. S. Anderson (Z. anorg. Chem., 1932, **208**, 238—248; cf. this vol., 920).—$Fe(CO)_2(NO)_2$ is formed by the action of NO on $Fe(CO)_4$ dissolved in $Fe(CO)_5$ at 60—100°, best at 95°. It can be separated from $Fe(CO)_5$ by fractional distillation at $-15°$. It forms red crystals, m.p. 18·5°, d_4^{20} 1·56, b.p. (by extrapolation) 120°; v.p. between 0° and 80° are given. The substance decomposes above 70°, and is rapidly oxidised by air or O_2 at room temp. Its relationship to other metal carbonyls is discussed. F. L. U.

Effect of hydrogen sulphide on corrosion of iron by salt solutions. S. C. Britton, T. P. Hoar, and U. R. Evans.—See B., 1932, 1035.

Corrosive action of potassium (and other alkali) salt solutions on metals. I. Cast iron and lead. V. K. Pershke and G. I. Chufarov.—See B., 1932, 985.

Persulphatopentamminocobaltic sulphate. (Mme.) R. Duval and C. Duval (Bull. Soc. chim., 1932, [iv], **51**, 1035—1040).—A reply to Klément (A., 1931, 1140). Previous work on the above compound (A., 1931, 53) has been repeated and its structure confirmed. Klément's compound probably exists, but is distinct from that prepared by the authors. The Co in cobaltiammines does not liberate I from aq. KI. D. R. D.

Molybdates and tungstates of complex cobaltammines. E. Neusser (Z. anorg. Chem., 1932, **207**, 385—394).—The following *compounds* are described:
$[Co(NH_3)_6]MoO_4Cl,3H_2O$; $[Co(NH_3)_6]WO_4Cl$;
$[Co(NH_3)_6](MoO_4)_2Mo_2O_7,6H_2O$ (impure);
$[Co(NH_3)_6](WO_4)_2W_2O_7,6H_2O$;
$[Co(NH_3)_5H_2O]_2MoO_4(MoO_7)_2,4H_2O$(?);
$[Co(NH_3)_5H_2O]_2(WO_4)_3,3H_2O$;
$[Co(NH_3)_5H_2O]_2(WO_4)_2W_2O_7,6H_2O$;
$[Co(NH_3)_5Cl]WO_4$; $[Co(NH_3)_5NO_2]MoO_4$;
$[Co(NH_3)_5NO_2]WO_4$; $[Co(NH_3)_5NO_3]W_2O_7,2H_2O$;
$[Co(NH_3)_5CNS]WO_4,2H_2O$;
$[Co(NH_3)_4CO_3]_2MoO_4,2H_2O$;
$[Co(NH_3)_4CO_3]_2WO_4,2H_2O$; $[Co(NH_3)_4C_2O_4]_2MoO_4$;
$[Co(NH_3)_4C_2O_4]_2WO_4$;
$[Co(NH_3)_4(NO_2)_2]_2MoO_4,5H_2MoO_4$(?). H. F. G.

Analysis of small quantities of volatile material by determination of the vapour pressure and mol. wt. during distillation. B. G. Šimek and R. Kassler (J. Amer. Chem. Soc., 1932, **54**, 3962—3969).—A method for ascertaining the behaviour of small quantities of material during distillation is described; temp. are measured in a tension eudiometer at 20 mm. It is possible to calculate the behaviour of a substance in a regular A.S.T.M. distillation or in the Krämer–Spilker method. The mean mol. wt. of the fractions may be determined simultaneously in the tension eudiometer. Tests are reported for C_6H_6, 4 gasolines, and motor and commercial benzol. C. J. W. (*b*)

Systematic qualitative analysis of anions. E. W. Flosdorf and C. M. Henry (Ind. Eng. Chem.

[Anal.], 1932, 4, 434).—A scheme for the group separation of anions in qual. analysis is suggested. E. S. H.

Systematic detection of anions. R. Montequi (Anal. Fís. Quím., 1932, 30, 567—599).—Eight groups are recognised, containing respectively anions (1) directly detectable (CO_3'', OAc'); (2) pptd. by KCl from AcOH solution; (3) pptd. by $Zn(OAc)_2$ from AcOH solution; (4) pptd. from AcOH solution by $Ca(OAc)_2$; (5) pptd. from neutral solution by Ca or Zn acetate; (6) pptd. by $Ba(OAc)_2$ from AcOH solution; (7) pptd. by $Ag^{\cdot}$ from HNO_3 solution; and (8) not already included. Full details are given of the group separations and of sp. tests for the anions. H. F. G.

Radium rays as a means of examining solid materials. K. Przibram (Z. Elektrochem., 1932, 38, 490—496).—The coloration produced in certain salts by Becquerel-ray irradiation is of val. for identification, and serves also to provide information regarding the structure of the material. Application of the method to study of the recrystallisation velocity of compressed rock-salt shows that the velocity increases with increase of the degree of deformation, whilst the temp. coeff. diminishes. The inhibition of the recrystallisation by intensive irradiation indicates that the coloration involves those points which are primarily concerned with the beginning of the recrystallisation process. H. F. G.

Rock sampling for chemical analysis. F. F. Grout (Amer. J. Sci., 1932, [v], 24, 394—404).—Reasoned suggestions are made. C. W. G.

Spectrographic detection of minute amounts [of elements]. W. Späth (Monatsh., 1932, 61, 107—115).—An apparatus is described for the spectrographic detection of elements in which the following sensitivities were observed: (spark) 10^{-10} g. Cd, 10^{-10} g. Mn, 10^{-8} g. Tl, 10^{-7} g. Te, 10^{-7} g. As, 10^{-9} g. Li, 10^{-11} g. Sr; (arc) 10^{-10} g. Cd, 10^{-8} g. Mn, 10^{-9} g. Te, 10^{-9} g. Tl. The prep. of Ag sufficiently free from Cd for use as an electrode for its detection is described. H. A. P.

Applications of the spectrograph in specific analysis and in the detection of vapours and suspended matter. F. Wirth and E. Goldstein (Angew. Chem., 1932, 45, 641—646).—Details are given of the apparatus and procedure employed when using the quartz spectrograph in conjunction with the condensed W spark and the H discharge tube, and of the interpretation of the results. The determination of C_6H_6, PhMe, etc. vapour in air by the direct method and by removal with EtOH is described in detail; 60—100 mg. of C_6H_6 per cu. m. of air may be detected. The sp. character of the results obtained by the spectrographic method, as compared with those given by refractometric and interferometric methods, is emphasised. H. F. G.

Application of antimony and manganese electrodes to determination of [H˙]. I. I. Shukov and J. A. Boltunov (J. Gen. Chem. Russ., 1932, 2, 407—414).—The p_H vals. of solutions containing org. acids as determined using Sb electrodes are considerably higher than when the H or quinhydrone electrode is used, whilst with Mn electrodes the difference is so great as to render the results completely untrustworthy. R. T.

Application of hydrogen and quinhydrone electrodes to mixed solvents. I. I. Shukov and I. G. Vorochobin (J. Gen. Chem. Russ., 1932, 2, 399—406).—The p_H of buffer solutions containing EtOH, MeOH, or $COMe_2$ rises with the org. solvent content for both acid and alkaline solutions; this effect is not shown by glycerol. The p_H vals. given by H and glass electrodes are in all cases higher than those given by the quinhydrone electrode, which should not be applied to such solutions. R. T.

Use of the antimony electrode in the determination of acidity. T. Gysinck (Arch. Suikerind. Ned.-Indië, 1932, 711—749; Chem. Zentr., 1932, ii, 409).—Gentle stirring gives the most const. vals. Cast Sb electrodes are preferred; they give the most reproducible results shortly after prep. Sb deposited electrolytically on Pt wire rapidly loses reproducibility. p_H–e.m.f. curves consisted of two almost straight and practically parallel sections. Between p_H 7·12 and 8·17 there was an inflexion which might disappear with purer electrodes. A. A. E.

Colorimetric determination of p_H of solutions containing chlorine or hypochlorites, and the stability of indicators. H. F. Lewis and S. I. Kukolich.—See B., 1932, 1028.

Effect of manganese salts on acidimetric titrations in presence of methyl-orange. A. Perret and A. M. Krawczynski (Bull. Soc. chim., 1932, [iv], 51, 1014—1019).—On running aq. NaOH into an acid solution containing a $Mn^{\cdot\cdot}$ salt and Me-orange, $Mn(OH)_2$ is pptd. and oxidised by the air to manganous acid, which destroys the Me-orange. Titration in boiling solution in an atm. of H_2 inhibits this effect, but the best results are obtained by the addition of reducing agents, of which quinol is the most efficient. $Co^{\cdot\cdot}$ does not interfere with Me-orange titrations. D. R. D.

Detection of chloride in presence of cyanide. R. Montequi and E. Otero (Anal. Fís. Quím., 1932, 30, 564—566).—The reagent used is prepared by dissolving $AgNO_3$ (4·25 g.) and $Hg(NO_3)_2$ (2·7 g. $HgO+10$ c.c. conc. HNO_3) in H_2O (to 50 c.c.); when it is added to a dil. solution containing Cl' and CN', non-ionised $Hg(CN)_2$ is formed, together with AgCl. The solution should contain $\not>0\cdot5\%$ of alkali cyanide, as otherwise an insol. complex is formed. The reagent will detect easily 0·2 mg. of NaCl in 5 c.c. of solution. It may be used in presence of $Fe(CN)_6'''$ and/or $Fe(CN)_6''''$, but preliminary pptn. with $2N$-$Zn(OAc)_2$ is necessary. H. F. G.

Micro-determination of perchlorate by titanous chloride. A. Rosenberg (Z. anal. Chem., 1932, 90, 103—109).—The liquid is decomposed with sufficient conc. H_2SO_4 to give a 50% H_2SO_4 solution after addition of aq. $TiCl_3$. When CO_2 has been allowed to pass for 15 min. a slight excess of $0\cdot01N$-$FeCl_3$ is added and the flask placed in boiling H_2O for 30 min. After cooling in ice-H_2O the solution is diluted with aq. CO_2 and, after addition of 5 c.c. of 40% KCNS, is titrated back with $0\cdot01N$-$FeCl_3$. The passage of CO_2 must be continued throughout the analysis. M. S. B.

Determination of iodine in cuprous iodide. A. ROUSSY.—See B., 1932, 980.

Use of metallic lithium in analysis of gases. Determination of nitrogen in inert gases. J. H. SEVERYNS, E. R. WILKINSON, and W. C. SCHUMB (Ind. Eng. Chem. [Anal.], 1932, 4, 371—373).—Molten Li reacts quantitatively with N_2, O_2, and H_2O vapour, giving non-volatile products. An apparatus which enables the purity of He to be calc. from the change in pressure when these gases are removed by electrically heated Li is described. E. S. H.

Selenium in determination of nitrogen by Kjeldahl method. J. TENNANT, H. L. HARRELL, and A. STULL (Ind. Eng. Chem. [Anal.], 1932, 4, 410). —Evidence is given to show that Se is a more efficient catalyst than $CuSO_4$. E. S. H.

Detection of ammonia in the atmosphere. I. M. KORENMAN (Z. anal. Chem., 1932, 90, 115—118).—When filter-paper, soaked in a solution of certain freshly-diazotised amines, is exposed to air containing NH_3, a colour is developed on the filter-paper. NH_2Ph, sulphanilic acid, benzidine, $NHPh{\cdot}NH_2$, Ursol DW and DS, α- and β-$C_{10}H_7{\cdot}NH_2$, atoxyl, and *p*-nitroaniline (I) react; the sensitivity varies from 0·0025 mg. of NH_3 per litre for *p*-nitroaniline (red) to 0·07 mg. for α-$C_{10}H_7{\cdot}NH_2$ (violet-red) and Ursol DS (rose-red). $NPhEt_2$, $NHPh_2$, *m*-$C_6H_4(NH_2)_2$, antipyrine, brucine, quinine, etc. do not react. Halogens inhibit the reaction, H_2S affects only Ursol DW, and SO_2 (I). C_5H_5N has no effect on the reaction, but NH_2Ph or CH_2O inhibits it in the case of (I). M. S. B.

Microchemical reaction for ammonia and test for its presence in pyridine. I. M. KORENMAN (Z. anal. Chem., 1932, 90, 114—115).—If a little of a solution containing free NH_3 is placed at the bottom of a porcelain crucible covered with a glass from which hangs a drop of a solution containing a Cu salt and picric acid, characteristic greenish-yellow crystals of a compound of NH_3, Cu, and picric acid can be observed under the microscope. The presence of C_5H_5N does not interfere with the test. The limiting amount of NH_3 detected is 2 mg. M. S. B.

Simple apparatus for absorption of small amounts of gas : detection of nitric oxide with ferrous sulphate. K. TÄUFEL and P. SADLER (Z. anal. Chem., 1932, 90, 20—23).—A micro-gas absorption apparatus suitable for the detection and determination of NH_3, CO_2, NO, etc. is described. For detection of traces of NO it is preferable to absorb the gas in conc. H_2SO_4 and then apply the brown ring test with $FeSO_4$, rather than to absorb in $FeSO_4$ directly. J. W. S.

Polarographic studies with the dropping mercury cathode. XXVII. Electro-reduction and determination of nitrates and nitrites. M. TOKUOKA (Coll. Czech. Chem. Comm., 1932, 4, 444—455).—The reduction of nitrates and nitrites at the dropping Hg cathode has been studied polarographically from current–voltage curves. In neutral or alkaline solution reduction occurs only in presence of bi- or ter-valent cations; in 0·1*N*-$LaCl_3$ the reduction potential is −1·2 volt (HgCl zero). SO_4'' hinders the reaction. The increase of current caused by electro-reduction of NO_3' is eight times the current depositing an equiv. amount of metallic cation. Hence NO_3' takes up eight faradays to give NH_3. The saturation currents due to reduction of NO_3' and NO_2' are proportional to their concn., whilst NO_2' is decomposed by strong acids, yielding electro-reducible NO. Hence small quantities of NO_2' and NO_3' can be determined in this way. It is supposed that the strong field in the neighbourhood of the cathode splits the ions into elementary N^{5+} and N^{3+} ions, high-valency cations serving to drag the anions towards the cathode surface. J. W. S.

Diphenylbenzidine as a test for nitrates and nitrites. H. STROMBERG (Proc. Staff Mtgs. Mayo Clinic, 1932, 7, 254—256).—The specimen (free from proteins and Cl) is diluted and 1 c.c. (0·0002—0·0009 mg. N as NO_3' or NO_2') is treated with 0·1 c.c. of NaCl solution (12·5 mg. per c.c.), 10 c.c. of the diphenylbenzidine solution (50 mg. in 200 c.c. H_2SO_4 diluted with 200 c.c. H_2O), and 10 c.c. of conc. H_2SO_4. The glass-stoppered tubes are inverted twice, kept in ice for 20 min., allowed to reach room temp., and compared after 1·75 hr. with a standard (0·0005 mg. N as NO_3'). CH. ABS.

Determination of phosphoric acid in the presence of pyrophosphoric acid. V. NJEGOVAN and V. MARJANOVIĆ (Chem. Listy, 1932, 26, 449—451).—The solution, containing 0·1—0·5 g. of P_2O_5, is evaporated to dryness, and 5 c.c. each of H_2SO_4 and of saturated aq. $MgSO_4$ are added. The solution is then made alkaline to phenolphthalein by a mixture of conc. aq. NH_3 and 25% NH_4OAc, H_2O is added to 200 c.c., and, after heating 1 hr. at 100°, the cooled solution is filtered, and the residue of $MgNH_4PO_4$ is washed and ignited. An accuracy of 99·7% is obtained. R. T.

Phosphate determination in boiler water. A. SULFRIAN.—See B., 1932, 963.

Determination of phosphoric acid with benzidine. F. UKRADIGA.—See B., 1932, 1027.

Identification of arsenic. M. SAUVÉ (Bull. Biol. Pharm., 1932, 280).—An apparatus is described for the identification of AsH_3 by means of the yellow stain obtained on paper moistened with aq. $HgCl_2$. A. L.

Determination of arsenic. Iodometric acidimetric method. R. C. WILEY, J. P. BEWLEY, and R. IREY (Ind. Eng. Chem. [Anal.], 1932, 4, 396—397).—The As compound is converted into AsH_3, which is absorbed by standard I solution. The residual I is titrated and the result checked by titrating the acids formed in the oxidation. It is possible to determine 0·00002 g. As. E. S. H.

Determination of boron spectroscopically. J. S. MCHARGUE and R. K. CALFEE (Ind. Eng. Chem. [Anal.], 1932, 4, 385—388).—The following procedure is suitable for determining the B content of plant and animal tissues. The material is ashed at or below 400° with excess of K_2CO_3, and the ash dissolved in aq. citric acid. B is converted into Me_3BO_3 by means of MeOH and H_3PO_4, and the vapour is burned in O_2 in a special apparatus. The spectrum is viewed through a glass cell containing H_2O, to which a standard solution of $KMnO_4$ is added until the bright green band is eliminated. The method gives an accuracy of $\pm0{\cdot}0095$ mg. on samples containing 0·05—0·3 mg. of B. E. S. H.

Displacement of end-point in titration of solutions of boric acid and mannitol–boric acid. F. L. Hahn, R. Klockmann, and K. Schulz (Z. anorg. Chem., 1932, 208, 213—216; cf. A., 1928, 857).—The observation by van Liempt (A., 1920, ii, 331) that a very small proportion of mannitol (I) enables H_3BO_3 to be neutralised by the theoretical amount of NaOH was due to an error in determining the end-point. When due precautions are taken the excess alkali required decreases as the proportion of (I) increases. If CO_2 is present the amount of (I) necessary greatly exceeds its solubility, and better results are obtained with glycerol. F. L. U.

Determination of carbon dioxide in gas mixtures. Potentiometric method. P. W. Wilson, F. O. Orcutt, and W. H. Peterson (Ind. Eng. Chem. [Anal.], 1932, 4, 357—361).—The gas mixture is bubbled through about 10 c.c. of aq. Na_2CO_3, the p_H of which is then determined by means of the glass electrode. The CO_2 is calc. from a calibration curve. The procedure is suitable for 0·03—7% CO_2 in the mixture and the error in rapid routine work is about 4%. Greater accuracy may be obtained by incorporating certain refinements. The method can be modified for use with a p_H colorimeter. E. S. H.

Apparatus for the determination of carbon dioxide. A. Hanak (Chem.-Ztg., 1932, 56, 672).—The apparatus comprises a conical decomp. flask (*A*) in the neck of which fits a bulb (*B*) for the dil. HCl, through the upper neck of which fits a second bulb (*C*) containing H_2SO_4 for drying the issuing gas. (*C*) has a long tube (*D*) passing through (*B*) into (*A*); the upper part of this tube terminates at the top of the inner bulb of (*C*), the lower end of which is provided with small holes to allow the gas to bubble through the acid from the inner to the outer bulb of (*C*). A small tube at the lower end of (*D*) communicates with a hole in the wall of (*D*) at the lower end of (*B*) so that by rotating (*A*) in one direction the HCl can be kept from running into (*A*) while the apparatus and contents are weighed and by rotating it in the other direction the HCl is allowed to fall on to the material being analysed. A. R. P.

Test paper for carbon disulphide. V. I. Kuznetzov (Anilinokras. Prom., 1932, 2, No. 3, 1—2).—Paper treated with a solution of Cu or Co salt in excess of $NHMe_2$, $NHEt_2$, or $C_5H_{11}N$ becomes brown in presence of CS_2 or H_2S. For the detection of CS_2 in presence of H_2S a CN' solution is added, to exact decolorisation, to the Cu–$NHMe_2$ complex; this becomes yellow to brown with CS_2, and remains colourless with H_2S, whilst with both the wet paper is coloured yellowish-green and becomes brown on drying. The reagent detects 0·001 g. of CS_2 in 1 litre of air, and 1—2% of CS_2 in H_2S. Ch. Abs.

New source of error in the separation of K_2PtCl_6. R. Strebinger and H. Holzer (Z. anal. Chem., 1932, 90, 81—86).—In the analytical separation of K_2PtCl_6 by EtOH reduction takes place if the EtOH contains MeCHO. This is an important source of error in micro-analytical work where the amount of EtOH is relatively large. K_2PtI_6, used in the colorimetric determination of Pt, is still more sensitive. The action is photochemical. M. S. B.

Visual conductivity titrations and measurements. G. Jander and H. Schorstein (Angew. Chem., 1932, 45, 701—703).—With the aid of a sensitive a.-c. galvanometer it is possible to titrate small amounts of substances in the presence of excess of electrolytes, *e.g.*, 5 c.c. of 0·01*N*-NaI and 130 times as much $NaNO_3$. Zn can be determined by adding to Na_2S and titrating excess of Na_2S with HCl. A. G.

Detection of silver in very dilute solutions by physical development. A. J. Velculescu (Z. anal. Chem., 1932, 90, 111—113).—One drop of very dil. aq. $AgNO_3$ to be tested is put on a marked spot on a piece of filter-paper, treated with 0·02*M*-KBr, and thoroughly washed, leaving the spot impregnated with AgBr. This is then treated with a developer of the following composition: 500 c.c. H_2O, 10 g. metol, and 50 g. citric acid, and to 50 c.c. of this mixture 2 c.c. of 0·1*M*-$AgNO_3$ are added immediately before use. The presence of AgBr on the filter-paper causes a considerable portion of Ag from the developer to be pptd. as metal, whether exposed to light or not. The limiting concn. which has been detected is 1 part in 10^7, but it is possible that the dilution might be carried further. Free HNO_3, but not H_2SO_4, is detrimental. Pb has no effect even when its concn. is 2000 times that of Ag. Hg behaves similarly to Ag and so must be removed previously by heating. M. S. B.

Application of catalysis to the detection of certain cations. Silver and copper. Applications. G. Denigès (Bull. Soc. chim., 1932, [iv], 51, 1096—1100).—2×10^{-4} mg. of $Ag^{\cdot}$ and 5×10^{-3} mg. of $Cu^{\cdot\cdot}$ in 10 c.c. of solution may be detected by the following tests, depending on their activity as catalysts in the oxidation of $Mn^{\cdot\cdot}$ to MnO_4'. To 10 c.c. of the Ag solution are added 20 drops of H_2SO_4, 2 drops of 0·4% $MnSO_4,5H_2O$, and 0·10 g. of $K_2S_2O_8$ or $Na_2S_2O_8$. On heating at 100° on a water-bath, the pink colour and characteristic absorption spectrum of MnO_4' appear. Hg and Co produce a similar effect, but their catalytic activity is, respectively, 1/50 and 1/200 of that of Ag. The method may be applied to the detection of Ag in coinage etc., a minute drop of HNO_3 being placed on the metal and after 8—10 sec. washed off and the solution tested as above. The method can be used for the colorimetric determination of Ag. To test for Cu, to 10 c.c. of the solution are added 5 drops of 0·4% $MnSO_4,5H_2O$ and 5 drops of aq. NaOBr, prepared by dissolving 1 c.c. of Br in 30 c.c. of 3·3*N*-NaOH. The mixture is heated on the water-bath for 2 min., cooled, and centrifuged to separate the MnO_2 ppt., when the colour of MnO_4' can be seen in the clear solution. Ni and Co act similarly, but their activity is only 1/12 and 1/45, respectively, of that of Cu. The application to the analysis of natural waters and to the colorimetric determination of Cu is considered. D. R. D.

Composite reagent for calcium. G. J. Cox and M. L. Dodds (Ind. Eng. Chem. [Anal.], 1932, **4**, 361).—$H_2C_2O_4,2H_2O$ (200 g.) and NH_4Cl (500 g.) are dissolved in H_2O (3500 c.c.), and AcOH (1000 c.c.) and 0·4% Me-red (10 c.c.) are added, any ppt. formed being filtered off. The composite reagent is satisfactory for pptg. CaC_2O_4 from bone ash solutions. E. S. H.

Precipitation of calcium by potassium ferrocyanide. R. Chandelle (Bull. Soc. chim. Belg., 1932, **41**, 420—429).—Ca salts give a ppt. on adding aq. $K_4Fe(CN)_6$ in presence of a large excess of NH_4Cl or KCl. In the first case, the ppt. is $Ca(NH_4)_2Fe(CN)_6$; in the second, it is $Ca_2Fe(CN)_6$. D. R. D.

Determination of radium in insoluble substances. A. Karl (Bull. Soc. chim., 1932, [iv], **51**, 1023—1029).—The emanation method (this vol., 355) is described. D. R. D.

Beryllium. IV. Micro-qualitative analysis of beryllium. H. S. Booth and S. G. Frary (J. Physical Chem., 1932, **36**, 2641—2650).—Of existing micro-analytical methods, the K oxalate method is the most satisfactory, and the H_2PtCl_6 method satisfactory under certain conditions. The use of K malonate similarly to K oxalate, and of the basic acetate, recrystallised from glacial AcOH, as a confirmatory test are suggested. I. J. P. (*c*)

Rapid determination of small amounts of magnesium in presence of phosphates. W. E. Thrun (Ind. Eng. Chem. [Anal.], 1932, **4**, 426—427).—Mg is determined colorimetrically by the formation of a lake with curcumin in presence of NaOH. The colour is affected by PO_4''', but not by its amount; $Ca_3(PO_4)_2$ is dissolved, therefore, in the colour standard. E. S. H.

Determination of zinc in brass and other alloys by the oxalate–permanganate method. E. Knoppick.—See B., 1932, 986.

Detection of cations of group IIb. A. Scheinkmann (Pharm. Zentr., 1932, **73**, 681—682; cf. A., 1931, 1260).—The sulphides are dissolved in HCl and H_2O_2, and Pb, Hg, and Bi pptd. with aq. NH_3. The Pb and Hg are extracted with NH_4OAc and detected by the usual methods. The Bi in HNO_3 solution gives $BiPO_4$ with Na_2HPO_4, or bismuthyl dichromate with $K_2Cr_2O_7$. The Na_2SnO_2 test for Bi is untrustworthy. Alternatively the $Pb(OH)_2$, $HgClNH_2$, and basic Bi salt are dissolved in NH_4OAc and AcOH. Pb is then detected as $PbSO_4$, Hg with $SnCl_2$, and Bi as above, $K_2Cr_2O_7$ being used only in the absence of Pb. Cd in a solution decolorised with KCN gives a yellow ring at its junction with an aq. H_2S layer. A. A. L.

Separation and determination of traces of lead in presence of small quantities of iron. J. H. Hamence (Analyst, 1932, **57**, 622—626).—Fe is removed as $Fe(CNS)_3$, which is extracted by equal vols. of Et_2O and amyl alcohol, and Pb is determined as PbS. If much SO_4 is present, Pb may be pptd. as $PbSO_4$; this is avoided by using smaller quantities or by the addition of NH_4OAc. NH_4 citrate is added to retain Ca in solution. T. McL.

Determination of thallium after oxidation with bromine. P. E. Browning (Ind. Eng. Chem. [Anal.], 1932, **4**, 417).—Tl (0·1 mg. in 10 c.c.) can be detected by the dark coloration produced by adding Br and excess of NaOH. The presence of Fe, Mn, Co, or Ni interferes. The test may be made quant. by heating the ppt. at 150—200° and weighing as Tl_2O_3. E. S. H.

[Copper zinc mercurothiocyanate test for copper.] R. Montequi (Anal. Fís. Quím., 1932, **30**, 600).—A claim for priority. H. F. G.

Dry test for copper. B. Batscha (Z. physikal. Chem. Unterr., 1932, **45**, 117—118; Chem. Zentr., 1932, ii, 411).—The manipulation of the borax bead test is discussed. A. A. E.

Determination of traces of mercury as comparable rings of mercuric iodide. A. Delauney (Ann. Falsif., 1932, **25**, 409—412).—Hg deposited on a brass or Au electrode is volatilised on to a cool portion of a hard glass tube (6 mm. diam.) in a current of air at a dull red heat. I is then passed over the Hg at 135—140° and the HgI_2 deposited in a further portion of the tube. Comparisons are made after the HgI_2 has turned red. T. McL.

Determination of metals in organic combination. D. L. Tabern and E. F. Shelberg (Ind. Eng. Chem. [Anal.], 1932, **4**, 401—403).—A mixture of $H_2S_2O_7$ and 30% H_2O_2 destroys rapidly all the org. matter in organometallic compounds of Hg, As, Sb, Bi, Au, Ag, and Ge. The metal is obtained in solution, generally as sulphate, and may be determined by the usual methods. E. S. H.

Separation of aluminium from zinc, using hydrazine carbonate. A. Jílek and J. Vřešťál (Chem. Listy, 1932, **26**, 497—503).—Al ($\ngtr$ 0·1 g.) is doubly pptd. as double salt with N_2H_4,H_2CO_3, ignited, and weighed as Al_2O_3. The mean error is ±0·5%. R. T.

Separation of aluminium as phosphate in the presence of calcium phosphate, with special reference to the action of milk on aluminium. A. G. G. Gwyer and N. D. Pullen (Analyst, 1932, **57**, 704—707).—A modification of Carnot's method is employed, the $AlPO_4$ being pptd. at p_H 4·0—4·5 in the presence of AcOH. Milk has no action on Al. T. McL.

Rapid analysis of manganate–permanganate mixtures. J. E. Orlov (Z. anal. Chem., 1932, **90**, 35—38).—The method suggested for analysis of mixtures containing $KMnO_4$, K_2MnO_4, MnO_2, K_2CO_3, and KOH consists in determination of (*a*) total oxidising constituents iodometrically; (*b*) of K_2CO_3+KOH; (*c*) $MnO_4'+MnO_4''$ by centrifuging with $CaCl_2$ and determining oxidising constituents in the

solution; (*d*) KOH by titration of alkali in the last solution; (*e*) the MnO_4' : MnO_4'' ratio colorimetrically.
J. W. S.

Analytical chemistry of rhenium. VII. Detection and determination of small quantities of rhenium by the aid of potassium thiocyanate and stannous chloride. W. GEILMANN, F. W. WRIGGE, and F. WEIBKE (Z. anorg. Chem., 1932, **208**, 217—224; cf. A., 1931, 328).—A yellow to orange-red coloration is produced when KCNS and $SnCl_2$ are added to a solution, acidified with HCl, containing a small quantity of a perrhenate. The colour can be conc. by extraction with Et_2O. The min. quantity of Re detectable is 5×10^{-7} g. in 10 c.c. The reaction has been used as the basis of a colorimetric method of determining Re, details of which are given.
F. L. U.

Analytical chemistry of rhenium. E. KRONMANN (Z. anal. Chem., 1932, **90**, 31—34).—Re can be separated quantitatively from minerals by distillation of a conc. H_2SO_4 solution in a stream of air (for separation from W) or HCl (to separate from Mo). Apparatus is described.
J. W. S.

Iodometric determination of iron. A. V. FILOSOFOV and S. MELNIK (J. Appl. Chem., Russia, 1932, **5**, 219—220).—2·7 g. KI per 0·1 g. Fe, and HCl $\not>$ 0·1*N* are recommended.
CH. ABS.

Determination and separation of cobalt as the cobaltic nitrosonaphthol compound. C. MAYR and F. FEIGL (Z. anal. Chem., 1932, **90**, 15—19).—Co can be determined, even in presence of Ni, Zn, or Al, by pptn. with a 2% solution of 1-nitroso-β-naphthol in 50% AcOH. A solution containing 1—30 mg. Co as $CoSO_4$, $CoCl_2$, or $Co(NO_3)_2$ in 10—20 c.c. is made slightly acid and treated with 5—10 drops of "perhydrol" and then with 2*N*-NaOH until pptn. of $Co(OH)_3$ commences; 10—20 c.c. of AcOH are added, the ppt. is redissolved, and the solution diluted to 200 c.c. Co is pptd. by addition of 10—20 c.c. of the above reagent, the ppt. coagulated by boiling, and weighed in a Gooch crucible.
J. W. S.

Determination of cobalt, using dinitroresorcinol. O. TOMIČEK and K. KOMÁREK (Chem. Listy, 1932, **26**, 515—520).—Pptn. of Co by Orndorff and Nichols' method (A., 1923, ii, 584) is not quant., and both the composition of the ppt. and the amount of Co remaining in solution depend on the conditions of pptn. and on the concn. of Co and of other substances present. Under certain conditions incomplete pptn. is masked by adsorption of dinitroresorcinol and alkali on the ppt., which ordinarily contains $\not>$ 80% of Co dinitroresorcinol. Attempts at attaining quant. pptn. of Co by varying the conditions of reaction were unsuccessful.
R. T.

Spectro-identification of small quantities of nickel and chromium. A. J. DE A. GOUVEIA (Rev. Chim. pura appl., 1932, **5**, 41—43; Chem. Zentr., 1932, ii, 412).—The detection of Ni (5476·9 Å.) is sensitive to 0·05% and that of Cr (5208·4, 5206·0, 5204·5 Å.) to 0·005% when SiO_2 is present.
A. A. E.

Volumetric determination of molybdenum by oxidation of quinque- to sexa-valent molybdenum by means of ceric sulphate or potassium permanganate. B. STEHLIK (Chem. Listy, 1932, **26**, 533—537).—Mo is reduced to Mo^V by means of $TiCl_3$, $SnCl_2$, Pb, or Zn, 50% of conc. H_2SO_4 is added, and the hot solution is titrated with $Ce(SO_4)_2$ or $KMnO_4$ in presence of $MnSO_4$ and in an atm. of CO_2, the end-point being determined potentiometrically.
R. T.

Colorimetric determination of traces of tungsten. F. FEIGL and P. KRUMHOLZ (Angew. Chem., 1932, **45**, 674—675).—To 2 c.c of the slightly alkaline tungstate solution (0·5—0·05*N*-NaOH) 5 drops of 25% KCNS solution are added, and 10% $SnCl_2$ (in conc. HCl) is added to make a total vol. of 5 c.c. The yellow colour is compared with a standard after 30 min. The error, when 10—100 microg. W is present, is about 3%. Molybdate, but not phosphate, interferes.
H. F. G.

Rapid method of dissolving lead alloys preparatory to determination of tin and antimony. B. S. EVANS.—See B., 1932, 941.

Separation of titanium from aluminium and certain elements of groups II and III by means of guanidine carbonate in presence of tartrate. A. JÍLEK and J. KOŤA (Coll. Czech. Chem. Comm., 1932, **4**, 412—417; cf. this vol., 491).—Separation of Ti with guanidine carbonate is quant. in presence of an equal quantity of $Al^{\cdots}$, CrO_4'', WO_4'', MoO_4'', $UO_2^{\cdot\cdot}$, AsO_3''', or $Tl^{\cdot}$, provided a boiling neutral dil. solution is used under conditions which are detailed.
J. W. S.

Determination of bismuth. C. MAHR (Z. anorg. Chem., 1932, **208**, 313—316).—Bi is pptd. in acid solution by $K_3Cr(CNS)_6$ as red cryst. $BiCr(CNS)_6$, the solubility of which in 0·1*N*-HNO_3 is 9·6 mg. per litre. The ppt. may be weighed, or the Cr determined volumetrically after oxidation to CrO_4''. The method can be used in presence of compounds of Mo, Cr, Al, Fe, Zn, Mn, Ni, Co, Mg, alkaline earths, and alkalis.
F. L. U.

Separation of rhodium from iridium and the gravimetric determination of these metals. R. GILCHRIST (Bur. Stand. J. Res., 1932, **9**, 547—556).—Salts of Rh and Ir are evaporated with H_2SO_4 to convert them into sulphates. Addition of $TiCl_3$ ppts. metallic Rh; two pptns. effect a quant. separation. Rh is redissolved in conc. H_2SO_4, pptd. by H_2S, ignited in H_2, and weighed as metal. Ti is removed from the filtrate by means of cupferron, two pptns. being necessary to eliminate contamination with Ir. Ir is determined in the filtrate by hydrolysing with $NaHCO_3$. The pptd. IrO_2,aq. is ignited in H_2 and weighed as metal.
E. S. H.

Calorimetric apparatus and the degree of accuracy attainable. S. DE WAARD (Chem. Weekblad, 1932, **29**, 567—569).—An apparatus utilising electrical ignition is described. With BzOH results vary by $\not>$ 0·025%, and with paraffin by $\not>$ 0·0125%; it is suggested that the paraffin burns more uniformly. In determinations of the heat of combustion of coals, a tolerance of ±40 kg.-cal. is proposed, owing to variations arising from incomplete combustion and from differences of the ash and H_2O contents and of the fineness of different samples.
H. F. G.

Vacuum-furnace design. K. K. Kelley (Ind. Eng. Chem. [Anal.], 1932, 4, 391—392).—The apparatus described is designed for calorimetric measurements at high temp. At 1000° a vac. of 0·1 mm. may be maintained. E. S. H.

Modifications in the Haughton–Hanson thermostat. J. L. Haughton (J. Sci. Instr., 1932, 9, 310—315).—Improvements of an apparatus previously described (B., 1917, 1039). C. W. G.

Device for increasing effectiveness of freezing mixtures. R. C. Archibald (J. Amer. Chem. Soc., 1932, 54, 3886—3887).—A wire screen holder keeps the NaCl on top and the ice below, to aid convection. In a test, $-20°$ was reached within 30 min., and the temp. remained const. until the ice had melted. L. O. (*c*)

Adiabatic method for precise electrical calibration of thermometers. F. Barry, H. W. Webb, and A. K. Smith (J. Amer. Chem. Soc., 1932, 54, 3785—3799).—The procedure depends on the precise maintenance of an adiabatic condition for a few hr., electrical heat being generated at a const. rate within the calorimeter. G. M. M. (*c*)

Self-rectifying demountable *X*-ray tube of high power. C. E. Eddy (J. Sci. Instr., 1932, 9, 354—358).—The tube, of the thermionic type, can be used with either a line or circular focus, and has readily detachable electrodes mounted on ground metal joints. The metal portions can be degassed. In intermittent use the tube will pass 10 milliamp. at 95 kv. C. W. G.

Double-crystal *X*-ray vacuum spectrometer. L. G. Parratt (Physical Rev., 1932, [ii], 41, 553—560).—An instrument for operation in a vac., designed to allow the study of soft *X*-rays, is described. N. M. B.

Metal *X*-ray tubes for characteristic radiation. C. J. Ksanda (Rev. Sci. Instr., 1932, [ii], 3, 531—534).—The main body is of stainless steel. The cathode is in a standard fitting for interchangeability. C. W. G.

Influence of refractive index on mounting media. W. Marshall (J. Roy. Micros. Soc., 1932, [iii], 52, 275—280).—Vals. of *n* (1·33—2·00) of a large no. of mounting media have been determined and the general usefulness of the mountants has been examined. The max. val. for a mountant for use in histology is about 1·70, and for vals. approaching this, specially computed objectives are desirable. Otherwise the ordinary laboratory microscope cannot be used with success. The effect of high *n* of the mountant is comparable with that of a thick cover-glass and the tube length has in consequence to be shortened. M. S. B.

Apparatus for taking photomicrographs. M. H. Stow (Science, 1932, 76, 277). L. S. T.

Modified apparatus for Raman effect. B. Anand (J. Sci. Instr., 1932, 9, 324—325).—Further details of an apparatus previously described (this vol., 7) are given. C. W. G.

Measurements with the absolute colorimeter. A. Thiel and W. Thiel (Chem. Fabr., 1932, 409—411).—The Leitz colorimeter operates on the Duboscq principle employing monochromatic light with a series of filters. Half of the beam passes through the solution to be tested and half through a standard neutral grey solution of known extinction power for light of any wave-length. The immersions in the two tubes are adjusted until the light intensities in the fields are equal, when the sp. extinction of the solution can be read directly from a scale. The instrument is also applicable to quant. measurements of turbidity and fluorescence. The " grey solution " supplied as standard should be kept in the dark and is permanent for at least 6 weeks. C. I.

Absolute colorimetric measurements. A. Thiel (Z. Elektrochem., 1932, 38, 621—622).—Abs. measurements may be effected by using Diehl's grey solution (Marburger Sitzungsber., 1931, 66, 55) in an ordinary colorimeter, together with suitable light filters. H. F. G.

Reproducible spintharometer for quantitative spectroscopy. A. Occhialini and L. Gallino (Atti R. Accad. Lincei, 1932, [vi], 15, 559—563).—A metal plate placed between two auxiliary wedge-shaped electrodes forms an easily reproducible electrode for the method of quant. spectroscopy previously described. O. J. W.

Regulation of temperature of water for refractometric measurements. V. Čupr and T. Krempaský (Chem. Listy, 1932, 26, 522—525).—Apparatus for the continuous delivery of H_2O at const. temp. is described. R. T.

[Chemical] microscopy. G. L. Keenan (J. Assoc. Off. Agric. Chem., 1932, 15, 626—629).—The solid substance is examined microscopically in ordinary light and in both parallel and convergent polarised light (crossed nicols) to determine whether it is singly- or doubly-refractive. *n* is then measured by immersion in suitable mixtures of mineral oil (*n* 1·490), $C_{10}H_7Cl$ (*n* 1·64), and CH_2I_2 (*n* 1·74); the line of contact between the solid and liquid disappears when their vals. of *n* are equal. J. G.

Illuminating device for use in experiments with filtered ultra-violet light. J. Grant (J. Sci. Instr., 1932, 9, 359—360).—To obviate the difficulty of reading a burette when working in the dark with ultra-violet light, a weighted float containing acidified quinine is used. C. W. G.

Sputtering and manipulation of replica gratings. L. G. Wilson (J. Sci. Instr., 1932, 9, 360).—More brilliant spectra are obtained if the gratings are sputtered with Pt. C. W. G.

Vacuum-tube potentiometer for p_H measurement with glass electrodes. F. Rosebury (Ind. Eng. Chem. [Anal.], 1932, 4, 398—401).—The construction and operation of the apparatus are described. Galvanometer drift is negligible. An accuracy of $\pm 0·03$ p_H is readily attainable. E. S. H.

Design of pressure ionisation chambers. J. H. Williams (Rev. Sci. Instr., 1932, [ii], 3, 586—592).—Constructional details of two metal ionisation chambers to be used at 30 and 60—100 atm., respectively, are given. C. W. G.

Distillation trap. E. S. West (Ind. Eng. Chem., [Anal.], 1932, 4, 445).—The trap may be used as a connecting bulb in Kjeldahl distillations. E. S. H.

Laboratory extractor. H. G. Tanner (Ind. Eng. Chem. [Anal.], 1932, 4, 397).—An extractor is assembled from common laboratory apparatus. E. S. H.

Large-capacity Soxhlet extractor and reflux condenser. A. E. Cameron (Ind. Eng. Chem. [Anal.], 1932, 4, 394—395).—Modified apparatus is described. E. S. H.

Static method for accurate vapour-pressure determination at high temperatures, and its application to the fixing of the hundred point on the temperature scale. H. Moser (Ann. Physik, 1932, [v], 14, 790—808).—The construction of a glass membrane manometer and its application for the determination of v.p. in the neighbourhood of 100° or higher are described. It has been used to fix the 100° point of the temp. scale with an accuracy of $\pm 0{\cdot}001°$. The dependence of v.p. of H_2O on temp. in the neighbourhood of the b.p. has been determined. A. J. M.

Low vapour-pressure gauge. K. Newbury and C. L. Utterback (Rev. Sci. Instr., 1932, [ii], 3, 593—595).—Depression of the surface of a Hg column moves a float, causing rotation of a small mirror. The instrument is calibrated against a McLeod gauge. C. W. G.

Accurate viscosimeter for volatile and hygroscopic liquids. E. N. da C. Andrade and K. E. Spells (J. Sci. Instr., 1932, 9, 316—319).—A completely closed all-glass viscosimeter is described. Resetting is carried out by means of a magnetically actuated Fe plunger, which does not come into contact with the liquid. C. W. G.

Apparatus for the determination of water by the xylene method. F. Eck (Glas u. Apparat, 1932, 13, 51—52; Chem. Zentr., 1932, i, 3469).

Improved micro-fractionating flask. H. Alber (Z. anal. Chem., 1932, 90, 100—103).—A form of micro-fractionating flask, which is simple, durable, and easily cleaned, is described. The best results are obtained for quantities of liquid $\nless 0{\cdot}2$ c.c. and the flask can also be employed for distillation under reduced pressure. M. S. B.

Manufacture of glass apparatus for microchemical work. P. de Fonbrune (Compt. rend., 1932, 195, 706—707).—The essential points are: heating the glass on the microscope stage by a Pt–Ir wire with regulated electric current in a regulated current of air, with means for moving the glass or wire at any desired speed. C. A. S.

Differential multiple condensation ebullioscope and its application. W. Swientosławski (Chem. Listy, 1932, 26, 442—444).—The difference between the b.p. of an azeotropic mixture and the condensation point of its vapours varies at different levels of the rectifying column; by substituting a no. of columns in series, each fitted with a receiver for the condensate, which then passes through the succeeding column, information may be obtained as to the nature of the components of an azeotropic mixture, and as to the degree of purity of a given liquid. R. T.

Automatic percolator. L. E. Warren (J. Assoc. Off. Agric. Chem., 1932, 15, 629—632).—The substance (*e.g.*, drug) to be extracted is placed on a wad of cotton-wool in the bottom of a glass cylinder terminating in a capillary tube at the lower end, and is covered with washed sand. The shoulder of this cylinder rests on glass knobs at the base of an outer jacket, the lower constricted end of which encloses the capillary of the cylinder and passes through a cork into the extraction flask, the upper end being attached to a condenser. J. G.

Rapid filtration apparatus. G. Müller (Chem. Fabr., 1932, 339—341).—The apparatus is a modified vac. filter in which the paper is placed in a perforated porcelain cone. E. S. H.

Aliquot and filter devices for analytical laboratories. T. M. Shaw (Ind. Eng. Chem. [Anal.], 1932, 4, 409—410).—A device for withdrawing an aliquot part from a suspension at any given depth is described. It is intended primarily for soil analysis. A rack for the simultaneous vac. filtration of several samples is described. E. S. H.

Glass and quartz filters for handling gases. P. H. Prausnitz (Ind. Eng. Chem. [Anal.], 1932, 4, 430—434).—The application of sintered glass and quartz filters to mercury traps, explosion safety-valves, dust filters, and gas–liquid reaction vessels is discussed. E. S. H.

Baro-burette. III. Application to gas density determinations. H. S. Booth and K. S. Willson (Ind. Eng. Chem. [Anal.], 1932, 4, 427—429; cf. A., 1930, 885, 1151).—The *d* of gases may be determined by measuring the pressure, vol., and temp. of a small sample in the baro-burette and determining its wt. by adsorption and weighing in a tube filled with C. Results are given for O_2 and CCl_2F_2. E. S. H.

Use of the bromine water pipette in exact chemical analysis. G. R. Schultze (Angew. Chem., 1932, 45, 573—575).—The only advantage the Br pipette has over the $KMnO_4$ pipette for determining olefines is its rapidity; in fact reasonably correct results are obtained with Br only with a short time of contact, a low temp., absence of direct light, and absence of O_2 in the gases. In sunlight and at temp. $> 25°$ C_2H_6 and higher paraffins are fairly readily attacked by $Br\text{-}H_2O$. A. R. P.

Comparative efficiencies of gas-washing bottles. S. Halberstadt (Ind. Eng. Chem. [Anal.], 1932, 4, 425—426; A., 1930, 1151).—The experiments show the superiority of glass-filter washers, particularly when the gaseous component to be absorbed is at a low concn. The spiral gas-washer can be employed only up to a max. velocity of 60 litres per hr., independently of the concn. of gas. E. S. H.

Improved McLeod gauge and manometer. H. S. Booth (Ind. Eng. Chem. [Anal.], 1932, 4, 380—382).—Two modified forms of apparatus are described, permitting the measurement of pressures from 760 to 0·00001 mm. E. S. H.

Modification of Poth's carbon dioxide generator. E. W. Lowe and W. S. Guthmann (Ind. Eng. Chem. [Anal.], 1932, **4**, 440—441).—Undesirable features of the original apparatus (A., 1931, 706) are eliminated. E. S. H.

Esterification resin as a ground-joint lubricant. T. P. Sager (Ind. Eng. Chem. [Anal.], 1932, **4**, 388).—The resin obtained by heating 1 mol. of citric acid and 1·5 mols. of tetraethylene glycol together at 180—185° for 90 min. is insol. in both aromatic and aliphatic hydrocarbons and is a suitable lubricant for use in the distillation of these liquids. The resin is sol. in H_2O, EtOH, and $COMe_2$. E. S. H.

Collecting train for recovering traces of iodine from ashed samples. G. M. Karns (Ind. Eng. Chem. [Anal.], 1932, **4**, 375—377).—The products of combustion are led through a train of freezing tubes (ice and NaCl, and solid CO_2 and $COMe_2$) and Cottrell precipitators. E. S. H.

Mol. wt. micro-method. A. C. Bratton, jun., and H. L. Lochte (Ind. Eng. Chem. [Anal.], 1932, **4**, 365—367).—The principle of the apparatus described is that of the Victor Meyer method, using samples of 2—10 mg. To avoid measuring the vol. of vapour produced, the change in pressure at const. temp. before and after vaporisation is determined. The error is $<2{\cdot}5\%$. E. S. H.

Absorption tube. E. F. Degering (Ind. Eng. Chem. [Anal.], 1932, **4**, 356).—A combination of Folin and Meyer absorption tubes provides a more efficient gas scrubber than either of these tubes separately, especially for high rates of gas flow. E. S. H.

Simple apparatus for carrying away corrosive or inflammable vapours in the laboratory. C. O. Guillaumin (Bull. Soc. chim., 1932, [iv], **51**, 1021—1023).—The vapours given off during a reaction or evaporation are sucked through an absorbing apparatus by means of a filter pump. D. R. D.

Laboratory apparatus. S. Rothenfusser (Z. Unters. Lebensm., 1932, **64**, 114—118).—A stand to hold a no. of separating funnels, a stand to hold a no. of burettes, a lamp for refractometers, and pocket apparatus for detection of heated milk by the Rothenfusser method are described. E. B. H.

Mercury traps. L. Marton (Nature, 1932, **130**, 739).—Glass-electrolysis is used to introduce clean Na into closed glass vessels to form a trap to prevent Hg vapour diffusing back into a vac. from a Hg pump. L. S. T.

Apparatus for automatic registration of dehydration with increasing temperature. S. Skramovský (Chem. Listy, 1932, **26**, 521—522).—The substance is suspended on the arm of a balance, which registers loss of wt. R. T.

Spectrophotometric development for biological and photochemical investigations. F. S. Brackett and E. D. McAlister (Smithsonian Miscell. Coll., 1932, **87**, 1—7).—A method and apparatus for investigating the effect of radiation on biological material, exposed to several wavelengths at the same time, are described, and illustrated for the Hg spectrum in the range 2500—3000 Å., and unicellular algæ. N. M. B.

Graphical method for converting atomic per cent. into weight per cent. A. Ölander (Ind. Eng. Chem. [Anal.], 1932, **4**, 438). E. S. H.

Geochemistry.

Salinity of the Rance at Chatelier determined by means of electric conductivity. P. Chauchard (Compt. rend., 1932, **195**, 621—623; cf. A., 1928, 147).—Using the method previously described, the salinity of the H_2O immediately above the tidal lock at Chatelier has been determined, showing the variations with tide and river flow, and the connexion between salinity and aquatic vegetation. C. A. S.

Natural waters containing radium and mesothorium. V. Chlopin and V. Vernadski (Z. Elektrochem., 1932, **38**, 527—530).—A comprehensive survey has been made of the waters in the neighbourhood of petroleum and mineral deposits in the U.S.S.R. H_2O adjacent to petroleum has a high Ra content (2×10^{-11} to $1{\cdot}8\times10^{-9}\%$), and usually considerable quantities of meso-Th-I and Th-*X* are present. U and Th are present in $<1\%$ of the equilibrium amounts. The minerals examined usually contained $<10\%$ of the quantity of Ra found in the H_2O. H. F. G.

Thermal springs of Sambor. S. S. Miholić (Bull. Soc. Chim. Yougoslav., 1932, **3**, 91—103).—The inorg. constituents of the waters of two springs examined are practically pure Mg and Ca H carbonates, whilst a third spring contains also Na, K, SO_4'', and Cl'. R. T.

Distribution of iodine in Alberta in relation to the prevalence of goitre. I. Iodine in water supplies. O. J. Walker (Canad. J. Res., 1932, **7**, 137—148).—The I content of the surface H_2O in Alberta is usually <1 in 10^9, but in the H_2O from deep wells it ranges from 0 to 663 in 10^9. There is no immediately apparent connexion between the I content of the H_2O supplies and the prevalence of goitre in different parts of the province. H. F. G.

Action of iodine on marine waters. G. Denigès (Compt. rend., 1932, **195**, 669—671).—Superiodised sea-water (5 samples), as also the intervalvular H_2O of superiodised oysters (4 samples), contains 36—145 mg. of I per litre, of which 30—139·5 is in the form of I' and 0·5—9 in that of IO_3', free I (17 mg. per litre) being found only once. Comparison of the interaction of I and H_2O, aq. NaCl, aq. $CaH_2(CO_3)_2$, and sea-water shows the action of the two last to be similar, 75% of the I forming I' and IO_3' in the approx. ratio 5 : 1, and 25% being dissolved as I; this last is absorbed by animal or vegetable matter, alive or dead ($HX+2I=XI+HI$). C. A. S.

Stability of the liquid carbon dioxide in the ocean. W. VERNADSKY (Nature, 1932, **130**, 661—662).—A reply to criticism (this vol., 829). L. S. T.

Geological structure of the potassium salt-beds of Stebnik. C. KUŹNIAR (Bull. Acad. Polonaise, 1932, A, 183—191).—Chemical analyses are given. E. S. H.

Granophyry and porphyry from the Carpathians in the neighbourhood of Sanok. A. GAWET (Bull. Acad. Polonaise, 1932, A, 145—157).—Chemical and mineralogical analyses of these rocks are given. E. S. H.

Tertiary dolomite of the Kerchensk Peninsula. S. V. KONSTANTOV (Min. Suir., 1930, **5**, 1081—1093).—The average composition is: CaO 31·7, MgO 18·14, R_2O_3 0·87, insol. residue 1·72%. CH. ABS.

Ore deposits in south Osetii. F. I. ABRAMOV (Min. Suir., 1930, **5**, 1036—1049).—The ore of the Karsman deposits contains: sphalerite 26·2, pyrite, 23·5, galena 6·5, arsenopyrite 1·5, calcite 17·2%, with small amounts of chalcopyrite and tennantite. Galena from Rasdaran-Kom contains Pb 30·91, Cu 0·06, Zn 0·14, Fe 0·62, Al_2O_3 4·06, TiO_2 trace, CaO 14·02, MgO 0·2, CO_2 12·22, SiO_2 29·42, S 4·21%. Pyrite ore from Moguta contains: pyrite 36·7, galena 7·8, sphalerite 4·4, chalcopyrite 0·5, siderite 17% (29% carbonate). CH. ABS.

Geochemistry of rhenium. E. KRONMANN (Z. physikal. Chem., 1932, **161**, 395—396).—It is probable that Re accumulates in rocks rich in C which also contains S (cf. A., 1931, 707). R. C.

Radium content of some Hungarian rocks. S. S. DE FINÁLY (Amer. J. Sci., 1932, [v], **24**, 306—310).—Samples of granite contained 1·43—3·69 $\times 10^{-12}$, of andesite 1·64—2·38 $\times 10^{-12}$, and of basalts 1·48—1·93 $\times 10^{12}$ g. Ra per g. of rock. C. W. G.

Manganese minerals of a vein near Bald Knob, N. Carolina. C. S. ROSS and P. F. KERR (Amer. Min., 1932, **17**, 1—18).—Alleghanyite, *d* 4·020, orthorhombic, n_α 1·756, n_β 1·780, n_γ 1·792, occurring as pink grains of $5MnO,2SiO_2$ in calcite, contained SiO_2 24·90, Al_2O_3 trace, FeO 1·40, MnO 70·35, MgO 2·16, CaO 0·74, total 99·55%. Galaxite, *d* 4·234, *n* 1·923, MnO,Al_2O_3, black with a reddish-brown streak, contained SiO_2 0·96, TiO_2 trace, Al_2O_3 45·71, FeO 16·36, MnO 34·03, MgO 1·50, CaO and ZnO trace, total 98·56%. Mn-bearing calcite, tephroite, rhodonite, and spessartite are also described. CH. ABS.

Pumpellyite from California. J. IRVING, M. VONSEN, and F. A. GONYER (Amer. Min., 1932, **17**, 338—342).—Green and brown varieties are chemically similar. The formula $Ca_4R_6Si_6O_{23}(OH)_3,2H_2O$, where $R=(Al:Mg+Fe=5:1)$, is derived. CH. ABS.

Gadolinite from Loughborough Township, Frontenac Co., Ontario. H. V. ELLSWORTH (Amer. Min., 1932, **17**, 96—97).—The mineral, $n>1·75$, *d* 4·101, contained SiO_2 25·97, ThO_2 0·14, $(Ce,La,Di)_2O_3$ 2·85, $(Yt,Er)_2O_3$ 46·47, Fe_2O_3 2·34, FeO 5·82, MnO 1·17, BeO 10·29, Al_2O_3 0·32, CaO 2·36, MgO 0·55, Na_2O+K_2O 0·09, H_2O 1·23, P_2O_5 trace, U 0, total 99·60%. CH. ABS.

Ptilolite from Utah. W. T. SCHALLER (Amer. Min., 1932, **17**, 125—127).—The mineral, $10SiO_2,Al_2O_3,(Ca,K_2Na_2)O,7H_2O$, n_α 1·473, n_β 1·475, n_γ 1·478, contained SiO_2 67·35, Al_2O_3 11·49, CaO 3·87, K_2O 0·11, Na_2O 2·63, H_2O- 5·13, H_2O+ 8·82, total 99·40%. CH. ABS.

Mordenite–ptilolite group; clinoptilolite. W. T. SCHALLER (Amer. Min., 1932, **17**, 128—134).—Three species are distinguished: mordenite, $9SiO_2,Al_2O_3,(Ca,K_2,Na_2)O,6H_2O$, monoclinic or triclinic; ptilolite, $10SiO_2,Al_2O_3,(Ca,K_2,Na_2)O,7H_2O$, orthorhombic; clinoptilolite, a dimorphous form of ptilolite, monoclinic tabular. Vals. of *n* are, respectively: α 1·472, 1·474, 1·476; β 1·474, 1·478, 1·479; γ 1·476, 1·480, 1·479. CH. ABS.

Cæsium biotite from Custer County, S. Dakota. F. L. HESS and J. J. FAHEY (Amer. Min., 1932, **17**, 173—176).—The Cs biotite, *d* 3·10, n_α 1·573, n_β 1·620, n_γ 1·620, contained SiO_2 36·97, TiO_2 2·64, Fe_2O_3 2·26, Al_2O_3 17·51, FeO 14·81, MnO 0·22, MgO 8·45, Li_2O 0·65, Na_2O 0·45, K_2O 8·04, Cs_2O 3·14, H_2O- 0·32, H_2O+ 2·48, F 3·17, less O for F 1·34, total 99·77%. CH. ABS.

Montmorillonite or smectite as constituents of fuller's earth and bentonite. P. F. KERR (Amer. Min., 1932, **17**, 192—198).—Montmorillonite and smectite are identical; the former term is preferred. European fuller's earth was formed by the alteration of volcanic ash, like bentonite. CH. ABS.

Composition of cuprotungstite. W. T. SCHALLER (Amer. Min., 1932, **17**, 234—237).—Analysis of material from Cave Creek, Arizona, indicates the formula $WO_3,2CuO,H_2O$. CH. ABS.

Joaquinite. C. PALACHE and W. F. FOSHAG (Amer. Min., 1932, **17**, 308—312).—Joaquinite is orthorhombic, $a:b:c=0·919:1:2·14$; *a* 9·61, *b* 10·45, *c* 22·4 Å.; *d* 3·89; n_α 1·748, n_β 1·767, n_γ 1·823; it contains SiO_2 35·27, TiO_2 29·53, FeO 3·41, BaO 23·91, CaO 0·27, MgO 0·07, ignition 0·47, Na_2O 4·47, total 97·40%, corresponding with $NaBa(Ti,Fe)_3Si_4O_{15}$. The unit cell contains 4 mols. CH. ABS.

Sanbornite from Mariposa County, California. A. F. ROGERS (Amer. Min., 1932, **17**, 161—172).—Sanbornite, triclinic $BaSi_2O_5$, has n_α 1·597, n_β 1·616, n_γ 1·624. CH. ABS.

Minerals from the rhodolite quarry near Franklin, North Carolina. E. P. HENDERSON (Amer. Min., 1931, **16**, 563—568).—Gedrite, *d* 3·178, n_α 1·642, n_β 1·655, n_γ 1·661, contains SiO_2 44·22, Al_2O_3 23·79, FeO 9·21, CaO 0·62, MgO 20·69, MnO 0·16, H_2O 1·42, Fe_2O_3 0·20, total 100·31%. Hypersthene, n_α 1·685, n_β 1·696, n_γ 1·699, contains SiO_2 52·36, Al_2O_3 4·29, FeO 16·90, CaO 0·44, MgO 25·89, H_2O 0·34, total 100·22%. Rhodolite has *n* 1·758; biotite, FeO 5·78, Fe_2O_3 0·72%, has n_α 1·565, $n_\beta=n_\gamma=1·607$. CH. ABS.

Triclinic manganiferous pyroxenes. N. SUNDIUS (Amer. Min., 1931, **16**, 411—429, 488—518).—A discussion of the composition and stability relationships of rhodonite, bustamite, fowlerite, Fe rhodonite, sobralite, and pyroxmangite. CH. ABS.

Negative crystal cavities of certain galenas and their brine content. M. J. BUERGER (Amer. Min., 1932, 17, 228—233). CH. ABS.

Uraninite from Huron Claim, Winnipeg River area, Manitoba. J. S. DELURY and H. V. ELLSWORTH (Amer. Min., 1931, 16, 569—575).—The uraninite (small cubic crystals in pink albite) is rich in Pb and Th; the high Pb ratio (0·260—0·265) indicates that it is the oldest uraninite known. CH. ABS.

Uraninite from Henry Township, Parry Sound district, Ontario. H. V. ELLSWORTH (Amer. Min., 1931, 16, 576—579).—The uraninite (*d* 8·173, Pb ratio 0·117) is associated with thucolite in pink perthitic microcline, and is in the second stage of alteration. CH. ABS.

***X*-Ray study of psilomelane and wad.** L. S. RAMSDELL (Amer. Min., 1932, 17, 143—149).—Of the four types of pattern observed, one is arbitrarily selected as that of " true " psilomelane (I). (I) containing Ba and lithiophorite are distinct species. " (I) " may be either of the above, pyrolusite, braunite, or wad; " wad " may be pyrolusite or (I). CH. ABS.

Perthites. H. L. ALLING (Amer. Min., 1932, 17, 43—65).—Processes capable of forming perthitic felspars are discussed. CH. ABS.

Determination of manganese in a rock from Miranda do Corvo. A. J. DE A. GOUVEIA (Rev. Chim. pura Appl., 1932, 5, 44—45; Chem. Zentr., 1932, ii, 412).

Deuteric and later alterations of the uncompahgrite of Iron Hill, Colorado. E. S. LARSEN and E. A. GORANSON (Amer. Min., 1932, 17, 343—356).—The processes are discussed. Juanite, $10CaO,4MgO,Al_2O_3,11SiO_2,4H_2O$, has n_α 1·640, n_γ 1·647; cebollite is orthorhombic, n_α 1·592, n_β 1·597, n_γ 1·630. CH. ABS.

Solubility of cassiterite in distilled water. S. J. THUGUTT (Arch. Min. Soc. Sci. Varsovie, 1932, 8, 122—133).—A sample of Bolivian cassiterite, containing SnO_2 93·36, TiO_2 0·49, Nb_2O_5 2·82, Ta_2O_5 3·71, and H_2O 0·39%, was heated with H_2O at 211—215°. The solution contained 0·00026% of dissolved substances, in colloidal solution. R. T.

Composition of pegmatic felspars as a criterion of their hydrogenetic origin. E. ZANIEWSKA-CHLIPALSKA (Arch. Min. Soc. Sci. Varsovie, 1931, 7, 49—81).—Klesów microcline has the composition: SiO_2 64·55, Al_2O_3 18·90, Fe_2O_3 0·33, BaO 0·20, CaO 0·32, K_2O 13·13, Na_2O 2·7, H_2O 0·38%. Felspars of igneous origin have the ratio $Al_2O_3 : SiO_2 = 1 : 6$; for those of pegmatitic origin it is $1 : < 6$. This indicates the hydrogenetic origin of such felspars, which would have been deposited from colloidal solutions of igneous felspar. R. T.

Composition of predazzite. M. KOŁACZKOWSKA (Arch. Min. Soc. Sci. Varsovie, 1932, 8, 149—165).—Predazzite is a mixture of calcite and brucite. R. T.

Epinatrolite, a component of hydronephelinite. S. J. THUGUTT (Arch. Min. Soc. Sci. Varsovie, 1932, 8, 141—144).—Hydronephelinite is a mixture of epinatrolite and hydrargyllite. R. T.

Microcline of Maczulanka (Volhynia) grey granite. E. S. LITMANOWICZÓWNA (Arch. Min. Soc. Sci. Varsovie, 1931, 7, 82—130).—Maczulanka granite consists of quartz, biotite, acid oligoclase, and microcline, the crystallographic data for which are given. R. T.

Silver–tin deposits of Oruro, Bolivia. B. KOZŁOWSKI and S. JASKÓLSKI (Arch. Min. Soc. Sci. Varsovie, 1932, 8, 1—121).—A detailed list of the minerals found in these deposits is given, together with crystallographic and analytical data. The minerals of the veins are partly of hydrothermal origin. R. T.

Phillipsite from the Pacific Ocean. S. J. THUGUTT (Arch. Min. Soc. Sci. Varsovie, 1932, 8, 134—140).—Phillipsite is formed by hydrolysis of nepheline, with loss of 4 mols. of $Na_2Al_2O_4$. Its composition is $8Na_2Al_2Si_3O_{10},3K_2Al_2Si_3O_{10},55H_2O$. The higher K content found by Murray and Renard (H.M.S. " Challenger " Rept., 1891) was due to their use of Thoulet's reagent for isolation of phillipsite. R. T.

Rocks of the gabbroid massif of the Bükk Mts., Hungary. S. VON SZENTPÉTERY (Chem. Erde, 1932, 7, 351—382).—Forty-one analyses of plutonic rocks ranging from peridotite to andesinite are tabulated and the mol. ratios plotted on diagrams for the purpose of showing the relation between the different types. L. J. S.

New type of Fe Al phosphate deposit in Brazil. F. BRANDT (Chem. Erde, 1932, 7, 383—425).—Phosphatised laterite overlying diabase contains small white to brown spherulites and " octahedra " (perhaps pseudomorphs after pyrite) which contain P_2O_5 25·7—36·4, SiO_2 0·2—1·7, TiO_2 0·8—2·0, Al_2O_3 24·5—33·4, Fe_2O_3 3·8—26·5, Na_2O 2·0—4·7, H_2O 16·9—19·1%; *d* 2·781—2·798 *n* 1·602—1·618. A formula $6Al_2O_3,4P_2O_5,17H_2O$ (differing from wavellite in containing less H_2O) is deduced and the mineral is named harbortite. At greater depths in the laterite there are tubular concretions of Al Fe phosphate, some of which is dufrenite. Analyses of materials from borings indicate that the phosphate was derived from the diabase. L. J. S.

Weathering of andesite from Java. E. BLANCK and E. VON OLDERSHAUSEN (Chem. Erde, 1932, 7, 426—433).—Analyses are given of the fresh rock, of material from different weathered zones, and of the resulting soil. L. J. S.

Cryoconite from the East Greenland pack-ice. E. BLANCK, H. POSER, and E. VON OLDERSHAUSEN (Chem. Erde, 1932, 7, 434—440).—Analyses of a fine grey dust collected from the surface and from pockets in the pack-ice gave SiO_2 61·12—64·24, Al_2O_3 15·19—15·70, Fe_2O_3 6·49—7·38, ignition loss 5·86—9·43, etc. L. J. S.

Synthesis of polianite, braunite, and hausmannite. F. KRÜLL (Chem. Erde, 1932, 7, 473—482).—Minutely (0·1 mm.) crystalline MnO_2 is best prepared by the slow decomp. of $Mn(NO_3)_2$ at 154°/20 mm.; Mn_2O_3 by heating cryst. MnO_2 in O_2 at 550°;

and Mn_3O_4 by heating pptd. MnO_2 in H_2 at 200°. The MnO_2 (*d* 4·94) and Mn_3O_4 (*d* 4·89) so obtained show the same microscopical characters and *X*-ray patterns as polianite and hausmannite, respectively, but artificial Mn_2O_3 (*d* 4·77) shows some differences from braunite. L. J. S.

New hexahedrite from Cerros del Buen Huerto, Chile. F. Heide, E. Herschkowitz, and E. Preuss (Chem. Erde, 1932, 7, 483—502).—A polished section of this meteorite, *d* 7·822, shows one very prominent set of Neumann lines, nodules and plates of troilite with some enclosed daubreelite, and plates and needles of schreibersite arranged parallel to (100), (210), and (211), along which directions the mass can be broken. The following *X*-ray determinations were made: kamacite, body-centred cubic, *a* 2·859 Å.; troilite, hexagonal, *a* 3·439, *c* 5·855 Å.; schreibersite (rhabdite), body-centred tetragonal, *a* 9·013, *c* 4·424 Å., with 8 mols. $(Fe,Ni,Co)_3P$, *d*(calc.) 7·44; daubreelite, cubic with spinel structure, *a* 9·966, *d* 3·81 (calc. 3·87). Analysis of the kamacite with enclosed rhabdite needles gave Fe 93·75, Ni 5·43, Co 0·58, S 0·08, P 0·19=100·03. Spectroscopic analysis showed also Cr, V, Mo, Mn, Pt, Cu, Ag, Au, Zn ?, Ga, Si, Ge, Sn, Pb. L. J. S.

Radioactivity and current geological problems. V. Vernadski (Z. Elektrochem., 1932, 38, 519—527).—A crit. review of the present state of knowledge of the geochemistry of Pb and of the distribution of radioactive elements in the earth's crust, and of the determination of geological time by the methods of radioactivity. H. F. G.

Minerals and Wood's light. A. Estrafallaces (L'Ind. Chimica, 1932, 7, 1360—1366).—213 minerals were subjected to Wood's light and those showing fluorescence were examined spectroscopically. This fluorescence is not produced by monochromatic light and does not show a characteristic spectrum line or zone capable of identifying the mineral under examination. Two specimens of fluorite from the same locality gave different emissions. The observed emissions extend between 4000 Å. up to the vals. given, except for two specimens of topaz in which the emission varied between 4750 and 5600 Å. and 4600 and 6050 Å., respectively. O. F. L.

Metallic meteorite from Ogallala, Nebraska. H. H. Nininger (Amer. Min., 1932, 17, 221—225).—The meteorite (3300 g.) contains Fe 90·10, Ni 7·93%, with small amounts of Co, Cu, Cr, P, S, C, Si, and O. Ch. Abs.

Petrological and mineralogical study of the under-clays of Illinois coal. V. T. Allen (J. Amer. Ceram. Soc., 1932, 15, 564—573).—The clays consist chiefly of potash beidellite purified before deposition in H_2O together with felspars, muscovite, quartz, etc. in the warm Pennsylvanian period. Later leaching by soil-forming processes has removed the carbonates. J. A. S.

Metamorphosis of coals and the problem of artificial coalification. W. Gropp and H. Bode (Braunkohle, 1932, 31, 277—284, 299—302, 309—313; Chem. Zentr., 1932, ii, 150).—Cellulose, wood, humic acid, peat, and lignite were heated at 300° at. pressures up to 2000 atm.; in all cases the volatile constituents diminished and the fixed C increased. The H_2O content diminished towards vals. for bituminous coal. At 300° transformation into typical lignites, but not into bituminous coals, could be effected. The duration of the process is of secondary importance. A. A. E.

Genesis of coals. V. E. Berl and A. Schmidt.—See B., 1932, 917.

Formation of bituminous coal, mineral oil, and asphalt. E. Berl.—See B., 1932, 918.

Mechanical and chemical composition of loess and genetically related rocks. S. S. Morozov (Pedology, 1932, 27, 232—259).—A series of loesses from various parts of European Russia showed a complete absence of particles > 1 mm. in diameter, and a fair constancy in the amounts of the various other fractions present. The chemical composition of the individual fractions showed great similarity and suggests a single place of origin for all samples. This is probably the N.W. part of the U.S.S.R., the source of the Würm glacier. A. M.

Soil types from different climatic areas of S. Africa. F. Behrend and K. Utescher (Z. Pflanz. Düng., 1932, 26A, 175—203).—Analytical data for a red loam and a black earth soil derived from the same parent rock are recorded. Differences between the two soils are attributable entirely to climatic conditions. A. G. P.

Rôle of forest (oak) in soil formation. N. N. Stepanov (Pedology, 1932, 27, 163—177).—The invasion of chernozem steppe by oak forest results in a degradation of the soil; $Ca^{\cdot\cdot}$ and $Mg^{\cdot\cdot}$ are leached to lower horizons, $H^{\cdot}$ taking their place, and there is an increase in soluble electrolytes in the *A* horizon. These changes are due to the litter of oak forest and its decomp. products. A. M.

Colours and signs for soil maps. L. I. Prasolov (Pedology, 1932, 27, 149—162).—Colours and symbols used for the soil maps of Russia are reproduced and their merits discussed. A. M.

Contradictory processes as a basis for genetic soil classification. N. P. Remezov (Pedology, 1932, 27, 178—211).—A philosophical discussion of soil classification giving a new scheme based on the differences in humus formation in different climates. A. M.

Rôle of organic matter in the classification of forest soils. M. F. Morgan and H. A. Lunt (J. Amer. Soc. Agron., 1932, 24, 655—662).—The nature and distribution of org. matter in various soil types are examined. A. G. P.

Saline soils. L. Pozdena (Chem. Erde, 1932, 7, 441—472).—The alkaline (soda) soils of the western Hungarian plain are discussed in detail with many mechanical and chemical analyses. L. J. S.

Important soil profiles of southern Puerto Rico. J. Thorp (Soil Sci., 1932, 34, 241—257).—Soils described are chernozem and chocolate-coloured clay pans with "alkali spots" in marshy coastal areas. Analyses, profile characteristics, and natural flora are recorded and discussed. A. G. P.

Organic Chemistry.

Natural classification of chemical compounds. II. F. M. Schemjakin (J. Gen. Chem. Russ., 1932, **2**, 128—134; cf. A., 1931, 1357).—The "structural no." of a given mol. is a numerical expression giving the combination of atoms and at. groups which constitute the mol. By arranging isomeric compounds in accordance with their structural nos., the "normal geometrical series" is obtained which is the same for all classes of org. compounds, and is of the type $[R_2'R_n'']$, $[R_3'R_nR''']$, $[R_4'P_n''R''']$, etc., the index of R showing the valency. Each member of the normal series can be the parent of a new series differently oriented, and is thus termed the top member. By plotting the physical consts. of the geometrical series of the top members for certain classes of org. compounds it is seen that complete analogies exist between the curves for different consts. and between the curves for the same const. of different classes of compounds arranged in normal geometrical series according to their structural nos. The conception is further developed and illustrated by three-dimensional space diagrams. Formulæ can be developed to express the abs. b.p., *d*, and *n* in terms of the b.p. and at. nos. of neon, and the mol. nos. and symmetry of the mol. M. Z.

Natural classification of catalytic organic reactions. A. A. Balandin (J. Gen. Chem. Russ., 1932, **2**, 166—182; cf. A., 1929, 1245).—Consideration is devoted to org. compounds containing C, H, and O, and possessing only single and double linkings, and in which there is no change of valency, the reactions being limited to those with doublet indices, *i.e.*, in which two linkings only are broken and remade. All possible types of compounds are examined and grouped in nine classes. M. Z.

Synthesis, purification, and physical constants of the normal hydrocarbons from pentane to dodecane, of *n*-amyl bromide, and of *n*-nonyl bromide. B. J. Mair (Bur. Stand. J. Res., 1932, **9**, 457—472; cf. A., 1931, 792).—The b.p., f.p., and n_D^{25} for the *n*-paraffins C_5 to C_{12} and for *n*-amyl and *n*-nonyl bromide (preps. described) are accurately determined. *n*-Nonyl bromide is isolated in two forms, m.p. —29·06° and —30·71°. J. L. D.

Slow combustion of β-methyltricosane. S. Landa and J. Pokorný (Coll. Czech. Chem. Comm., 1932, **4**, 456—462, and Chem. Listy, 1932, **26**, 512—515).—Slow combustion of β-methyltricosane (I) yields the following identified products: CH_2O, MeCHO, EtCHO, MeOH, and $COMe_2$; the $COMe_2$ originates from the $\cdot CHMe_2$ group of (I). The production of $COMe_2$ from natural paraffin (cf. A., 1930, 190) indicates the presence of branched-chain hydrocarbons. β-Methyltricosan-β-ol (*phenylurethane*, m.p. 86°) has m.p. 63° (cf. A., 1930, 1268). H. B.

Addition of hydroxyl groups to ethylallene. M. Bouis (Bull. Soc. chim., 1932, [iv], **51**, 1177—1178).—$\Delta^{\alpha\beta}$-Pentadiene shaken with aq. 10% $AgClO_3$ containing 0·15% of osmic acid gives a small amount of unstable material, b.p. 92—95°/11 mm., and (mainly) acetylethylcarbinol, which is formed thus: $CH_2{:}C{:}CHEt + 2OH = CH_2{:}C(OH){\cdot}CHEt{\cdot}OH \longrightarrow CHAcEt{\cdot}OH$. H. B.

Catalytic hydrogenation of unsaturated compounds. VI. *iso*Propyl- and phenyl-acetylene. S. V. Lebedev and V. J. Schtern (J. Gen. Chem. Russ., 1932, **2**, 249—259).—Addition of H_2 to the ethylenic products of hydrogenation of C_2H_2 derivatives takes place simultaneously with their formation, the proportion of H_2 combining at a given moment with each component of the mixture depending on the relative concn. of $CR{\vdots}CH$ to $CHR{:}CH_2$ ($R=Pr^{\beta}$ or Ph) and on the nature of R. R. T.

Acetylene polymerides and their derivatives. III. Addition of hydrogen chloride to vinylacetylene. W. H. Carothers, G. J. Berchet, and A. M. Collins (J. Amer. Chem. Soc., 1932, **54**, 4066—4070).—The initial product in the (1 : 4-) addition of HCl to $CH{\vdots}C{\cdot}CH{:}CH_2$ (I) is *δ-chloro-$\Delta^{\alpha\beta}$-butadiene* (II), b.p. 87·7—88·1°, which readily undergoes isomerisation to chloroprene ($CH_2{:}CCl{\cdot}CH{:}CH_2$) (III), which always constitutes a part of the reaction product. The Cl atom of (II) is very reactive; (II) does not react with maleic anhydride or with naphthaquinone, does not give a $Cu^{\cdot}$ derivative, with O_3 it yields CH_2O and (after oxidation with $KMnO_4$) $CH_2Cl{\cdot}CO_2H$, with $KMnO_4$ gives $CH_2Cl{\cdot}CO_2H$, and with cold conc. H_2SO_4 affords δ-chlorobutan-β-one, b.p. 120—122°/760 mm. The formation of (II) is accelerated by certain salts. (III), which is the main product when the reaction is carried out in presence of CuCl, reacts further with HCl to give *βδ-dichloro-Δ^{β}-butene* (IV), b.p. 53—54°/50 mm., 127—129°/756 mm. (II) is transformed into (III) by powdered KOH, by quinoline at 140—150°, by heat (290°) in presence of silica gel, and by hot dil. HCl; the best conditions are heating with CuCl in 18% HCl [(IV) is recovered unchanged under these conditions]. (IV) undergoes no change when heated at 50°/6000 atm. for 45 hr. (II) shows no tendency to polymerise. C. J. W. (*b*)

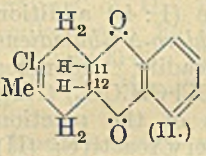
3-Nitrophthalimide as reagent for the identification of organic halogen compounds. P. P. T. Sah and T. S. Ma (Ber., 1932, **65**, [*B*], 1630—1633).—The alkyl halide is gradually heated under reflux to 120—200° with *K 3-nitrophthalimide* (improved prep. of 3-nitrophthalic acid given). Reaction is discontinued when the mixture has become homogeneous and the cold product is boiled with H_2O to extract K halide and hydrolyse unchanged 3-nitrophthalimide. The following *N*-substituted 3-nitrophthalimides are described: *Me*, m.p. 112—113°; *Et*, m.p. 105—106°; *Pr^{α}*, m.p. 84—85°; *Bu^{α}*, m.p. 71—72°; iso*amyl*, m.p. 93—94°; *allyl* m.p. 100—101°; β-*bromoethyl*, m.p. 115—116°; *CH_2Ph*, m.p. 142—143°; p-*nitrobenzyl*, m.p. 181—182°; *acetonyl*, m.p. 152—153°; *carbethoxymethyl*, m.p. 79—80°. H. W.

Oxidation of solutions of iodoform. R. Dubrisay and G. Emschwiller.—See this vol., 1215.

Photolysis of chloropicrin in aqueous solution. E. V. Alexeevski.—See this vol., 1215.

Synthesis of ethylene bromide from acetylene and hydrogen bromide. F. De Carli (Annali Chim. Appl., 1932, **22**, 455—462).—Combination of C_2H_2 and HBr over $FeBr_3$ or $CuBr_2$ at 160—170° gives ethylene and ethylidene bromides (cf. A., 1931, 598), and a product shown by *d*, viscosity, m.p., and Br content to be a complex partly brominated mixture, from which $CH_2Br\cdot CH_2Br$ is not easily isolated. E. W. W.

New synthetic rubbers. II. Homologues of chloroprene and their polymerides. W. H. Carothers and D. D. Coffman (J. Amer. Chem. Soc., 1932, **54**, 4071—4076).—$CH_2{:}CMe\cdot C{:}CH$, b.p. 34°, shaken with conc. HCl, CuCl, and NH_4Cl, gives 40% of β-*chloro-γ-methyl*-$\Delta^{\alpha\gamma}$-*butadiene* (I), b.p. 37°/105 mm., 93°/760 mm. with polymerisation, which with α-naphthaquinone affords 2-*chloro*-3-*methyl*-1 : 4 : 11 : 12-*tetrahydroanthraquinone* (II), m.p. 165—166°, oxidised by air in dil. EtOH–NaOH to 2-chloro-3-methylanthraquinone, m.p. 214—215°. (I) polymerises very rapidly to a rubber-like polymeride, which after vulcanisation is less extensible than the corresponding product from chloroprene (B., 1932, 156). $CHMe{:}CMe\cdot C{:}CH$ similarly gives 22% of β-*chloro-γδ-dimethyl*-$\Delta^{\alpha\gamma}$-*butadiene*, b.p. 57—60°/96 mm., converted (as above) into 2-*chloro*-3 : 4-*dimethyl*-1 : 4 : 11 : 12-*tetrahydroanthraquinone*, m.p. 107°, and thence into 2-*chloro*-3 : 4-*dimethylanthraquinone*, m.p. 171·5°. This Cl-derivative polymerises very slowly; the product, even after vulcanisation, is soft and lacking in "nerve." 1-Ethinyl-Δ^1-*cyclo*hexene gives 32% of β-*chloro-γδ-tetramethylene*-$\Delta^{\alpha\gamma}$-*butadiene* [1-α-*chlorovinyl*-Δ^1-cyclo*hexene*], b.p. 55—57°/1 mm., convertible into 2-*chloro*-3 : 4-*tetramethylene*-1 : 4 : 11 : 12-*tetrahydroanthraquinone*, m.p. 191—192°, and thence into 2-*chloro*-3 : 4-*tetramethyleneanthraquinone*, m.p. 191—192°. This Cl-derivative also polymerises very slowly; the product is very soft, plastic, and sticky. Since butadiene, isoprene, and βγ-dimethylbutadiene do not differ greatly in the rate of their spontaneous polymerisation, this indicates that Me is not an activating group. The fact that chloroprene polymerises about 700 times as fast as isoprene illustrates the powerful activating effect of Cl in the β-position. The introduction of Me at C_γ does not greatly modify this effect, although the polymeride is somewhat less extensible; the introduction of a second Me at one of the terminal C atoms almost completely checks the activating effect of the Cl atom. C. J. W. (*b*)



(II.)

Safe preparation of dichloroacetylene as lecture experiment. L. Metz (J. pr. Chem., 1932, [ii], **135**, 142—144).—C_2Cl_2 is prepared without risk of explosion by interaction of dry KOH with $C_2H_2Cl_4$ in xylene in N_2 at 95—100°. An apparatus in which the spontaneous inflammation of C_2Cl_2 in air is demonstrated is described. H. A. P.

Oxidising properties of the halogenated dinitromethanes. A. E. Kretov and N. N. Melnikov (J. Gen. Chem. Russ., 1932, **2**, 202—207).—Bromopicrin reacts with thiophenol or thiocresol to give the corresponding disulphides with evolution of oxides of N considerably more than in the case of chloropicrin. With KI, a complicated reaction takes place, CI_4, much free I, CO_2, CO, N oxides, and N_2 being evolved. With alkali sulphides the reaction is also complicated, a mixture of COS, CS_2, S, and alkali nitrite and halide being obtained, whilst CO, CO_2, N_2, and N oxides are evolved. With NaHS the reaction is still more complicated, since in addition to the products enumerated above, NH_3 and salts of HNO_3 are obtained. Mechanisms for the above various reaction schemes are suggested, and it is concluded that the halogenated dinitromethanes react as oxidising agents, attacking C atoms in the first instance. M. Z.

Reaction between *p*-nitrophenylcarbimide and some higher alcohols. W. J. Hoppenbrouwers (Rec. trav. chim., 1932, **51**, 951—954).—The following are thus prepared: *nonyl*, m.p. 104°, *undecyl*, m.p. 99·5°, n-*cetyl*, m.p. 117—118°, and *cholesteryl*, m.p. 204—205°, p-*nitrophenylurethane*. Myricyl alcohol and phytosterol react only with great difficulty and no derivative could be obtained from pentaerythritol. J. W. B.

Preparation of acetone-chloroform [ααα-trichloro*tert*.-butyl alcohol]. P. P. T. Sah, M. Lei, and S. Ma (Sci. Rep. Nat. Tsing Hua Univ., 1932, **1**, 209—214).—The prep. is modified. R. S. C.

Dehydration of *tert*.-carbinols containing a neopentyl system. I. Methylethyl*tert*.-butylcarbinol and dimethyl*tert*.-amylcarbinol. F. C. Whitmore and K. C. Laughlin (J. Amer. Chem. Soc., 1932, **54**, 4011—4014).—$CMeEtBu^\gamma\cdot OH$, b.p. 76°/40 mm., obtained in 60% yield from MgEtBr and $COMeBu^\gamma$, refluxed with a trace of I, gives a mixture of 80% of $CMe_3\cdot CMe{:}CHMe$, b.p. 109°/740 mm., and 20% of $CH_2{:}CMe\cdot CMe_2Et$ (I), b.p. 106—106·7°/742 mm.; none of the olefine postulated by Clarke and Jones (A., 1912, i, 150) is found. Dehydration of dimethyl*tert*.-amylcarbinol gives mainly (I). C. J. W. (*b*)

Ether-esters of glycerol or ether-glycerides of shark-liver oil, *Scymnorhinus lichia*, Bonnaterre. E. André and A. Bloch.—See this vol., 1275.

New catalysts for hydrolysis. Hydrolysis of diethyl ether. A. A. Balandin, N. I. Schujkin, M. P. Nesvishski, and T. K. Kosminskaja (Ber., 1932, **65**, [*B*], 1557—1561).—At 275—300°/100 atm., hydrolysis of Et_2O does not occur in presence of Al_2O_3, Fe_2O_3, or active C. With Al_2O_3 95%–NiO 5% (I) or Al_2O_3 90%–ZnO 10% extensive hydrolysis is observed; Al_2O_3 50%–Fe_2O_3 50% (II) and Al_2O_3 63%–Fe_2O_3 37% are also serviceable. With (I) and (II) decomp. of Et_2O with production of (?) C_2H_4 is observed, whereas gas is not formed with the other catalysts. H. W.

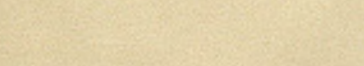
Ether-like compounds. VII. Preparation of the simpler, mixed formals. M. H. Palomaa and K. K. Kantola (Ber., 1932, **65**, [*B*], 1593—1598; cf. this vol., 833).—The requisite chloromethyl alkyl ether is added slowly and with agitation to an ice-cold mixture of the requisite alcohol and C_5H_5N and the mixture is boiled until the upper layer no longer increases. This layer is washed, dried over K_2CO_3, purified by Na, and fractionally distilled (apparatus described). The following compounds are described: *Me ethers*; ethoxymethyl (methylethylformal), b.p. 65·06—65·18°/744·6 mm.; n-*propoxymethyl*, b.p. 92·7°/761·3 mm.; n-*butoxymethyl*, b.p. 119·5°/760·9 mm.; n-*amyloxymethyl*, b.p. 144·5°/757·4 mm.; n-*hexyloxymethyl*, b.p. 167·7°/757·4 mm.; *Et ethers*; n-*propoxymethyl*, b.p. 113·4°/762·6 mm.; n-*butoxymethyl*, b.p. 137·6°/744·9 mm.; n-*amyloxymethyl*, b.p. 161·9°/757·4 mm.; n-*hexyloxymethyl*, b.p. 184·0°/760 mm.; Pr^{α} n-*butyloxymethyl ether*, b.p. 160·2°/755 mm. H. W.

Esters of monofluorophosphoric acid. W. Lange and G. von Krueger (Ber., 1932, **65**, [*B*], 1598—1601; cf. A., 1929, 662).—Me_2 *monofluorophosphate* (I), b.p. 150·1°/759 mm., is prepared from MeI and Ag_2PO_3F at 50°. Et_2PO_3F has b.p. 171·5—172°/757 mm. At 200°, the esters are unimol. (I) is readily hydrolysed by aq. alkali, whereas (II) is only slowly affected by KOH–EtOH, whereby it is ultimately transformed into dialkyl phosphate. The esters have very marked physiological action. H. W.

ββ-Dichloro- and ββ-dibromo-divinyl sulphoxides. A. E. Kretov and S. M. Klieger (J. Gen. Chem. Russ., 1932, **2**, 322—326).—Divinyl sulphoxide, prepared by the action of $NaHCO_3$ on ββ′-dichlorodiethyl sulphoxide, is chlorinated in EtOH to αα′ββ′-tetrachlorodiethyl sulphoxide, m.p. 122·5° (80—85% yield), converted into ββ′-dichlorodivinyl sulphoxide (A., 1926, 1224), b.p. 86—87°/10 mm., m.p. 15°. *αα′ββ′-Tetrabromodiethyl sulphoxide*, m.p. 120·8°, is similarly obtained (35—50% yield), and is converted by $NaHCO_3$ into *ββ′-dibromodivinyl sulphoxide*, m.p. 40·5—42° (75% yield). Neither this nor the Cl_2-compound could be reduced. G. A. R. K.

Dithiomethionic acid. H. J. Backer (Rec. trav. chim., 1932, **51**, 981—987).—Oxidation of K or Ba thiolmethanedisulphonate with I in neutral aq. solution affords *di(thiomethanedisulphonic) acid*, $[(SO_3H)_2CH\cdot S\cdot]_2+6H_2O$ (I) (*K_4* $+2H_2O$, *Tl_4*, *Ba*, and *strychnine* $+6H_2O$ salts). The *Pb*, *Ag*, *Cu*, and *Hg* salts are unstable, decomp. of the Pb salt occurring thus: $2\{Pb(O_3S)_2CH\cdot S\cdot\}_2 \longrightarrow Pb\{Pb(O_3S)_2CH\cdot S\cdot\}_2 + Pb\{SC(SO_3H)\cdot SO_3\cdot\}_2$, the second product not being isolated. Oxidation of (I) with Cl_2 in neutral aq. solution gives $CH(SO_3H)_3$, whilst H_2S is obtained by reduction with Zn. (I) is decomposed in presence of excess of alkali: $(I)+H_2O \longrightarrow HS\cdot CH(SO_2H)_2$ (II)+ $HO\cdot S\cdot CH(SO_3H)_2$ (III), (II) being isolated as its Tl salt, whilst (III) accounts for the yellow colour formed in the presence of alkalis, but is further decomposed thus: $(III)+KOH \longrightarrow K_2SO_3+OH\cdot SO\cdot SO_3K+H_2O$. J. W. B.

Reaction of potassium disulphomethanemonothiosulphate with mercuric oxide. H. J. Backer (Rec. trav. chim., 1932, **51**, 988—990).—That the acid previously designated thiolmethanetrisulphonic acid is actually *disulphomethanemonothiosulphuric acid* (A., 1931, 600) is confirmed, since dissolution of HgO in an aq. solution of its K salt gives the *K Hg* salt of thiolmethanedisulphonic acid (cf. this vol., 1018): $(SO_3K)_2CH\cdot S_2O_3K+HgO \longrightarrow$



$$SO_3K\cdot CH{<}\genfrac{}{}{0pt}{}{S-}{SO_3}{>}Hg+K_2SO_4.$$

J. W. B.

Relation between Kolbe's reaction and hydrogen-ion concentration. VII. H. R. Matsuda.—See this vol., 1214.

Electrolysis of fused acetates and propionates. G. B. Moorhouse.—See this vol., 1213.

Maximum rotations and correlation of disubstituted acetic acids containing a methyl group. P. A. Levene and R. E. Marker (J. Biol. Chem., 1932, **98**, 1—7).—Contrary to those in the series previously investigated (this vol., 365), the max. vals. of $[M]_D$ (given in parentheses) for the acids of the homologous series $CHMeR\cdot CO_2H$ increase progressively towards the left as the size of R is increased. *l*-α-Methyl-*n*-butyric (−18°); -n-*valeric*, b.p. 96°/15 mm., $[\alpha]_D^{25}$ −18·4° (−21·4°), -n-*hexoic*, b.p. 105°/5 mm., $[\alpha]_D^{25}$ −18·7° (−24·3°), -n-*nonoic*, b.p. 115°/1 mm., $[\alpha]_D^{21}$ −15·9° (−27·3°), and d-*methyl*-n-*dodecoic*, b.p. 150°/1 mm., $[\alpha]_D^{25}$ +12·85° (+27·5°), *acid*, are obtained by resolution of the *dl*-forms. Correlation of the configurations of β-methyl-*n*-hexoic and α-methyl-*n*-valeric acids is afforded by their conversion into the same *d*-α-amino-β-methyl-*n*-pentane, $[\alpha]_D^{25}$ +4·09° (A., 1930, 63). J. W. B.

α- and β-Forms of the higher polybromo-fatty acids (octa- and deca-bromides of behenic acid). H. Rudy (Z. physiol. Chem., 1932, **210**, 236—245).—The α- and β-octabromides of the unsaturated acids of brain kephalin are shown to consist of mixtures of isomerides of different solubility and m.p. by re-brominating the Br-free acids derived from each group. In each case mixtures of α- and β-octabromides were obtained differing in the percentage of each group present according to the method of bromination. In between the α (insol.) and β (sol.) groups there are bromides of intermediate solubility, the whole forming a graded series. J. H. B.

Polymerisation and ring formation. XVII. Friedel–Crafts syntheses with the polyanhydrides of dibasic acids. J. W. Hill (J. Amer. Chem. Soc., 1932, **54**, 4105—4106).—The polyanhydride (A., 1930, 1558) from adipic acid with C_6H_6 and $AlCl_3$ gives δ-benzoylvaleric acid, m.p. 70—71°, and αδ-dibenzoylbutane, m.p. 105—106°, according to the equation $[\cdot OC(CH_2)_nCO\cdot O]_x+C_6H_6=\frac{x}{4}(CH_2)_nBz_2+\frac{x}{2}Bz(CH_2)_nCO_2H+\frac{x}{4}(CH_2)_n(CO_2H)_2$. Similarly, sebacic polyanhydride gives θ-benzoylnonoic acid, m.p. 77—78°, and αθ-dibenzoyloctane, m.p. 92—93°. This furnishes a convenient method of prep. of ω-benzoylated fatty acids. C. J. W. (*b*)

Identification test for oxalic acid. E. R. Caley (Ind. Eng. Chem. [Anal.], 1932, **4**, 445).—Only $H_2C_2O_4$ and dihydroxytartaric acid give a ppt. when 1 c.c. of 6*N*-NaOH is added with vigorous shaking to 0·1 g. of the solid in 2 c.c. of cold H_2O. E. S. H.

Reaction between ethyl oxalate and phosphorus pentabromide. V. V. Tschelincev and V. I. Esafov (J. Gen. Chem. Russ., 1932, **2**, 217—224).—$Et_2C_2O_4$ and PBr_5 react incompletely at atm. pressure, but on heating in an autoclave at 100° for 8—10 hr. some 72% reacts, forming *ethoxalyl bromide*, b.p. 150—152°, PBr_3, and EtBr; PCl_2Br_2

cannot be used in place of PBr_5. $CBr_3{\cdot}CO_2H$, HBr, and PBr are produced in side-reactions.

G. A. R. K.

Reduction of unsaturated organic acids at the dropping mercury cathode. L. Schwaer (Chem. Listy, 1932, 26, 485—489).—Unsaturated carboxylic acids possessing conjugated double linkings, *e.g.*, pyruvic, maleic, fumaric, citraconic, mesaconic, aconitic, cinnamic, and sorbic acids, are readily reduced at a dropping Hg electrode, using a potential of —0·4 to 1·0 volt in acid and —1·2 to —2·1 volt in alkaline solution. Fumaric acid differs from maleic acid in its smaller reduction potential (—1·69 and —1·89 volt, respectively). Citric, malonic, and tartaric acids can be determined polarographically after conversion into the corresponding unsaturated acids.

R. T.

Preparation of glutaconic ester and acid. B. S. Gidvani (J.C.S., 1932, 2666).—The prep. from Et β-hydroxyglutarate and $SOCl_2$ in C_5H_5N is described; the ester is hydrolysed by 50% aq. HCl.

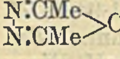
F. R. S.

***cis–cis*-Muconic acid and its oxidation by potassium permanganate.** J. Böeseken and C. L. M. Kerkhoven (Rec. trav. chim., 1932, 51, 964—970).—Muconic acid, m.p. 187—188° [improved prep. by Farmer's method (J.C.S., 1923, 123, 2540) and by oxidation of PhOH, o-$C_6H_4(OH)_2$ or *o*-benzoquinone with AcO_2H], is the *cis–cis*-modification and on oxidation with $KMnO_4$ at 0° gives (besides $H_2C_2O_4$) only mesotartaric acid unmixed with any *dl*-form. Such absence of configurational changes during $KMnO_4$ oxidation confirms Behrend and Heyer's conclusion (A., 1919, i, 521) that muconic acid, m.p. 298°, is the *trans–trans*-form.

J. W. B.

Constitution of the safran dye, crocetin. Synthesis of perhydrobixin ethyl ester and perhydronorbixin. P. Karrer, P. Benz, R. Morf, H. Raudnitz, M. Stoll, and T. Takahashi (Helv. Chim. Acta, 1932, 15, 1218—1219).—Perhydrococetin, when treated successively with Br and KOH, gives the *αα′-dihydroxycarboxylic acid*, changed by MgMe·Hal to the *di*tert.-*carbinol*, which with $Pb(OAc)_4$ yields βο-*diketo*-ζλ-*dimethyl*-n-*hexadecane*, b.p. 135—138°/0·2 mm. (*disemicarbazone*, m.p. 168°). Crocetin is, therefore, $(\colon CH{\cdot}CH\colon CMe{\cdot}CH\colon CH{\cdot}CH\colon CMe{\cdot}CO_2H)_2$. Perhydrobixin (I) gives similarly βζλο-*tetramethylhexadecane*-απ-*dialdehyde*, b.p. 185—190°/0·3 mm., oxidised to the corresponding *dicarboxylic acid*, b.p. 220°/0·1 mm. In accordance with these constitutions, oxidation of tetrahydrocrocetin gives methylsuccinic acid (II), but not succinic acid (III), and of tetrahydrobixin (III), but not (II). Et_2 sodiomethylmalonate and αγ-dibromopropane give *Et_4 αε-dimethyl*-n-*pentane*-ααεε-*tetracarboxylate*, whence the *dicarboxylic acid* was obtained. Reduction of the *ester* of this gives the *dialcohol*; the corresponding *dibromide* with Et_2 sodiomalonate gives *Et_4 γη-dimethyl*-n-*nonane*-ααιι-*tetracarboxylate*, which was changed to the *K* salt of the *acid ester* of the corresponding *dicarboxylic acid*; this on electrolysis gives the di-ester of (I), identified as *diamide*, m.p. 110·5°, and *di*-2 : 4 : 6-*tribromoanilide*, m.p. 83°.

R. S. C.

Formation of triacetylacetic ester. K. von Auwers (Ber., 1932, 65, [*B*], 1561—1563).—Et *o*-acetylacetoacetate and N_2H_4,H_2O give 3-methylpyrazol-5-one and Et 3 : 5-dimethylpyrazole-4-carboxylate in varying ratio. Correspondingly, Et diacetoacetate reacts normally in part and, in part, loses Ac, whilst its *O*-Ac derivative gives essentially Et dimethylpyrazolecarboxylate with, occasionally, methylpyrazolone; Seidel's compound,  $\begin{matrix}N\colon CMe\\N\colon CMe\end{matrix}\!\!>\!CAc{\cdot}CO_2Et$, m.p. 188° (this vol., 931), is never encountered. On theoretical grounds the existence of Seidel's Et triacetylacetate is doubted and the constitution of the compound, m.p. 188°, is regarded as unproven.

H. W.

Action of sodium ethoxide on itaconic, citraconic, and mesaconic esters. E. H. Coulson and G. A. R. Kon (J.C.S., 1932, 2568—2573).—The addition of NaOEt to citraconic, itaconic, and mesaconic esters results in the formation of some 50% of OEt-ester at the end of 5 min. and reaches a max. of 80%. The reaction is reversible. The unsaturated ester recovered consists of the two αβ-forms (citraconic and mesaconic) only, except in the short-time experiments, when a small amount of itaconic acid is obtained. This shows that the 3-C change is more rapid than the addition of EtOH. The OEt-acid has been synthesised from Et_3 ethane-ααβ-tricarboxylate and $CH_2Cl{\cdot}OEt$, and is identical with that obtained by Hope's method (J.C.S., 1912, 101, 895). The three isomeric esters are not equilibrated unless EtOH is added.

F. R. S.

[Attempted] synthesis of αα′-diketoadipic acid. H. Sutter (Annalen, 1932, 499, 47—59).—Addition of Et_2O–C_5H_5N to succinyl chloride and anhyd. HCN in Et_2O gives 18% of *αα′-diketoadiponitrile*, m.p. 98°, which with $NHPh{\cdot}NH_2$ affords succinphenylhydrazide and is hydrolysed by conc. HCl at about 5° to 40% of *αα′-diketoadipamide*, m.p. 230—235° (decomp.) (darkens at 200°). This is hydrolysed by dil. NaOH to a little *αα′-diketoadipamic acid*, m.p. 152° (decomp.); definite products could not be isolated from acid hydrolysates. Et sodio-oxaloacetate and Br in cold $CHCl_3$ give *Et αδ-diketobutane-αβγδ-tetracarboxylate*, m.p. 83°, which when hydrolysed by dil. HCl affords *furan*-2 : 3 : 5-*tricarboxylic acid* (I), m.p. 273° (decomp.); treatment of the product from the acid mother-liquors with diazomethane gives a small amount of a *substance*, $C_{12}H_{14}O_{10}$, m.p. 160° (not sharp). Et sodio-oxaloacetate and $CH_2Br{\cdot}CO{\cdot}CO_2Et$ (II) yield *Et β-carbethoxy-αα′-diketoadipate*, m.p. 79°, also hydrolysed by dil. HCl or H_2O to (I); hydrolysis with aq. $Ba(OH)_2$ gives $H_2C_2O_4$. Definite products could not be isolated from (II) and "mol." Ag. Oxidation of αα′-dihydroxyadipic acid with aq. $KMnO_4$ at 5° gives a little α-hydroxy-α′-ketoadipic acid (as 2 : 4-*dinitrophenylhydrazone*, m.p. 213°); with Br-H_2O, a compound (2 : 4-*dinitrophenylhydrazone*, decomp. 237°) results. Oxidation with O_2 in presence of Cu powder and H_2O gives a little of the diketo-acid (?) [*di*-(2 : 4-*dinitrophenylhydrazone*)]; with H_2O_2 and $FeSO_4$, succinaldehyde results.

H. B.

Isolation of hexuronic acid. E. K. Nelson (Science, 1932, 76, 345).—Difficulties encountered in King's method are pointed out. L. S. T.

Polygalacturonic acid diacetate and dinitrate. K. Smoleński and W. Pardo (Chem. Listy, 1932, 26, 446—449).—Polygalacturonic acid yields a *diacetate*. $[C_6H_6O_4(OAc)_2]_8$, and *dinitrate*, $[C_6H_6O_4(NO_3)_2]_8$, indicating that it contains $\ngtr$ 2 OH groups. R. T.

Complex types involved in the catalytic oxidation of thiol acids. M. Schubert (J. Amer. Chem. Soc., 1932, 54, 4077—4085).—Complexes of $Fe^{\cdot\cdot}$ with cysteine and thiolacetic acid and its Et ester are prepared in absence of O_2; their structures are discussed in detail. The rôle of these complexes in the catalytic oxidation of SH-acids in presence of Fe salts is indicated and a theory of the mechanism of this catalysis is presented. If an air-free solution of $Fe^{\cdot\cdot}$ and twice as many mols. of thiolacetic acid is mixed in H_2 and air-free KOH is added dropwise, a yellow colour soon develops and further slow addition ppts. the yellow salt, $Fe(S{\cdot}CH_2{\cdot}CO_2),1{\cdot}5H_2O$; further addition of KOH causes this to dissolve, giving a deep orange to orange-red solution, from which $Fe(S{\cdot}CH_2{\cdot}CO_2K)_2$ is isolated; if enough KOH is added, $Fe(OH)_2$ is pptd. The same sequence of changes occurs with cysteine or when Fe is replaced by Co (the colours are different). C. J. W. (*b*)

Fission of mercaptal- and mercaptol-acetic acids $[CR_1R_2(S{\cdot}CH_2{\cdot}CO_2H)_2]$. B. Holmberg (J. pr. Chem., 1932, [ii], 135, 57—100).—Ethylidenebisthiolacetic acid may be determined by addition of $HgCl_2$ or $HgSO_4$, and titration of the acid liberated or (iodometrically) of the Hg compound formed according to the equation $CHMe(SR)_2+2HgCl_2+H_2O = MeCHO + 2HgCl{\cdot}SR + 2HCl$ [or, perhaps, $CHMe(SR)_2 + HgCl_2 + H_2O = MeCHO + Hg(SR)_2 + 2HCl$]. Reaction is retarded by the presence of Br′ or I′, particularly the latter, and is very slow in EtOH; it is rather faster with $HgSO_4$ than with $HgCl_2$. It is generally applicable to compounds of the type $CRR'(S{\cdot}CH_2{\cdot}CO_2H)_2$, with the exception of those from CH_2O and phenolic aldehydes, and also to glucose diethylmercaptal (cf. A., 1894, i, 269). Trustworthy results are obtained with the phenolic aldehydes by substitution of $CdSO_4$ for the Hg salt in a solution buffered with NaOAc or $CO(NH_2)_2$ and iodometric titration; this method gives sharper end-points in many other cases, but fails with the derivatives of CH_2O, $CHO{\cdot}CO_2H$, $CH_2Ph{\cdot}CHO$, and $CHPh{:}CH{\cdot}CHO$. Direct iodometric titration gives consistently high results. The course of reaction may be followed kinetically; it is complicated, but its velocity is governed essentially by the equations $CRR'(S{\cdot}CH_2{\cdot}CO_2H)_2 + I_2 + H_2O = (S{\cdot}CH_2{\cdot}CO_2H)_2 + CRR'{:}O+2HI$, and $2I+I' \rightleftharpoons I_3'$. The reaction velocity is increased by added $(S{\cdot}CH_2{\cdot}CO_2H)_2$, which is therefore responsible for the increase in velocity coeff. as the reaction proceeds. CH_2O displaces other aldehydes from their thiolacetic acid derivatives with formation of $CH_2(S{\cdot}CH_2{\cdot}CO_2H)_2$; the reaction is apparently irreversible.

The thiolacetic acid derivatives were prepared by direct condensation with the aldehydes, if necessary in presence of a little HCl (cf. A., 1888, 479); the following are new: *propylidene-*, m.p. 74—75°; 3 : 4-*dihydroxybenzylidene-*, m.p. 150—151° (decomp. ?); *vanillylidene-*, m.p. 136—138°; *veratrylidene-*, m.p. 124—126°; *piperonylidene-*, m.p. 138—139°; β-*phenylethylidene-*, m.p. 99—100°; *hydrocinnamylidene-*, m.p. 110—111°; *furfurylidene-*, m.p. 108—109°; β-*butylidene-*, m.p. 109—111°; *carboxy*iso*propylidene-*, m.p. 146—147° [from the Et ester, m.p. 99—101° (*loc. cit.*)], and cyclo*hexylidene-*, m.p. 138—140°, *-bisthiolacetic acids*. H. A. P.

Identification of aldehydes and primary alcohols by dimethyldihydroresorcinol. C. H. Kao and J. Y. Yen (Sci. Rep. Nat. Tsing Hua Univ., 1932, 1, 185—188).—The prep. of dimethyldihydroresorcinol (I) is modified. Details are given for the $K_2Cr_2O_7$–H_2SO_4 oxidation of primary alcohols and condensation of the resulting aldehydes with (I). The *alkylidenebisdimethyldihydroresorcinols* from the following aldehydes are new, or have been previously assigned incorrect m.p.: Pr^aCHO, m.p. 133·8°; Bu^aCHO, m.p. 104·5°; *n*-hexaldehyde, m.p. 108·5°; *n*-heptaldehyde, m.p. 101·7°; *n*-octaldehyde, m.p. 89·8°; *n*-nonaldehyde, m.p. 86·3°; *n*-decaldehyde, m.p. 91·7°. R. S. C.

Distyryl ketone and triphenylmethane. XV. Thermal decomposition of α-alkoxylalkyl chlorides. F. Straus and H. J. Weber [with N. Stancovici].—See this vol., 1132.

Oxidation of methylglyoxal to pyruvic acid with molecular oxygen. C. Neuberg and M. Kobel (Biochem. Z., 1932, 252, 215—230).—Within the range p_H 5·8—8·1 the H sulphite compound of methylglyoxal in aq. solution in presence of phosphate (or, to a smaller extent, in that of borate) takes up O_2 with formation of $AcCO_2H$. At p_H 6·8 and 37° the reaction is quant. Free methylglyoxal reacts much more slowly and to a much smaller extent. In Na_2CO_3 solution the reaction also proceeds anäerobically, but the yields of $AcCO_2H$ are poor. W. McC.

Reactions of methylglyoxal with nitrogen-free compounds. C. Neuberg and J. Burkard (Biochem. Z., 1932, 253, 222—224).—Although oxalacetic and acetonedicarboxylic acids do not reduce Fehling's solution and methylglyoxal reduces it only very slightly, mixtures of the acids with the keto-aldehyde in dil. aq. solution reduce it readily. The condensation products responsible for the reduction react with hydrazine derivatives. W. McC.

Correlation of the Walden inversion with the pinacol and Beckmann changes. J. Kenner (Nature, 1932, 130, 309).—A discussion. L. S. T.

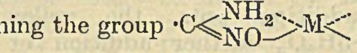
Detection of acetone. R. Raw (J.S.C.I., 1932, 51, 276T).—The condensation of $COMe_2$ and $o\text{-}NO_2{\cdot}C_6H_4{\cdot}CHO$ (I) to indigotin can be used as a test for small quantities of the former by heating the solution containing $COMe_2$ in an org. solvent, *e.g.*, MeOH or EtOH, with a few crystals of (I) for about 1 min., pouring into an equal vol. of 10% aq. NaOH, and heating for a few min. at 80—90°. Addition of aq. NaOH at the commencement of the test retards the reaction.

Condensation products of propanone; mesityl oxide and derivatives. G. GALLAS and F. G. GONZÁLEZ (Anal. Fís. Quím., 1932, 30, 645—654).—$CMe_2Cl\cdot CHAc\cdot OH$ may be prepared by adding mesityl oxide to a solution of HOCl (3% free Cl) and extracting with Et_2O after 24 hr. With primary and *sec.* amines it yields *compounds* of the type $NHR\cdot CMe_2\cdot CHAc\cdot OH$; the compound obtained with *iso*amylamine has m.p. 212°; that with NH_2Ph, m.p. 189° (*Bz* derivative, m.p. 155°; *oxime*, m.p. about 250°); with $NHPr_2$, m.p. 180°; and with toluidine, m.p. 206°; the *hydrochlorides* of the products obtained with NH_2Et, NH_2Pr, and NH_2Bu have m.p. between 150° and 190°. $NHEt_2$, NHPhEt, NHPhMe, and NHPhPr formed deep red condensation products which could not be isolated. H. F. G.

Catalytic decomposition of diethyl ketone phenylhydrazone. A. E. ARBUSOV and V. A. ROTERMEHL (J. Gen. Chem. Russ., 1932, 2, 397—398).—Et_2 ketone phenylhydrazone, b.p. 144°/9 mm., on heating with a trace of $ZnCl_2$ gives NH_3 and a 69% yield of 3-*methyl*-2-*ethylindole*, b.p. 153°/10 mm., m.p. 59·5° (*dipicrate*, m.p. 150·5°). G. A. R. K.

Triacetylmethane. K. VON AUWERS (Ber., 1932, 65, [*B*], 1634—1636).—Comparison of the optical consts. of triacetylmethane (Birckenbach and others, this vol., 933) with those of the acetate of diacetoacetic ester, ethoxymethyleneacetone, and acetylacetone acetate shows that it is enolised to the extent of at least 75%. Its salts are therefore *O* derivatives. Its presence predominatingly as ketone in H_2O or HCl–H_2O is in harmony with the known ketonising power of these media. H. W.

[**Triacetylmethane.**] L. BIRCKENBACH, K. KELLERMANN, and W. STEIN (Ber., 1932, 65, [*B*], 1636—1637; cf. this vol., 933).—In reply to von Auwers (preceding abstract) it is stated that the salts of triacetylmethane (I) are derived initially from the enolic form. Dissolution in H_2O causes extensive hydrolysis into KOH and free (I), which becomes extensively ketonised. The K salt is hydrolysed rapidly, the Ag salt slowly. The contradiction that (I) can be sharply titrated in presence of phenolphthalein, but is completely enolised only by a large excess of KOH, is merely apparent, depending on the widely differing concn. of KOH employed. Conclusions with respect to the constitution of homogeneous (I), particularly on its keto-enolic equilibrium, cannot be based on measurements of its absorption in H_2O. H. W.

Influence of the vicinity of amino-groups on the formation of salts of α-dioximes (oxamidedioxime). J. V. DUBSKÝ and A. OKÁČ (Coll. Czech. Chem. Comm., 1932, 4, 388—399).—Gradual addition of an aq. solution of 3 mols. of oxamidedioxime (I), $[NH_2\cdot C(:N\cdot OH)\cdot]_2$ (designated OxH_2), m.p. 204° (lit. 195° and 200°), to a solution of 1 mol. of $CuSO_4$ in aq. NH_3 gives the *salt* $Cu(OxH)_2,2H_2O$ (II), decomp. about 200°, which is completely sol. only in 4 mols. of HCl (0·1*N*), and is thereby converted (mainly) into the tetrammine *salt* (III), $Cu(OxH_2)_2Cl_2$, decomp. explosively at about 142° [corresponding *dinitrate* (IV), decomp. explosively at about 128°], which is also prepared from (I) (3 mols.) and $CuCl_2$ (1 mol.) in dil. HCl. The conversion of (II) into (III) is considered to occur by way of an unstable intermediate formed by addition of 4HCl to the NH_2-groups of (II). Aq. solutions of (I) (3 mols.) and $CuSO_4$ (1 mol.) afford a *complex*, $Cu_2(OxH_2)_5SO_4,4H_2O$, decomp. about 158° (slight explosion). (I) and an excess of $CuCl_2$ give the *salt* $Cu(OxH_2)Cl_2$ (V), decomp. explosively about 169°, also formed in small amount when (II) is dissolved in 0·1*N*-HCl (above), and converted by $AgNO_3$ into (IV): $2Cu(OxH_2)Cl_2+4AgNO_3 \longrightarrow 4AgCl+Cu(NO_3)_2+Cu(OxH_2)_2(NO_3)_2$. Addition of aq. NH_3 to an aq. solution of (V) ppts. a *complex*, $3CuOx,Cu(OH)_2,6H_2O$, decomp. about 196° (slight explosion), also formed from an equimol. mixture of (I) and $CuCl_2$ (or $CuSO_4$) in H_2O and aq. NH_3, in which the $:NO\cdot Cu\cdot ON:$ group probably occurs. The proximity of the NH_2 to the $:N\cdot OH$ groups should suppress the basic function of the latter, thereby causing them to react as acids; it should, therefore, be possible to prepare complexes containing the group  $\cdot C\!\!<\!\!\begin{smallmatrix}NH_2\\NO\end{smallmatrix}\!\!>\!\!M\!<$.

The salt $Ni(OxH)_2,2H_2O$ (Tschugaev and Surenjanz, A., 1907, i, 198) is converted by conc. HCl (4 mols.) into the *salt* $Ni(OxH_2)_2Cl_2$, decomp. about 216°; the *sulphate* ($+4H_2O$), decomp. about 219°, is similarly prepared. H. B.

Identification of common carbohydrates. W. M. DEHN, K. E. JACKSON, and D. A. BALLARD (Ind. Eng. Chem. [Anal.], 1932, 4, 413—415).—Colour reactions given by many reagents with common carbohydrates are listed so as to form a scheme of identification. Single-test identifications are given for cellulose, starch, glycogen, dextrin, pectin, fructose, mannose, maltose, and rhamnose; other carbohydrates require two or more tests. E. S. H.

Determination of reducing sugars. Application of Shaffer and Hartmann iodometric cuprous titration. G. L. MARSH and M. A. JOSLYN (Ind. Eng. Chem. [Anal.], 1932, 4, 368—371).—Sources of error in the procedure (A., 1921, ii, 417) have been examined and modifications are suggested. E. S. H.

Formation of furfuraldehyde from methylated pentoses. H. G. BOTT and E. L. HIRST (J.C.S., 1932, 2621—2624).—Me_3 derivatives of arabo- and xylo-furanose and -pyranose are decomposed readily by 12% aq. HCl with formation of furfuraldehyde in good yield. The mechanism of the reaction is discussed. F. R. S.

Ribosephosphoric acid from xanthylic acid. II. P. A. LEVENE and S. A. HARRIS (J. Biol. Chem., 1932, 98, 9—16).—Methylation of the *d*-ribosephosphoric acid (I), $[\alpha]_D^{26}$ $-8\cdot93°$ as its Na salt in H_2O, obtained from xanthylic acid (this vol., 497) by the action of MeI on the Ag salt of its methylriboside, affords *dimethylphosphordimethyl*-n-*methylriboside*, b.p. 128—133°/0·1 mm., $[\alpha]_D^{28}$ $-17\cdot2°$, which could not be completely hydrolysed to the methylated ribose. Oxidation of (I) with HNO_3 gave only $H_2C_2O_4$. Reduction of  $O\!<\!\begin{smallmatrix}CH(OH)\cdot CH(OH)\\CH_2\text{——}CH(OH)\end{smallmatrix}\!>\!CH\cdot OPO_3H_2$ (I) (as its Ba salt) with H_2–PtO_2 affords an inactive ribitolphosphoric acid. This, with results previously obtained (this vol., 1043), proves the structure assigned to (I). J. W. B.

Influence of bile acids on the mutarotation of glucose. T. Hosizima (J. Biochem. Japan, 1932, **16**, 153—161).—The influence of Na cholate in presence of liver-enzyme preps. on the mutarotation of glucose was investigated. F. O. H.

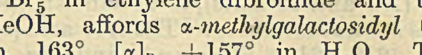
New anhydroglucose. L. Reichel and G. Erdös (Ber., 1932, **65**, [*B*], 1618—1623).—The " stable γ-dextrose " of Pringsheim and Kolodny (A., 1926, 822) is best obtained by the action of conc. HCl (*d* 1·19, 10 c.c.) on β-glucosan (20 g.) at 16—18° during 120 hr. Small amounts of glucose are removed by fermentation and the unattacked portion is treated with AcOH, whereby the ash content is reduced to 0·5—1%. The product is an *anhydroglucose*, $C_6H_{10}O_5$ (not $C_6H_{12}O_6$ as recorded by Pringsheim), decomp. 135—140°, $[\alpha]_D^{20}$ +96·9° in H_2O (non-mutarotatory). It reduces Fehling's solution, NH_3–$AgNO_3$, and Hg^I salts. It does not yield a phenylosazone and cannot be fermented. It is stable towards AcOH, but quantitatively hydrolysed by 2*N*-HCl to glucose. With HBr–AcOH it affords an unstable *acetobromoanhydroglucose*, m.p. 100° after softening, $[\alpha]_D^{22}$ +135° in C_6H_6, thus establishing the presence of the free OH at 1. With Ac_2O in C_5H_5N it gives a *triacetate*, m.p. 118°, $[\alpha]_D^{20}$ +90·8° in C_6H_6, and with Me_2SO_4 and NaOH at 60—70° it yields *dimethylanhydroglucose*, m.p. 90°, $[\alpha]_D^{20}$ +82·8° in H_2O. It is probable that 2—4 and 1—5 oxygen bridges are present. H. W.

Relations between rotatory power and structure in the sugar group. XXXI. α- and β-Forms of ethyl-*d*-glucoside and their tetra-acetates. J. H. Ferguson (J. Amer. Chem. Soc., 1932, **54**, 4086—4090; cf. A., 1930, 1024).—Details are given for the prep. of the α-, m.p. 114·6°, $[\alpha]_D^{28}$ +152·01° in H_2O (tetra-acetate, m.p. 61·8°, $[\alpha]_D^{30}$ +132·13° in $CHCl_3$), and β-, m.p. 90·4°, $[\alpha]_D^{29·5}$ −36·7° in H_2O (tetra-acetate, m.p. 106·8°, $[\alpha]_D^{22·5}$ −22·67° in $CHCl_3$), -forms of ethyl-*d*-glucoside. The results confirm Hudson's second rule of isorotation when they are compared with other substances of the glucoside series. A test of the first rule of isorotation, made by comparing certain of them with the rotation of β-ethylmaltoside hepta-acetate, also shows confirmation. C. J. W. (*b*)

Use of 1-bromotetramethylglucose for the synthesis of methylated glucosides. P. A. Levene and F. Cortese (J. Biol. Chem., 1932, **98**, 17—19).—Tetramethylglucose is converted by Ac_2O and NaOAc into its *Ac* derivative, b.p. 133—138°/high vac., which with HBr in AcOH affords 1-*bromo*-2 : 3 : 4 : 6-*tetramethylglucose* (unstable). This with MeOH and Ag_2CO_3 gives a mixture of tetra- (33%) and penta- (66%) -methylglucose, and with Ag theophylline affords *theophylline*-2 : 3 : 4 : 6-*tetramethylglucoside*, b.p. 180—220°/0·006 mm.

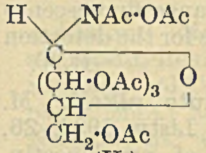
J. W. B.

[3 : 6-]Anhydrogalactose. F. Valentin (Coll. Czech. Chem. Comm., 1932, **4**, 364—375).—α-Methylgalactoside (modified prep.), when treated in C_5H_5N with CPh_3Cl and then with Ac_2O, gives 2 : 3 : 4-*triacetyl*-6-*triphenylmethyl*-α-*methylgalactoside*, m.p. 179—181°, $[\alpha]_D$ +56° in C_6H_6, which, when treated with PBr_5 in ethylene dibromide and then with NH_3–MeOH, affords α-*methylgalactosidyl* 6-*bromide*, decomp. 163°, $[\alpha]_D$ +157° in H_2O. This with $Ba(OH)_2$ yields 3 : 6-*anhydro*-α-*methylgalactoside*, m.p. 141—142°, $[\alpha]_D$ +82·4° in H_2O, hydrolysed by 1% H_2SO_4 to 3 : 6-*anhydrogalactose* (I), amorphous, $[\alpha]_D$ in H_2O +37·6°, changing to +27·2° [*phenylosazone*, m.p. 215° (decomp.), $[\alpha]_D$ +48·2° in MeOH]. The possibility that (I) contains an ethylenic linking is excluded by its stability to halogens, and the constitution of the 3 : 6-ring follows from stereochemical reasons and the formation of the osazone. (I) decolorises Schiff's reagent in 3—4 sec. and is considered to be an anhydro-aldehyde. Mutarotation is due to opening of the 1 : 5-ring, and not the more stable 3 : 6-ring, and equilibrium is between (I) and the aldehyde. For stereochemical reasons the pyranose ring can re-form only in one direction. R. S. C.



$$\mathrm{CH(OH)\cdot CH(OH)\cdot CH\cdot CH(OH)\cdot CH\cdot CH_2}$$ (I.)

Ring–chain isomerism in the acetates of galactoseoxime. M. L. Wolfrom, A. Thompson, and L. W. Georges (J. Amer. Chem. Soc., 1932, **54**, 4091—4095).—α-Galactoseoxime (I), m.p. 176—178°, $[\alpha]_D$ (in H_2O) +84° ⟶ +14·5°, with Ac_2O in C_5H_5N gives α-*galactoseoxime hexa-acetate* (II), m.p. 130°, $[\alpha]_D^{23}$ +33·7° in $CHCl_3$ (unchanged after 18 hr.). Aldehydo-galactose penta-acetate Et hemiacetal, NH_2OH,HCl, and KOAc in H_2O give the *monohydrate* (III), m.p. 112—114°, $[\alpha]_D^{23}$ +32° in $CHCl_3$, of *aldehydogalactoseoxime penta-acetate* (IV), which shows no tendency to mutarotate; deacetylation gives (I). (III) heated at 95—97° over $CaCl_2$ in vac. gives (IV), m.p. 118—120°, $[\alpha]_D^{25}$ +34° in $CHCl_3$, which when crystallised from hot H_2O gives (III). (III), Ac_2O, and C_5H_5N at 0° give *aldehydo-galactoseoxime hexa-acetate*, m.p. 145—146°, $[\alpha]_D^{24}$ +22·5° in $CHCl_3$, which has a solubility different from (II) and is deacetylated to (I). C. J. W. (*b*)



(II.)

Reduction of fructose at the dropping mercury cathode, and the polarographic determination of invert sugar. J. Heyrovský and I. Smoler (Chem. Listy, 1932, **26**, 479—484).—Fructose and sorbose, but not glucose, mannose, rhamnose, arabinose, lyxose, sucrose, maltose, or lactose, undergo reduction at a dropping Hg cathode at a potential of −1·60 volt. The increment in current during reduction is proportional to the concn. of carbohydrate, and this allows fructose in honey or invert sugar to be determined with an accuracy of ±2%, and in lower concn. than using Bertrand's method. R. T.

Crystalline esters derived from fructose. F. G. González (Anal. Fís. Quím., 1932, **30**, 611—644).—α- and β-Di*iso*propylidene-fructose and -glucose cannot be esterified by the action of $POCl_3$ in C_6H_6, C_5H_5N, or Et_2O, but a small yield of ester is obtained under these conditions from the first-named and PCl_5. With equimol. proportions of

$POCl_3$ and PCl_5, in Et_2O at room temp., a quant. yield of *tri-β-diisopropylidenefructose phosphate*, m.p. 136—137° (*Na* and *K* salts), is obtained; the other compounds are not esterified. The free acid [*cinchonidine*, m.p. 212—213° (decomp.), and *Ag* salts] is hygroscopic. *Me*, m.p. 109°, and *Et*, m.p. 113—114°, *di-β-diisopropylidenefructose phosphate* are described; on hydrolysis they yield, probably, *Na Et* and *Na Me β-diisopropylidenefructose phosphates*. H. F. G.

[Preparation of] sugars for microbiological uses. Maltose. A. Stepanov and A. Kuzin (Khim. Farm. Prom., 1932, No. 2—3, 57—64).—Starch solution (5%) is kept at 37° for 24 hr. with enzyme (0·8%) from malt extract; albumins are coagulated by warming and maltose from the filtrate is purified by recrystallisation. Ch. Abs.

3 : 6-Dinitro-2 : 7-dihydroxyfluoran as a reagent for the detection of reducing sugars. M. Dominikiewicz (Rocz. Chem., 1932, **12**, 686—692).—2 : 7-Dinitro-3 : 6-dihydroxyfluoran yields with KOH–EtOH an orange K salt, an orange-brown K_2 salt, and a violet K_3 salt; the last two dissociate on dilution with H_2O to yield the K salt. 3 : 6-Dinitro-2 : 7-dihydroxyfluoran (I) gives an orange-brown K_2 salt, which readily dissociates, yielding an orange K salt, reduced to 2 : 7-dihydroxyrhodamine by glucose, fructose, mannose, galactose, arabinose, xylose, lactose, and maltose, but not by sucrose, raffinose, starch, and inulin, or by sorbitol, dulcitol, mannitol, glycerol, glyoxal, glyceraldehyde, CH_2O, HCO_2H, or $H_2C_2O_4$. Reducing sugars are detected by adding (I) to the alkaline solution, when a cerise coloration develops, changing to an intense orange fluorescence on acidification. This method serves for the detection of $\nless$0·01275 mg. per c.c. of sugar. R. T.

Reaction of starch with dilute alkali. M. Samec [with S. Sazanow] (Chem. Listy, 1932, **26**, 451—454).—The titration curves of amylopectin, amylophosphoric acid, and phosphoric acid all exhibit a series of step-like breaks. The viscosity–c.c. of NaOH curve of amylopectin at first rises to a max. at 0·5 g.-equiv. of NaOH, then falls to a min. at 1 g.-equiv., after which it rises continuously. These observations support the author's theory of the constitution of starch. R. T.

Constitution of cellulose and its derivatives. III. Solid solutions and dyeing. (Mlle.) A. Dobry and J. Duclaux (Bull. Soc. chim., 1932, [iv], 51, 1172—1177).—Cellulose diacetate is dyed by the following complexes (in aq. solution): $Fe^{\cdots}$ (I), Co, and Mo thiocyanates; Au bromide (brown) (II); $FeCl_3$; phosphomolybdic acid; Fe nitrososulphide, $Fe_4KS_3(NO)_7$ (III). Dyeing of cellulose triacetate, ethylcellulose, and cellophane with (I), cellulose triacetate and ethylcellulose with (II), and ethyl- and benzyl-cellulose with (III), also occurs. Dyeing is considered to be due to the formation of solid solutions; the complexes used are sol. in Et_2O or EtOAc, and the cellulose derivatives which are dyed contain the same groupings. Of the complexes used, (III) only is sol. in PhOMe; the dyeing of benzylcellulose by (III) supports the solution theory. Cellulose di- and tri-nitrates are not dyed by any of the above complexes; this may be concerned with the cryst. structure of the nitrates. In accordance with this view, cellobiose octa-acetate is not coloured by crystallisation from an EtOH solution of (I), its Co analogue, or (III); amorphous cellodextrin acetates and the micro-cryst. acetates of (probably) cellotetraose and higher polymerides are coloured, thus indicating that the constitution of the compounds is only one aspect of the problem. H. B.

Resolution of racemic amines at low temperatures. T. D. Stewart and C. Allen (J. Amer. Chem. Soc., 1932, **54**, 4027—4039).—The method, which consists in salt formation between amine antipodes and optically active acids at −70°, is standardised with *dl*-α-phenylethylamine and 1-bromo-*d*-camphor-10-sulphonic acid; formation of cryst. salt is necessary for resolution. Success in the resolution appears to depend on a difference between the amine enantiomorphs in their rate of forming salt crystals from supersaturated solutions, rather than on a difference in the solubility of the non-enantiomorphic salts. Attempted resolution of an *as*-substituted amine, $NPhEt{\cdot}CH_2Ph$, failed. C. J. W. (*b*)

Action of alkali on ζ-bromo-*n*-hexylamine and η-bromo-*n*-heptylamine. A. Müller and P. Krauss (Monatsh., 1932, **61**, 219—228).—The action of KOH on ζ-bromo-*n*-hexylamine [hydrobromide, m.p. 142—143° (corr.) (lit., 89—90°)] gives only a little hexamethyleneimine (I), whilst with η-bromo-*n*-heptylamine no heptamethyleneimine is formed (cf. J. Pharm. Soc. Japan, 1928, **48**, 72; **534**, 368; **557**, 688). The primary amines were prepared by the phthalimide route, the following compounds being described: *α-bromo-ζ-phthalimido-*n*-hexane*, m.p. 57° (corr.); *α-bromo-η-phthalimido-*n*-heptane*, m.p. 34° (corr.), and *heptamethylenediphththalimide*, m.p. 129° (corr.). The chloroplatinate of (I) has m.p. 197° (decomp.); the form (+1H_2O), m.p. 149—150°, could not be obtained. H. A. P.

Racemisation of amino-acids in aqueous solution by acetic anhydride. V. du Vigneaud and C. E. Meyer (J. Biol. Chem., 1932, **98**, 295—308).—In extension of previous work (this vol., 753), the Na salts of either the Ac or formyl derivatives of various NH_2-acids are racemised by Ac_2O and thus are obtained: *acetyl*-dl-*methionine*, m.p. 114—115° [from *acetyl*-l-*methionine*, m.p. 111—111·5° (corr.), $[\alpha]_D^{25}$ −16·1°; identical with a specimen prepared by Ac_2O–NaOH on the *dl*-parent]; *dl*-glutamic acid (from acetyl-*d*-glutamic acid); formyl-*dl*-phenylalanine [from formyl-*l*-phenylalanine (brucine salt, m.p. 91—93°, $[\alpha]_D^{26}$ −7·3°; cf. Fischer and Schoeller, A., 1907, i, 1037) and from acetyl-*d*-phenylalanine, m.p. 172° (corr.), $[\alpha]_D^{26}$ −51° in EtOH (erroneously described by Knoop and Blanco, A., 1925, i, 1208, as the *l*-compound)]; and *acetyl*-dl-*arginine*+2H_2O, m.p. 108—110° (from *d*-compound). According to the conditions *l*-tyrosine with NaOH–Ac_2O affords *N*-acetyl-*l*-tyrosine or *diacetyl*-dl-*tyrosine*, m.p. 167—170° (corr.). Similar attempts to racemise diacetyl-*l*-cystine lead to decomp., whilst no racemisation of *acetyl*-l-*proline*+H_2O, m.p. 81—82°, and anhyd., m.p. 116—117° (corr.), could be effected by this method.

The rate of racemisation of acetyl-*d*-glutamic acid decreases with time, 50% being racemised in 0·25 hr. and 100% in 8 hr. No racemisation occurs with free NHAc-acids, but the action is not due to any sp. action of Na ions, since no racemisation occurs when NaCl is added. The determining factor is the p_H val., since racemisation occurs in the presence of NaOAc (inhibited by addition of H_2SO_4) or with C_5H_5N in place of NaOH. J. W. B.

Action of sugar on amino-acids. I. In alkaline media. J. Watanabe (J. Biochem. Japan, 1932, 16, 163—189).—Deamination of glycine, alanine, leucine, glutamic acid, and lysine in alkaline solution is accelerated by glucose, fructose, galactose, and glyceraldehyde, in presence of which formation of NH_3, CO_2, and aldehydes occurs. The influence of the sugar is proportional to its rate of decomp. by alkalis, a decomp. which also renders the sugar more reactive towards NH_2-acids. With the sugar and NH_2-acid at 100° the reaction is equimol. and irreversible. F. O. H.

Synthesis of ε-amino-*n*-heptoic acid. A. Müller and P. Krauss (Monatsh., 1932, 61, 206—211).—ε-Keto-*n*-heptoic acid, m.p. 33° (corr.), is conveniently prepared by interaction of $CHNa(CO_2Et)_2$ with $COCl\cdot[CH_2]_4\cdot CO_2Et$ and hydrolysis and decarboxylation of the product. Its *phenylhydrazone*, m.p. 67° (decomp.), is reduced by Al–Hg in aq. EtOH to NH_2Ph and ε-*amino*-n-*heptoic acid*, m.p. 188° (decomp.) [*hydrochloride*, m.p. 131° (corr.); *chloroplatinate*, m.p. 183° (decomp.); *Bz* derivative, m.p. 92·5° (*Me* ester, m.p. 68°), and *benzenesulphonyl* compound, m.p. 100°; *lactam*, m.p. 90—90·5° (*chloroplatinate*)]. H. A. P.

Trichloromethyl alkyl urethanes. N. N. Melnikov and M. M. Vinokurov (J. Gen. Chem. Russ., 1932, 2, 484—490).—CCl_3 chloroformate (I) with *p*-nitroaniline (II) in Et_2O yields *s*-dinitrophenylcarbamide (III) and CCl_3 N-p-*nitrophenylurethane* (IV), yellow crystals evolving $COCl_2$ and rapidly decomposing in moist air or with boiling H_2O giving (III) and a little (II). (IV) with NaOAc at 150—160° gives *p*-nitrophenylacetamide, whilst when heated alone or in CCl_4 on the water-bath it forms *p*-nitrophenylcarbimide, $COCl_2$, and HCl. With MeOH and EtOH it gives the corresponding alkyl urethanes. Pr^{α}, Bu^{β}, and iso*amyl* N-p-*nitrophenylurethanes* have m.p. 116°, 81°, and 98°; the corresponding dialkyl carbonates were also obtained, b.p. 167°, 186°, and 228°.

$NHPh_2$ and (I) in Et_2O furnish CCl_3 N-*diphenylurethane* (V), m.p. 61°. This on boiling with H_2O gives $NHPh_2$, on heating alone $COCl_2$ and diphenylcarbamyl chloride, and with NaOAc, $NAcPh_2$. With alcohols the following alkyl *N*-diphenylurethanes have been obtained: *Me*, m.p. 85°, *Et*, m.p. 84°, Pr^{α}, m.p. 85°, Bu^{β}, m.p. 87°, and iso*amyl*, m.p. 84°, together with the corresponding alkyl carbonates. G. A. R. K.

Flask for Van Slyke protein analysis. R. Patton (Ind. Eng. Chem. [Anal.], 1932, 4, 417). E. S. H.

Constitution of spilanthol, the pungent principle of para cress. M. Asano and T. Kanematsu (Ber., 1932, 65, [*B*], 1602—1604; cf. A., 1920, i, 654; 1922, i, 505).—Tetrahydrospilanthol is converted by 50% HBr at 160° into decoic acid (identified as the *p*-toluidide, m.p. 76—77°) and NH_2Bu^{β} (identified as *p*-toluenesulphon*iso*butylamide, m.p. 77°. Ozonisation of spilanthol in $CHCl_3$ and decomp. of the ozonide with warm H_2O affords HCO_2H, succinic acid (?), and $PrCO_2H$. The presence of a conjugated double linking is thus established and confirmed by the formation with maleic anhydride of the *compound* $C_{18}H_{27}O_4N$, m.p. 167—168°. Spilanthol is therefore regarded as $\Delta^{\gamma\epsilon}$-decadieno*iso*butylamide. H. W.

Aminobuiret and its formaldehyde derivative. P. P. T. Sah and S. Ma (Sci. Rep. Nat. Tsing Hua Univ., 1932, 1, 189—191).—The preps. of biuret, nitrobiuret, and aminobiuret hydrochloride (I) are modified. (I) with aq. CH_2O gives *methyleneaminobiuret*, m.p. 220°, but reacts only very slowly with a no. of other aldehydes and ketones. R. S. C.

Determination of the thiocyano-group in organic compounds. A. N. Pantschenko and G. S. Smirnov (J. Gen. Chem. Russ., 1932, 2, 193—196).—When org. CNS compounds are heated with Na_2S in EtOH the CNS group is quantitatively eliminated as NaCNS and can be titrated, after removal of excess of Na_2S, by Volhard's method. This method is rapid and accurate for compounds of the aliphatic, aromatic, and mixed series. The presence of the CO, CN, or NO_2 groups, as well as of As, N, and S (other than in the CNS group), does not affect the accuracy. M. Z.

Action of the Grignard reagent on aminonitriles. II. T. Thomson and T. S. Stevens (J.C.S., 1932, 2607—2612).—Interaction of $R''MgX$ and $NR'_2\cdot CHR\cdot CN$ ($R' = Me$) gives $NR'_2\cdot CHRR''$ (I) or $NR'_2\cdot CHR\cdot COR''$ (II) and no $(NR'_2)CH\cdot R\cdot CHR\cdot NR'_2$. The results obtained lead to the rules: (*a*) When R=H (II) predominates. (*b*) When R=lower alkyl (II) predominates if R''= alkyl, and (I) if R''=Ph or CH_2Ph. (*c*) When R=Ph the main product is (I). When $NR'=C_5H_{10}N$, (I) and not (II) is formed in all cases. Competition experiments with CH_2MeCN and $NC_5H_{10}\cdot CHMe\cdot CN$ and differing Grignard reagents show that the reaction is sensitive to small constitutional changes. The following are described: p-*bromophenacylobromide* of $NMe_2\cdot CHMe\cdot COEt$, m.p. 180—181° (decomp.); *Me* Pr^{α} *ketone* 2 : 4-*dinitrophenylhydrazone*, m.p. 142—143°; CH_2NMe_2 CH_2Ph *ketone hydrobromide*, m.p. 151—153°; cyclo*hexyl* $NMe_2\cdot CH_2\cdot CH_2$ *ketone* p-*bromophenacylobromide*, m.p. 213—214° (decomp.); β-*dimethylamino*-α-*phenylpropane methopicrate*, m.p. 103—105°; CH_2Ph *Et ketone* 2 : 4-*dinitrophenylhydrazone*, m.p. 140—141°; *propiophenone* 2 : 4-*dinitrophenylhydrazone*, m.p. 187—189°; α-*phenyl*-β-*piperidinopropane* p-*bromophenacylobromide*, m.p. 197—199°; and *picrates* of the following: $NMe_2\cdot CH_2\cdot CN$, m.p. 168—169°, NMe_2Pr^{α}, m.p. 240—241° (decomp.), $NMe_2\cdot CHMe\cdot COEt$, m.p. 166—168°, NMe_2Bu^{β}, m.p. 192—193°, $NMe_2\cdot CHEt\cdot COEt$, m.p. 161—163°, $NMe_2\cdot CHEt\cdot COPr^{\alpha}$, m.p. 200—201°, β-dimethylaminopentane, m.p. 208—210°, *cyclo*hexyl $NMe_2\cdot CH_2\cdot CH_2$

ketone, m.p. 165—167°, $NMe_2\cdot CHMe\cdot COBu^{a}$, m.p. 118—120°. F. R. S.

Mixed magnesium alkoxides and their molecular compounds. I. Molecular compounds of magnesium iodide alkoxide with benzophenone and other ketones. V. M. Tolstopiatov and B. N. Sverdlov (J. Gen. Chem. Russ., 1932, **2**, 105—127).—The mol. *compound* $CMe_3\cdot COMe,MgMeI,COPh_2$ is obtained on addition of $COPh_2$ to $CMe_3\cdot COMe,MgMeI$ or of $CMe_3\cdot COMe$ to $CPh_2Me\cdot OMgI$; on distillation it yields $CMe_3\cdot CMe_2\cdot OH$ and $COPh_2$, with about 5% of $CPh_2Me\cdot OH$. The *compounds* $R\cdot OMgI,COPh_2$ ($R=Me$, Et, Bu^{a}, Bu^{γ}), obtained similarly, and $R\cdot OMgI,Et_2O$ ($R=Me$, Et, Bu^{γ}, $CMe_3\cdot CMe_2$) are described. R. T.

Dehydrogenation of stereoisomeric dimethyl*cyclo*hexanes; contact transformation of the *cis*- into the *trans*-forms. N. D. Zelinski and E. I. Margulis (Ber., 1932, **65**, [*B*], 1613—1617).—Catalytic hydrogenation of *o*- and *p*-xylene in presence of Os at 50—70° produces the corresponding *cis*-dimethyl*cyclo*hexanes, whereas the *trans*-forms result in presence of Ni. In presence of Pt–C, Ni, or Os–asbestos, *m*-xylene affords a mixture of the stereoisomeric forms. Ni as catalyst causes the transformation of *cis-o-* and *-p*-dimethyl*cyclo*hexanes into the *trans*-forms. Dehydrogenation of the *cis*- and *trans*-forms of the dimethyl*cyclo*hexanes follows the same course, but it remains undecided whether the change is preceded by isomerisation of the *trans*- into the *cis*-variety. H. W.

Reactions of etherates of aluminium and thallium trichlorides in benzene. L. I. Kaschtanov (J. Gen. Chem. Russ., 1932, **2**, 515—523).—$TlCl_3$ reacts like $TiCl_4$ (A., 1928, 876), causing condensation of C_6H_6 with alkyl radicals of esters but not with the acid radicals; $AlCl_3$ reacts more vigorously, causing both radicals of an ester to combine. The following were condensed with C_6H_6 in presence of $TlCl_3$: CH_2PhCl or $CH_2Ph\cdot OEt$ to yield CH_2Ph and *m*- and *p*-$C_6H_4(CH_2Ph)_2$; BzCl to $COPh_2$; AcCl to COPhMe; *iso*amyl acetate and benzoate, no reaction (?). With C_6H_6 and $AlCl_3$, $CH_2Ph\cdot OEt$ gives PhEt, CH_2Ph_2, *m*- and *p*-$C_6H_4(CH_2Ph)_2$; EtOAc gives PhEt and ethylacetophenone; *iso*amyl acetate, COPhMe and *p*-di*iso*amylbenzene; Et valerate, PhEt, *ethylvalerophenone* (semicarbazone, m.p. 191—192°), and valeric acid; *iso*amyl benzoate, a *hydrocarbon*, $C_{17}H_{20}$, and a *product*, b.p. 295—300°, giving terephthalic acid on oxidation; $CH_2Ph\cdot OBz$, CH_2Ph_2, *m*- and *p*-$C_6H_4(CH_2Ph)_2$ and BzOH, but no $COPh_2$. This appears to be the only difference between the Friedel–Crafts reaction and that now described.

G. A. R. K.

Reaction of nitrobenzene. L. Pavolini (Riv. Ital. Ess. Prof., 1932, **14**, 110—111; Chem. Zentr., 1932, i, 3508—3509).—$PhNO_2$ in AcOH is reduced by Mg first to azoxybenzene; then under the influence of H_2O and rising temp. this is reduced to NH_2Ph, which reacts with the $PhNO_2$ and gives azoxybenzene. The presence of 1% of $PhNO_2$ in PhCHO is readily detected by the production of an orange coloration.

A. A. E.

Reaction between triarylmethyl halides and magnesium phenyl bromide. I. C. S. Schoepfle and S. G. Trepp (J. Amer. Chem. Soc., 1932, **54**, 4059—4065).—A theory postulating quinoidation of triarylmethyl halides is advanced to explain the supposedly abnormal reaction of these compounds with MgPhBr. *p*-$C_6H_4Cl\cdot CPh_2Cl$ and 3 mols. of MgPhBr give about 10% of p-*chlorotetraphenylmethane*, m.p. 227—227·5°, 28% of 4-*chloro*-4′-*phenyltriphenylmethane* (I), m.p. 102—103°, and 9% of $CHPh(C_6H_4Ph)_2$. Approx. the same results are obtained with p-*chlorotriphenylmethyl bromide*, m.p. 111—112°. *p*-$C_6H_4Br\cdot CPh_2Cl$ and MgPhBr give 13% of p-*bromotetraphenylmethane*, m.p. 245°, 7% of 4-*bromo*-4′-*phenyltriphenylmethane* (II), m.p. 82—84°, and 20% of $CHPh(C_6H_4Ph)_2$. *p*-$C_6H_4Cl\cdot COCl$, Ph_2, $AlCl_3$, and CS_2 give 63% of 4-*chloro*-4′-*phenylbenzophenone*, m.p. 169·5—170·5°, which with MgPhBr affords 4-chloro-4′-phenyltriphenylcarbinol; this did not crystallise readily and was converted into (I) by 57% HI in C_6H_6. (II) is prepared similarly. *p*-$PhC_6H_4\cdot CPh_2Cl$ and MgPhBr give 7—10% of p-*phenyltetraphenylmethane* (III), m.p. 197—198°, and 58—70% of $CHPh(C_6H_4Ph)_2$; (*p*-*p*′-diphenylylphenyl)-diphenylmethane could not be isolated. 4-*Amino*-4′-*phenyltetraphenylmethane*, m.p. 192°, obtained in 92% yield from *p*-$PhC_6H_4\cdot CPh_2Cl$ and NH_2Ph,HCl, is converted by the diazo-reaction into (III). *p*-$PhC_6H_4\cdot CPh_2Cl$ and NH_2Ph in C_6H_6 give 86% of N-*phenyl*-p-*diphenylyldiphenylmethylamine*, m.p. 154—155°; N-p-*diphenylyltriphenylmethylamine*, m.p. 179·5—180·5°, is prepared from CPh_3Cl and 4-aminodiphenyl. C. J. W. (*b*)

Bromonitro-derivatives of diphenyl. L. Guglialmelli and M. R. Franco (Anal. Asoc. Quím. Argentina, 1932, **20**, 8—50).—Bromination of 4-nitrodiphenyl in AcOH yields 4-bromo- and a small amount of 2-bromo-4′-nitrodiphenyl (I), m.p. 102—103° (A., 1927, 236, gives m.p. 82·5°). A 25% yield of (I) is obtained by bromination in H_2O ($+FeCl_3$). 4-Bromo-4′-aminodiphenyl yields the following derivatives: *benzylidene*, m.p. 182—183°; *piperonylidene*, m.p. 129°; *dimethylaminobenzylidene*, m.p. 236°; *thiocarbamide*, m.p. 226°. Reduction of (I) by $SnCl_2$ yields 2-*bromo*-4′-*aminodiphenyl*, m.p. 120—121° (derivatives: *Ac*, m.p. 155—156°; *benzylidene*, m.p. 126—127°; *piperonylidene*, m.p. 124°; p-*dimethylaminobenzylidene*, m.p. 183°; *thiocarbamide*, m.p. 207°), from which 2 : 4′-*dibromodiphenyl*, m.p. 109°, is prepared. The course of substitution in the diphenyl series is discussed. R. K. C.

Substitution in compounds containing two or more phenyl groups. III. Nitration and bromination of 2 : 4 : 6-trimethyldiphenyl. D. H. Hey (J.C.S., 1932, 2636—2640).—Four methods of prep. of 2 : 4 : 6-*trimethyldiphenyl* (I), b.p. 275—277°, are described, the most successful being from diazotised NH_2Ph and mesitylene in presence of aq. NaOH, and from nitrosoacetanilide and mesitylene. Nitration of (I) with HNO_3–AcOH at room temp. gives 3 : 4′-*dinitro*- (II), m.p. 120°, and with more conc. acid, 3 : 5 : 4′-*trinitro*-2 : 4 : 6-*trimethyldiphenyl* (III), m.p. 216°. A mononitro-product could not be prepared. Oxidation of (II) and (III) yields *p*-

nitrobenzoic acid. (II) is reduced and acetylated to 3 : 4′-*diacetamido-*, m.p. 293—294°, and (III) forms with $SnCl_2$, 3 : 5 : 4′-*triamino-*, m.p. 248°, and with Na_2S, 5-*nitro*-3 : 4′-*diamino*-2 : 4 : 6-*trimethyldiphenyl*, m.p. 194° (brominated to the 3′ : 5′-Br_2-compound, m.p. 238°). Bromination of (I) affords 3 : 5 : 4′-*tribromo*-2 : 4 : 6-*trimethyldiphenyl*, m.p. 223°.
F. R. S.

Stereochemistry of 2 : 2′-disubstituted diphenyls. II. Optical resolution of diphenyl-2 : 2′-disulphonic acid. (MISS) M. S. LESSLIE and E. E. TURNER (J.C.S., 1932, 2394—2396; cf. this vol., 942).—NH_4 salts obtained from distrychnine and dibrucine diphenyl-2 : 2′-disulphonates showed activity. From the strychnine H salt *strychnine H* d- ($+7\cdot5H_2O$), m.p. 275—276° (decomp., softens 135°), $[\alpha]^{20}_{5791}$ $-8\cdot5°$, dl- ($+7\cdot5H_2O$), m.p. 145° and 265° (decomp.), $[\alpha]^{20}_{5791}$ $-11\cdot0°$, and l-*diphenyl*-2 : 2′-*disulphonate* ($+4H_2O$), m.p. 143—145° and 209—210°, $[\alpha]^{20}_{5791}$ $-13\cdot8°$, are obtained. Racemic and active NH_4 salts are obtained from these, the latter being racemised at 100° in H_2O. A. A. L.

Chlorination of 1-nitronaphthalene. J. BUFFLE and J. CORBAZ (Arch. Sci. Phys. Nat., 1932, 14, 149—158).—Little HCl is evolved when $1\text{-}C_{10}H_7\cdot NO_2$ (0·5 g.-mol.) dissolved in 50 g. of C_6H_6, PhCl, or CCl_4 is treated with 35·5 g. of Cl_2 during 1 hr. in presence of I (0·635 g.) or $FeCl_3$ (2—3 g.). When the resulting product is heated in vac., progressive decomp. occurs from 100—105°; HCl and nitrogen oxides are evolved and $C_{10}H_8$, $C_{10}H_7Cl$, $C_{10}H_6Cl_2$ (mixture), and $C_{10}H_5Cl_3$, m.p. 102—103°, are isolated. The initial reaction gives a mixture of chloronitronaphthalenes and chlorides of $1\text{-}C_{10}H_7\cdot NO_2$; the chlorides subsequently decompose (when heated) to the above N-free substances. Chlorination during 1·5 hr. affords some *tetrachloronitronaphthalene*, m.p. 176·5°. H. B.

Anthracene derivatives. E. DE B. BARNETT (Ber., 1932, 65, [*B*], 1563—1566).—1 : 4-, 4 : 5-, and 2 : 3-Dichloroanthrone, like the 1 : 5- and 1 : 8-compounds, are reduced by Zn–HCl to the corresponding dichloroanthracenes. Dianthryls are produced from 2-, 3-, and 4-chloroanthrone. Among dimethylanthrones, the pinacol condensation appears to be hindered only when a Me group is in the *peri* position to CO. Oxidation of anthrones with $FeCl_3$ to dianthronyls appears generally independent of the presence of *Bz* substituents. The following substances are described: 1 : 1′-dichloro-, m.p. 288°; 3 : 3′-*dichloro-*, m.p. 288° after softening; 1 : 3 : 1′ : 3′-tetramethyl-, m.p. 284°, and 2 : 3 : 2′ : 3′-*tetramethyl-*, m.p. 310°, *-dianthryl*: 2 : 2′-*dichloro-*, darkens at about 240°; 2 : 3 : 2′ : 3′-*tetrachloro-*, blackens at about 250°; 1 : 4 : 1′ : 4′-*tetrachloro-*, m.p. 275° (decomp.); 2 : 2′-*dimethyl-*, m.p. 210°; 3 : 3′-*dimethyl-*, m.p. 239° (decomp.); 1 : 3 : 2′ : 3′-*tetramethyl-*, m.p. 193°: 1 : 4 : 1′ : 4′-*tetramethyl-*, m.p. 216°; 2 : 3 : 2′ : 3′-*tetramethyl-*, m.p. 222° (decomp.), *-dianthronyl*.
H. W.

Resin acids. I. Synthesis of phenanthrene hydrocarbons derived from *d*-pimaric acid, and a new route to phenanthrene. J. C. BARDHAN and S. C. SENGUPTA (J.C.S., 1932, 2520—2526).—Condensation of β-phenylethyl bromide and the K derivative of Et *cyclo*hexanone-2-carboxylate gives *Et* 2-β-*phenylethyl*cyclo*hexanone-2-carboxylate*, b.p. 184—185°/6 mm. (reduced to the *-hexanol-*, b.p. 182—183°/3 mm.), hydrolysed to 2-β-*phenylethyl*-cyclo*hexanone*, b.p. 154°/6 mm. [*semicarbazone*, m.p. 179—180° (decomp.)], which is reduced by Na and Et_2O to the *-hexanol* (I), b.p. 158—160°/6 mm. (*phenylurethane*, m.p. 115—116°). (I) gives with P_2O_5 1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-octahydrophenanthrene, b.p. 135°/9 mm. (also obtained from diketo-octahydrophenanthrene), dehydrogenated by Se to phenanthrene. 2-Methylphenanthrene, m.p. 54—55° (cf. Haworth, this vol., 608), is similarly prepared; *Et* 4-*methyl*-2-β-*phenylethyl*cyclo*hexanone-2-carboxylate*, b.p. 175—178°/3 mm.; 4-*methyl*-2-β-*phenylethyl*-cyclo-*hexanone*, b.p. 145—147°/3 mm. [*semicarbazone*, m.p. 187° (decomp.)], and *-hexanol*, b.p. 157—160°/6 mm.; 2-*methyl*-1 : 2 : 3 : 4 : 9 : 10 : 11 : 12-*octahydrophenanthrene*, b.p. 137°/6 mm., are the intermediate products.

2 : 5-*Dimethylbenzyl chloride*, b.p. 85—86°/7 mm., is converted into the *cyanide*, b.p. 115—119°/6 mm., which forms *Et* 2 : 5-*dimethylphenylacetate*, b.p. 114°/4 mm. The ester is reduced by Na to β-2 : 5-*dimethylphenylethyl alcohol*, b.p. 110—113°/5 mm., which yields the *bromide*, b.p. 104—106°/5 mm. 1 : 4-*Dimethylphenanthrene*, m.p. 77° (*picrate*, m.p. 155°), has been obtained from *Et* 2-(β-2′ : 5′-*dimethylphenylethyl*)cyclo-*hexanone-2-carboxylate*, b.p. 192—194°/4 mm., reduced to the *-hexanol-*, b.p. 195—198°/4 mm., converted into the corresponding octahydrophenanthrene derivative, b.p. 170—174°/4 mm. *Et* 4-*methyl*-2-(β-o-*tolylethyl*)cyclo-*hexanone-2-carboxylate*, b.p 185—187°/2 mm., is reduced to the *-hexanol-*, b.p. 195—197°/2 mm., converted into 1 : 7-dimethylphenanthrene, identical with the product obtained from *d*-pimaric acid. F. R. S.

Action of aniline on glucose in aqueous solution in presence of acetic acid. C. N. CAMERON and G. H. GUEST (Canad. J. Res., 1932, 7, 237—247).—NH_2Ph and glucose in H_2O react, more rapidly in presence of AcOH, to give a brown amorphous ppt., decomp. 140—146° after darkening at 119°; the reaction is faster in conc. than in dil. solutions. AcOH increases the reactivity of mixtures of NH_2Ph and glucose in H_2O with respect to quinone formation and Selivanov's reaction. It is suggested that there are formed successively glucose-α-anilide, -β-anilide, -anil, and AcCHO or (possibly) an indole derivative.
R. S. C.

Reactions of ω-substituted acetophenone derivatives. III. Comparison of the mechanism of interaction of ω-halogenoacetophenones and of benzyl halides with primary and tertiary bases. J. W. BAKER (J.C.S., 1932, 2631—2636).—The effects of substituents (R=*p*-OMe, *p*-Me, *m*- and *p*-NO_2) on the ψ-unimol. velocity coeffs. for the reactions $C_6H_4R\cdot CH_2\cdot Hal+NH_2Ph \longrightarrow C_6H_4R\cdot CH_2\cdot NHPh+HHal$ and $C_6H_4R\cdot CH_2\cdot Hal+C_5H_5N \longrightarrow C_6H_4R\cdot CH_2\cdot \overset{\oplus}{N}C_5H_5\}\overset{\ominus}{Hal}$ are determined; the reactions are carried out with 10 mols. of the base in *M*/40 solution in 90% EtOH at 30·5°. The above reactions are facilitated by an accession of electrons to the side-chain and they are of the opposite type to those with

$C_6H_4R{\cdot}CO{\cdot}CH_2{\cdot}Hal$ (this vol., 744); anionisation of the halogen is, therefore, the main factor in determining the velocity. The velocity increases in the order $Cl<Br<I$ when R is const. and is the reverse of the order expected. The factors operating in the above reactions are discussed. p-*Methoxybenzylpyridinium bromide* has m.p. 162—163° (decomp.). H. B.

Reactions of unsaturated compounds. I. Addition of arylamines to *cyclo*hexene and 1 : 4-dihydronaphthalene. W. J. Hickinbottom (J.C.S., 1932, 2646—2654; cf. this vol., 1124).—1 : 4-Dihydronaphthalene heated with NH_2Ph and its hydrochloride (hydrobromide, cobaltobromide, or cadmibromide) at 300° gives mainly 2-p-*aminophenyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m.p. 89—90° [*hydrochloride*; *hydrobromide*; *sulphate*; *picrate*, m.p. 186—188° (decomp.); *Ac*, m.p. 184—185°, m-*nitrobenzenesulphonyl*, m.p. 168—169°, and *phenylthiocarbamyl*, m.p. 154—155°, derivatives], together with another primary and a *sec.* amine (not identified). 2-*p*-Hydroxyphenyl-, m.p. 130—131° (softens at 129°) (lit. 129—130°), and 2-*p*-bromophenyl-1 : 2 : 3 : 4-tetrahydronaphthalenes are prepared by the usual methods; oxidation (CrO_3–AcOH) of the latter gives *p*-$C_6H_4Br{\cdot}CO_2H$. *cyclo*Hexene, NH_2Ph, and NH_2Ph,HCl at 230—250° give *o*-[*hydrochloride* (+H_2O); p-*toluenesulphonyl* derivative, m.p. 156—157°] and *p*-aminophenyl*cyclo*hexane (m-*nitrobenzenesulphonyl* derivative, m.p. 160—161°) and *N*-*cyclo*hexylaniline [Ac derivative, m.p. 69—70° (lit. 66°); *hydrochloride*; p-*toluenesulphonyl* derivative, m.p. 141—142° (crystallographic data by E. G. Cox)]. *cyclo*Hexene, *p*-$C_6H_4Me{\cdot}NH_2$, and *p*-$C_6H_4Me{\cdot}NH_2,HCl$ at 270—280° afford N-cyclo*hexyl*-p-*toluidine*, b.p. 161—161·5°/20 mm., m.p. 42—42·5° (also prepared from *p*-$C_6H_4Me{\cdot}NH_2$ and *cyclo*hexyl bromide at 130°) [*hydrochloride*; *Ac*, m.p. 87—88° (crystallographic data given), *NO*-, m.p. 57—58°, p-*toluenesulphonyl*, m.p. 133—134°, and m-*nitrobenzenesulphonyl*, m.p. 143—144°, derivatives], and 4-*amino*-3-cyclo*hexyltoluene*, b.p. 167—168°/21 mm. (*hydrochloride*; *Ac* derivative, m.p. 136—137°), separable through the differing solubilities of their oxalates in EtOH and H_2O. H. B.

Steric hindrance. VI. J. von Braun and K. Weissbach (Ber., 1932, 65, [*B*], 1574—1580; cf. A., 1931, 1407).—The extent to which *o*-substituted *sec.* bases react with CPhCl:NPh or $CPhCl{:}N{\cdot}C_6H_4Me$ in Et_2O at 25° during 120 hr. according to the equation 2 mols. base + 1 mol. imide chloride = 1 mol. amidine + 1 mol. base,HCl is measured and compared with the amounts of Ac and chloroacetyl compounds of the corresponding primary bases which after equally prolonged action of PCl_5 undergo further change as imide chlorides and with the extent to which the corresponding Me_2 bases add MeI. The first type of change is more impeded by Me than by halogen, in qual. agreement with the experiments on the Ac derivatives, but reversing the results of the addition of MeI. In the first type of change the difference in the influence of Cl and Br is sharply marked, but this is not the case with the second and third types. In the first type OMe has a smaller influence than Cl or Br and apparently no effect in the remaining types.

o-$C_6H_4Cl{\cdot}NMe_2$ is converted by β-phenylpropionic acid at about 225° into β-*phenylpropion*-o-*chlorophenylmethylamide*, b.p. 230—232°/15 mm., hydrolysed by conc. HCl at 130° to *o*-chloromethylaniline, b.p. 95°/14 mm. β-*Phenylpropion*-m-*chlorophenylmethylamide*, b.p. 239—241°/15 mm., and -m-*tolylmethylamide*, b.p. 211—214°/15 mm., similarly afford the corresponding pure *sec.* bases. *o*-$C_6H_4Cl{\cdot}NH_2$ is converted into the formyl derivative, which is treated successively with NaOEt and EtBr; hydrolysis and nitrosation afford *nitroso*-o-*chlorophenylethylamine*, b.p. 148—150°/14 mm., reduced by $SnCl_2$ and conc. HCl to *o*-chlorophenylethylamine, b.p. 99°/14 mm. (*picrate*, m.p. 124°). The formyl compound of *o*-$C_6H_4Br{\cdot}NH_2$ is transformed by Me_2SO_4, hydrolysis, and nitrosation into *nitroso*-o-*bromophenylmethylamine*, b.p. 154—156°/14 mm., and thence into *o*-$C_6H_4Br{\cdot}NHMe$, b.p. 117°/14 mm. (*picrate*, m.p. 105°). o-*Formamidodiphenyl ether*, m.p. 100°, is similarly converted into *nitrosomethylaminodiphenyl ether*, b.p. 198—200°/13 mm., and thence into o-*methylaminodiphenyl ether*, b.p. 170°/13 mm., m.p. 48° (*hydrochloride*, m.p. 134°; *picrate*, m.p. 149°). The following -*benzamidines* are described: N′-*phenyl*-N-o-*tolyl*-N-*methyl*-, b.p. 226—223°(?)/13 mm., m.p. 89° (*picrate*, m.p. 179°); N′-p-*tolyl*-N-o-*tolyl*-N-*methyl*-, b.p. 237—239°/12 mm., m.p. 94° (*picrate*, m.p. 128°); N′-*phenyl*-N-o-*tolyl*-N-*ethyl*-, b.p. 227—229°/14 mm., m.p. 76° (*picrate*, m.p. 76°); N′-*phenyl*-N-o-*chlorophenyl*-N-*methyl*-, b.p. 228—230°/13 mm., m.p. 120° (*picrate*, m.p. 175°); N-o-*chlorophenyl*-N′-p-*tolyl*-N-*methyl*-, b.p. 242—244°/12 mm., m.p. 116° (*picrate*, m.p. 209°); N′-*phenyl*-N-o-*chlorophenyl*-N-*ethyl*-, b.p. 240°/13 mm., m.p. 123° (*picrate*, m.p. 177°); N′-*phenyl*-N-o-*bromophenyl*-N-*methyl*-, b.p. 245°/13 mm., m.p. 107—110° (non-cryst. *picrate*); N-o-*bromophenyl*-N′-p-*tolyl*-N-*methyl*-, b.p. 250°/14 mm., m.p. 103° (*picrate*, m.p. 204°); N′-*phenyl*-N-o-*anisyl*-N-*methyl*-, b.p. 252—255°/13 mm., m.p. 114° (*picrate*, m.p. 137°); N-o-*anisyl*-N′-p-*tolyl*-N-*methyl*-, b.p. 252—255°/13 mm., m.p. 106° (*picrate*, m.p. 168°); N′-*phenyl*-N-o-*phenoxyphenyl*-N-*methyl*-, b.p. 275—280°/12 mm., non-cryst. (*hydrochloride*, m.p. 238°); NN′-*diphenyl*-N-*methyl*-, b.p. 226—228°/13 mm., m.p. 47° (*picrate*, m.p. 189°); NN′-*diphenyl*-N-*ethyl*-, b.p. 225°/13 mm., m.p. 88° (non-cryst. *picrate*); N′-*phenyl*-N-m-*tolyl*-N-*methyl*-, b.p. 232—234°/13 mm., m.p. 98° (*picrate*, m.p. 181°); N′-*phenyl*-N-m-*chlorophenyl*-N-*methyl*-, b.p. 238—240°/13 mm., m.p. 89° (*picrate*, m.p. 188°). H. W.

Decomposition of quaternary ammonium hydroxides. J. von Braun and K. Hamann (Ber., 1932, 65, [*B*], 1580—1586).—Quant. investigation of the mixture of propenes, $X{\cdot}C_6H_4{\cdot}CH{:}CH{\cdot}CH_2Ph$ and $X{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH{:}CHPh$, obtained by decomp. of quaternary hydroxides $X{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(NMe_3{\cdot}OH){\cdot}CH_2Ph$ indicates that the method is suitable for the comparison of the tenacity of H atoms in CH_2 groups in complicated CH_2Ph residues in which the effect of substituents in the C_6H_6 nucleus is not obvious. The mixture of propenes is ozonised and the aldehydes are determined by treatment with dil. H_2SO_4 and $CH_2Ph{\cdot}CHO$ followed by steam-distillation. It is found, for example, that treatment of *n* mols. of PhCHO and *m* mols. of $C_6H_4Me{\cdot}CHO$ with $n+m$ mols.

of $\mathrm{CH_2Ph\cdot CHO}$ yields an aldehyde distillate in which PhCHO and $\mathrm{C_6H_4Me\cdot CHO}$ are in the exact ratio $n : m$.

β-Phenyl-α-*p*-methylbenzylpropionyl chloride is converted into the *amide*, m.p. 134°, and thence by NaOMe and Br followed by dil. AcOH into the *urethane*, m.p. 67°, which when distilled with CaO in $\mathrm{N_2}$ affords *α-phenyl-γ-*p*-tolyl-β-propylamine*, b.p. 191—192°/12 mm. (*hydrochloride*, m.p. 214°; *picrate*, m.p. 158°; *Bz* derivative, m.p. 155°). The corresponding *methiodide*, m.p. 164°, when transformed into the hydroxide and decomposed by alkali yields 34% of α-phenyl-γ-*p*-tolyl-Δ^{β}-propene and 66% of α-phenyl-γ-*p*-tolyl-Δ^{α}-propene. *β-Phenyl-α-*m*-methylbenzylpropionamide*, m.p. 91°, affords the *urethane* $\mathrm{CH_2Ph\cdot CH(NH\cdot CO_2Me)\cdot CH_2\cdot C_6H_4Me}$, m.p. 56°, and *α-phenyl-γ-*m*-tolyl-β-propylamine*, b.p. 194—195°/12 mm. (*hydrochloride*, m.p. 161°; *picrate*, m.p. 175°; *Bz* derivative. m.p. 130°). The corresponding quaternary *iodide*, m.p. 134°, is transformed through the hydroxide into a mixture of 73% of α-phenyl-γ-*m*-tolyl-Δ^{β}-propene and 27% of α-phenyl-γ-*m*-tolyl-Δ^{α}-propene. *Et benzyl-*p*-chlorobenzylmalonate*, b.p. 245—250°/12 mm., yields the dicarboxylic acid and thence *β-phenyl-α-*p*-chlorobenzylpropionic acid*, b.p. 220—223°/0·2 mm., m.p. 88°, transformed through the *amide*, m.p. 151°, and *urethane*, m.p. 100°, into *α-phenyl-γ-*p*-chlorophenyl-β-propylamine*, b.p. 212—214°/12 mm. (*hydrochloride*, m.p. 212°; *Bz* derivative, m.p. 155°). From the *methiodide*, m.p. 216°, a mixture of 75% of α-phenyl-γ-*p*-chlorophenyl-Δ^{β}-propene and 25% of the -Δ^{α}-propene is obtained. *Et benzyl-*m*-chlorobenzylmalonate*, b.p. 240—245°/12 mm., affords successively the dicarboxylic acid, *β-phenyl-α-*m*-chlorobenzylpropionic acid*, b.p. 200—215°/0·1 mm., m.p. 71°, the *amide*, m.p. 69°, *methylurethane*, m.p. 99°, and *α-phenyl-γ-*m*-chlorophenyl-β-propylamine*, b.p. 210—213°/12 mm. (*hydrochloride*, m.p. 204°; *picrate*, m.p. 178°; *Bz* compound, m.p. 162°). The *methiodide*, m.p. 196°, affords a mixture of 77% of α-phenyl-γ-*m*-chlorophenyl-Δ^{β}-propene and 23% of the -Δ^{α}-propene. H. W.

Chromability rule concerning azo-dyes derived from hydroxyquinolines and additive rule relating to azo-dyes in general. C. COURTOT and H. HARTMAN (Bull. Soc. chim., 1932, [iv], **51**, 1179—1199).—Azo-dyes are prepared by coupling diazotised sulphanilic, metanilic, α-naphthylamine-5-sulphonic, amino-G, amino-R, naphthionic, and anthranilic acids with 3-, 5-, 6-, 7-, and 8-hydroxyquinolines; 2- and 4-hydroxyquinolines do not couple. The colours of the dyes on wool are recorded; the bathochromic effect of the OH group increases as it approaches the N atom. Only those hydroxyquinolines containing a OH group in an α-position of the benzenoid ring (*i.e.*, the 5- and 8-derivatives) confer chromability on their azo-dyes; this is the sixth rule of chromability. The azo-dyes derived from anthranilic acid and 3-, 6-, and 7-hydroxyquinolines are chromable, as are those obtained similarly using $\beta\text{-}\mathrm{C_{10}H_7\cdot OH}$, and R- and G-acids; in all these dyes the OH and $\mathrm{CO_2H}$ groups are both *ortho* to $\mathrm{\cdot N{:}N\cdot}$ (such an arrangement confers chromability; this is designated the fifth rule). The only exception to the above rules is the azo-dye from 7-hydroxyquinoline and amino-R-acid; this dye is chromable. The causes of chromability of azo-dyes are discussed briefly. H. B.

Azo chromophore. IV. J. S. P. BLUMBERGER (Chem. Weekblad, 1932, **29**, 454—464).—The idea that the colour of azo-dyes depends on an equilibrium between quinonoid and azoid forms (Hodgson, A., 1929, 1298; 1930, 596, 906) fails to account for the bathochromic effect of the *p*-$\mathrm{NO_2}$ group in *p*-nitrobenzeneazo-*p*-dimethylaniline and the sensitivity of disazo-dyes of the type sulphanilic acid$\longrightarrow$*p*-$\mathrm{C_6H_4(NH_2)_2}$$\longrightarrow$1 : 4-naphtholsulphonic acid, to alkalis. Similarly, Burawoy's views (A., 1931, 144, 544, 1052) are contrary to the ionogenic properties of these dyes. The light absorption curves and the sensitivity to acids and alkalis of a large no. of monoazo-dyes are satisfactorily explained on simple polarity relationships between chromophore and substituents (A., 1928, 966; 1931, 721). A *m*- or *peri*-$\mathrm{NH_2}$ group in *o*-hydroxyazo-dyes has an unexpectedly marked effect on shade. In disazo-dyes containing a system of two conjugated chromophores, the additional $\mathrm{PhN_2}$ group has a strong bathochromic effect, which may be greatly reduced or intensified by the position of a $\mathrm{SO_3H}$ group in the benzidine mol. On account of the co-ordination between the OH group and the azo-linking, *o*-hydroxyazo-dyes show greater differences in shade etc. than *p*-hydroxy- or *o*- or *p*-aminoazo-dyes. Non-conjugated chromophoric systems have little or no effect, the systems acting independently. Nearly 100 light absorption curves are given. S. C.

Formation of azoxy-, azo-, hydrazo-, and benzidine compounds and the dyes derived from the latter. R. N. SEN and R. SADASIVAM (J. Indian Chem. Soc., 1932, **9**, 403—411).—6-Nitrocoumarin is reduced by Zn dust and aq. $\mathrm{EtOH\text{–}NH_4Cl}$ to 6-aminocoumarin (30%) and 6 : 6′-*azoxycoumarin*, m.p. >300° (60%); a solution of the latter in aq. NaOH treated with HgO gives 5 : 5′-*azoxy-*o*-coumaric acid*, decomp. above 270° (*Et*$_2$ ester, m.p. > 250°). Reduction of *m*-$\mathrm{NO_2\cdot C_6H_4\cdot CO_2H}$ with Zn dust and aq. EtOH–NaOH gives *m*-hydrazobenzoic acid, rearranged by HCl to 4 : 4′-diaminodiphenic acid. *o*-$\mathrm{NO_2\cdot C_6H_4\cdot OH}$ is similarly reduced to *o-hydrazophenol*, m.p. 148° (*Bz*$_2$ derivative, m.p. 186°), rearranged to 3 : 3′-*dihydroxybenzidine* (I), m.p. 160° (*dihydrochloride*, m.p. 144°; *Bz*$_4$ derivative, m.p. 180°; *Br*$_2$-derivative, m.p. 174°), converted by boiling AcOH–NaOAc into the *dimethyldibenzoxazole*, m.p. 187°. *Dyes* (m.p. and shades on cotton quoted in parentheses) are prepared from tetrazotised (I) and $\beta\text{-}\mathrm{C_{10}H_7\cdot OH}$ (150°; pink), β-naphtholsulphonic acid (decomp. above 250°; pink), $\beta\text{-}\mathrm{C_{10}H_7\cdot NH_2}$ (>250°), $\mathrm{NPhMe_2}$ (>250°). 2 : 2′-Dihydroxybenzidine is similarly prepared from *m*-$\mathrm{NO_2\cdot C_6H_4\cdot OH}$. Reduction of *m*-$\mathrm{NO_2\cdot C_6H_4\cdot CHO}$ with Zn dust and aq. EtOH–NaOH gives *m-azobenzyl alcohol*, m.p. 117° (*Ac*$_2$ derivative), or *m-hydrazobenzyl alcohol*, m.p. 268° (*Ac*$_2$, decomp. above 220°, and *Bz*$_2$ derivatives); the latter is rearranged to 2 : 2′-*di(hydroxymethyl)benzidine*, m.p. 177° [*Bz*$_4$, m.p. 233°, *Ac*$_4$, m.p. >250°, and *Br*$_2$-, m.p. >270°, derivatives; *dyes* by coupling with $\beta\text{-}\mathrm{C_{10}H_7\cdot OH}$ (deep red on silk), β-naphtholsulphonic acid (deep red), $\beta\text{-}\mathrm{C_{10}H_7\cdot NH_2}$ (120°), and $\mathrm{NPhMe_2}$ (>250°)]. *o*-$\mathrm{NO_2\cdot C_6H_4\cdot CHO}$ is similarly reduced to o-*hydrazobenzyl alcohol*, m.p. 200° (*Ac*$_2$, m.p. >250°, and *Bz*$_2$, m.p. 107°, derivatives), rearranged to 3 : 3′-*di*(*hydroxymethyl*)*benzidine*, m.p. 185° [*Ac*$_4$, *Bz*$_4$, and *Br*$_2$-derivatives, all m.p. >250°; *dyes* by coupling with β-$C_{10}H_7$·OH (>250°; bluish-violet on silk), β-naphtholsulphonic acid (red), β-$C_{10}H_7$·NH_2 (>250°; reddish-orange on silk), $NPhMe_2$ (>250°; violet on silk)]. The ease of the benzidine rearrangement with the above substituted hydrazobenzenes is OH>CO_2H>CH_2·OH; the *m*-are generally transformed more readily than the *o*-compounds. H. B.

Sensitised photolysis of azo-compounds by zinc oxide. I. Fukushima, M. Horio, and M. Ohmori.—See this vol., 1215.

Losses in the production of benzidine bases and the reductive cleavage of aromatic hydrazo-compounds during rearrangement. III. V. A. Izmailski, E. P. Rustanovich, and P. T. Shpuntenok (Anilinokras. Prom., 1932, 2, No. 3, 10—16).—In the prep. of the hydrazo-compound the formation of NH_2Ph is decreased by carrying out the process in two stages: (1) reduction of $PhNO_2$ to azoxybenzene with Zn dust in alkaline medium, (2) reduction to hydrazobenzene at 57—65° at low alkali concn., preferably in 3—4% solution with Fe. Extraction of reduction sludge at ≮100° leads to much decomp. with formation of amines. Reductive decomp. is greater with HCl than with H_2SO_4. It is proposed that the sludge should be extracted at a lower temp. and that the rearrangement be effected without separation of hydrazo-compound from its solution in hydrocarbon. The best solvents are PhCl and liquid $C_6H_4Cl_2$. Ch. Abs.

Replacement of the diazonium group by chlorine or bromine. H. W. Schwechten (Ber., 1932, 65, [*B*], 1605—1607).—The base is diazotised and transformed by $HgCl_2$ in KCl or by $HgBr_2$ [or $Hg(NO_3)_2$] in KBr into the corresponding complex salt, which is collected and dried by $COMe_2$, MeOH, or Et_2O. Mixed with twice its weight of KCl or KBr it is heated from above in a vertical tube sufficiently strongly to cause complete decomp. of the diazonium salt; sometimes it is advisable to heat so that the halogeno-compound is volatilised. Examples cited are: 2 : 2′-diamino- to 2 : 2′-dibromo-diphenyl, m.p. 80—81° (yield 80%) and to 2 : 2′-dichlorodiphenyl, m.p. 60·5° (yield >80%); *p*-C_6H_4Br·NH_2 to *p*-C_6H_4ClBr, m.p. 66—67° (yield about 85%) [the double salt of C_6H_4Br·N_2Cl and $HgCl_2$ mixed with KBr gives mainly *p*-$C_6H_4Br_2$, which is the sole product from C_6H_4Br·N_2Br and $HgBr_2$ in presence of KCl]; β-$C_{10}H_7$·NH_2 to 2-$C_{10}H_7Br$ (yield about 65%). The use of complex salts containing $SbCl_3$ and $SnCl_4$ is also indicated. H. W.

Action of ethyl oxalate on *o*-aminophenols. E. Puxeddu and G. Sanna (Gazzetta, 1932, 62, 558—566).—*o*-NH_2·C_6H_4·OH condenses with $EtHC_2O_4$ or $Et_2C_2O_4$ to *NN′-bis*-o-*hydroxyphenyloxamide*, m.p. 280° (decomp.) (*Ac*$_2$ derivative, m.p. 201°). Similarly 3-amino-*p*-cresol yields *NN′-bis*-(4-*hydroxy*-m-*tolyl*)-*oxamide*, m.p. 282°, and 4-*hydroxy*-m-*tolyloxamic acid*, m.p. 170°, resolidifying to 6-methyl-2 : 3-diketophenmorpholine, form of m.p. 230° (cf. A., 1931, 747), which is also a product of the condensation. 5-Aminoeugenol with $EtHC_2O_4$ gives 4-*hydroxyeugenyl*-5-*oxamic acid*, m.p. 233—235°, but with $Et_2C_2O_4$ or $C_2O_2Cl_2$ the product is 6-*allyl*-8-*methoxy*-2 : 3-*diketophenmorpholine*. E. W. W.

Dimorphism of phenacetin [acet-*p*-phenetidide]. R. Fischer and A. Kofler (Arch. Pharm., 1932, 270, 433—435).—Phenacetin exists in stable, m.p. 134—135°, and metastable, m.p. 128—129°, modifications. H. B.

Resolution of α-*m*-hydroxyphenylethylmethylamine and preparation of *d*- and *l*-miotine (methylurethanes of *d*- and *l*-α-*m*-hydroxyphenylethyldimethylamine). J. M. Macdonald and E. Stedman (J.C.S., 1932, 2513—2519).—*dl*-α-*m*-Methoxyphenylethylmethylamine, b.p. 117—118°/15 mm. (*hydrochloride*, m.p. 152—153°), best prepared from the -ethyl bromide and NH_2Me in MeCN, is demethylated (aq. HBr) to *dl*-α-*m*-hydroxyphenylethylmethylamine, m.p. 160°, which is resolved by treatment of its *hydrochloride*, m.p. 160°, first with aq. NH_4 *d*- and then with NH_4 *l*-bromocamphor-π-sulphonate. d- and l-α-m-*Hydroxyphenylethylmethylamines*, m.p. 171°, $[\alpha]_D$ ±68° in C_5H_5N [*hydrochlorides*, m.p. 201°, $[\alpha]_D$ ±20° in H_2O; d- and l-*bromocamphor*-π-*sulphonates* (hydrated), m.p. about 193°, respectively], are converted by H_2 in presence of PtO_2, MeOH, and aq. CH_2O into d-, m.p. 116°, $[\alpha]_D$ +55·8° in EtOH {*hydrochloride*, m.p. 161°, $[\alpha]_D$ +15·2° in H_2O; *methylurethane* (=d-*miotine*), m.p. 85°, $[\alpha]_D$ +37° in EtOH [*hydrochloride*, m.p. 167° (decomp.) (sinters at about 160°), $[\alpha]_D$ +10·6° in H_2O]}, and l-α-m-*hydroxyphenylethyldimethylamine*, m.p. 116°, $[\alpha]_D$ −55·8° in EtOH {*hydrochloride*, m.p. 161°, $[\alpha]_D$ −15° in H_2O; *methylurethane* (=l-*miotine*), m.p. 85°, $[\alpha]_D$ −35·7° in EtOH [*hydrochloride*, m.p. 167° (decomp.), $[\alpha]_D$ −10·2° in H_2O]}, respectively. *dl*-α-*m*-Hydroxyphenylethyldimethylamine and its methylurethane (=*dl*-miotine) (A., 1929, 692) could not be resolved. H. B.

Recognition of dithio-*o*-toluidine as 2 : 2′-diamino-5 : 5′-ditolyl disulphide. R. Child (J.C.S., 1932, 2666).—The identification (cf. Hodgson and France, this vol., 943) was carried out by Child and Smiles (A., 1926, 1243) by a different method. F. R. S.

Preparation and germicidal properties of *p*-hydroxyphenyl alkyl sulphides. C. M. Suter and H. L. Hansen (J. Amer. Chem. Soc., 1932, 54, 4100—4104).—The following sulphides are prepared, generally from SHAr, alkyl bromide, and EtOH–NaOEt: PhSMe, b.p. 58—60°/6 mm.; *p*-OMe·C_6H_4·SMe, b.p. 99°/4 mm.; *p*-OMe·C_6H_4·SEt, b.p. 103°/5 mm.; *anisyl Pr*, b.p. 110°/5 mm., *Bu*, b.p. 120°/5 mm., *amyl*, b.p. 127°/5 mm., and *hexyl*, b.p. 142°/5 mm., *sulphides*; p-*ethoxyphenyl Me*, b.p. 98—100°/5 mm., m.p. 19—20°, and *Et*, b.p. 110—112°/6 mm., *sulphides*. *Anisyl Me*, m.p. 119—120°, and *Et*, m.p. 55—56°, and p-*ethoxyphenyl Me*, m.p. 89—89·5°, *sulphones* are prepared. The following *p*-hydroxyphenyl alkyl sulphides are prepared from the anisyl derivatives and HBr in AcOH: *Pr*, m.p. 33—33·5°; *Bu*, m.p. 36—37°; *amyl*, m.p. 55—56°; *hexyl*, m.p. 58—59°. The germicidal properties of these last sulphides are at a max. towards *B. typhosus* with the Bu and amyl derivatives. The hexyl compound is probably the most effective towards *S. aureus*, since its PhOH coeff. is not much higher than that of the amyl derivative. The at. refraction of S in these compounds is abnormally great. C. J. W. (*b*)

Manufacture of nitroaminodiphenyl sulphides. Soc. Anon. des Mat. Col. et Prod. Chim. de St. Denis, and R. Lantz.—See B., 1932, 974.

Action of gaseous cyanogen on phenols. I. The three dihydroxybenzenes. G. Machek (Monatsh., 1932, **61**, 87—98).—Gaseous $(CN)_2$ and aq. pyrocatechol in absence of air give 2 : 3-*dihydroxybenzonitrile* (I), m.p. 197—198° [3(?)-*Ac*, m.p. 182—184°, and *Bz* derivatives; the diacyl derivatives could not be prepared]. With excess of Me_2SO_4 and NaOH (I) gives veratrole and a small amount of unidentified *substance*, m.p. 214—216°, whilst under milder conditions a Me ether seems to be formed, but cannot be isolated. Attempts to hydrolyse (I) to the corresponding carboxylic acid gave only pyrocatechol and unidentified products. Under similar conditions resorcinol and quinol give with $(CN)_2$ additive *compounds*, $C_6H_6O_2,(CN)_2$, m.p. 92—94° (decomp.), and 120—121° (decomp.), respectively. H. A. P.

Styphnic acid. I. Preparation and properties. P. P. T. Sah (Sci. Rep. Nat. Tsing Hua Univ., 1932, **1**, 197—199).—Styphnic acid (modified prep.) with egg-white gives a ppt. of protein styphnate, and is reduced to styphnamic acid in hot, alkaline solution by glucose and by creatinine present in urine. When warmed with PCl_5 it explodes. R. S. C.

4-Aminoresorcinol and its reactions. N. N. Voroschcov and A. M. Gorkov (J. Gen. Chem. Russ., 1932, **2**, 421—432).—4-Aminoresorcinol, prepared by reduction of 4-benzeneazoresorcinol (I), is stable only as hydrochloride (N-*Ac* compound, m.p. 164—165°; Ac_3, m.p. 113°, and Ac_4 compound, m.p. 106—108°). It can be diazotised in presence of $CuCl_2$ or $NiCl_2$; the cryst., explosive product is probably a quinonediazide. An attempted Sandmeyer reaction gave an orange cryst. *product*, m.p. 126·5—127·5°, probably resorcinolazochlororesorcinol. *Resorcinolazoresorcinol* can be separated into two forms, both forming brown needles, by crystallisation from AcOH, one giving a cherry-red solution in H_2SO_4 and a reddish-violet one in aq. NH_3, the other brown solutions. *Resorcinolazo-β-naphthol*, m.p. 192°, gives brownish-red solutions in alkalis and violet ones in aq. NH_3. The Me_2 ether of (I) is reduced to 2 : 4-$NH_2·C_6H_3(OMe)_2$,HCl (Ac derivative, m.p. 115—116°), oxidised by $FeCl_3$ to 2-*methoxy*-3-1′ : 4′-*dimethoxyanilino*-p-*benzoquinone*, m.p. 153—154°. 2 : 4-*Dimethoxybenzeneazoresorcinol* has m.p. 178—179°, and 2 : 4-*dimethoxybenzeneazo*-β-*naphthol*, m.p. 148—149°. Benzenediazonium chloride couples with resorcinol Me ether to the *Me ether* of resorcinoldisazobenzene, m.p. 172—173°, further methylated by Me_2SO_4 and KOMe to the *Me_2 ether*, m.p. 151°. G. A. R. K.

Constitution of cholesterol. R. Robinson (Nature, 1932, **130**, 540—541).—A formula which identifies the cholesterol C skeleton with that of squalene less 3 C atoms has been devised. Cholesterol may be 2 : 6 : 22-trimethyl-(7 : 24)(8 : 22)(12 : 21)(16 : 20)-tetra*cyclo*tetracosen-$\Delta^{16:17}$-14-ol. The *sec.* alcoholic group and the double linking of cholesterol are better moved one position to the left in the graphic formula as usually given. L. S. T.

Constitution of cholesterol. R. Robinson (Nature, 1932, **130**, 665—666). L. S. T.

Dehydrogenation of phytosterols with selenium. H. Dieterle and A. Salomon (Arch. Pharm., 1932, **270**, 495—501).—Dehydrogenation of sterol acetates proceeds under milder conditions and gives better yields of products than with the sterols themselves.

[With C. Coester.] Lupeol is dehydrogenated by Se at 230—240° to a *compound*, $C_{27}H_{44}O$, m.p. 199—200°, whilst acetyl-lupeol similarly gives *lupane*, $C_{27}H_{48}$, m.p. 184—185°, *lupene* (I), $C_{27}H_{46}$, m.p. 180—181°, the *acetate*, m.p. 242—243°, of dihydrolupeol, m.p. 201° (Ruzicka *et al.*, A., 1929, 932), and a *substance*, $C_{24}H_{40}O$, m.p. 207—208°.

[With W. Rosenfelder.] α-Amyrin benzoate is dehydrogenated (cf. A., 1931, 624) to a hydrocarbon (b.p. 225—250°/11 mm.), $C_{15}H_{20}$ (*picrate*, m.p. 133°), and *amyranene*, $C_{27}H_{46}$, m.p. 182—183°, which is not identical with (I).

Betulin diacetate is dehydrogenated to (mainly) a *compound*, $C_{19}H_{32}O$, m.p. 167·5—168°, and betulin monoacetate, whilst cholesteryl acetate gives β-cholestane but no chrysene. H. B.

Halogen analogues of adrenaline and ephedrine. I. ω-3 : 4-Dichlorophenyl-β-aminoethanol. H. E. Glynn and W. H. Linnell (Pharm. J., 1932, **129**, 249—250).—*o*-$C_6H_4Cl_2$, $AlCl_3$, and $CH_2Cl·COCl$ give ω : 3 : 4-*trichloroacetophenone*, m.p. 44°, which with NH_3 or with NH_2Me in H_2O or C_6H_6 gives 3 : 4-*dichloro-ω-hydroxyacetophenone*, m.p. 137°. 3 : 4-Dichloroacetophenone (Roberts and Turner, A., 1927, 975) and amyl nitrite afford the *oximino*-derivative, m.p. 143°, reduced to 3 : 4-dichloro-ω-aminoacetophenone [*hydrochloride* (I) resinifies at 255°], and then to the *hydrochloride* (II) of β-amino-α-3 : 4-dichlorophenylethyl alcohol. The results of a pharmacological examination of (I) and (II) are given. W. S.

Benzyl alkyl ethers. P. P. T. Sah and M. Lei (Sci. Rep. Nat. Tsing Hua Univ., 1932, **1**, 193—195).—The b.p., n_D, and *d* at 20° and 25° are recorded for the following benzyl alkyl ethers (prepared from CH_2PhCl, Na alkoxide, and the corresponding alcohol): Me, Et, Pr^{α}, Pr^{β}, Bu^{α}, Bu^{β}, and *iso*amyl. R. S. C.

Comparative stability of isomerides according to their absorption spectra. Transpositions in the arylglycol series. (Mme.) Ramart-Lucas and F. Salmon-Legagneur (Bull. Soc. chim., 1932, [iv], **51**, 1069—1087).—The dehydration (by heat) of arylethylene glycols to aldehydes or ketones and the transformation (by heat) of aldehydes into ketones are studied. The results agree with those predicted from the rules previously proposed (A., 1928, 760) for the relationship between intramol. transformations and absorption spectra. Thus, hydrobenzoin passes at about 300° into (mainly) $CHPh_2$·CHO but at 450° deoxybenzoin (also formed from $CHPh_2$·CHO at 500°) results; αα-diphenylethylene glycol similarly gives $CHPh_2$·CHO or deoxybenzoin; *αα-di-*p*-tolylethylene glycol*, m.p. 110° (from Mg *p*-tolyl bromide and CH_2OH·CO_2Et), affords di-*p*-tolylacetaldehyde at 160—190°/0·7—1 mm. or *p*-tolyl *p*-methylbenzyl ketone at 250—450°; β-phenylpropane-αβ-diol yields CHPhMe·CHO at 250—300° or benzyl Me ketone at 550°; β-phenylbutane-αβ-diol (improved prep. given) furnishes α-phenylbutaldehyde at 300° or benzyl Et ketone at 460°; *βγ-diphenylpropane-αβ-diol*, m.p. 73° (obtained together with a *compound*, $C_{22}H_{22}O$, m.p. 92°, probably β-phenyl-ββ-dibenzylethyl alcohol, from CH_2Ph·MgCl and benzoylcarbinyl acetate), gives αβ-diphenylpropaldehyde (*semicarbazone*, m.p. 120—121°) and a trace of a *hydrocarbon*, $C_{15}H_{12}$, m.p. 167°, at 300° [at 500°, the hydrocarbon is the sole product, and it is obtained similarly from αβ-diphenylpropaldehyde, Ph β-phenylethyl ketone, or dibenzyl ketone; the hydrocarbon is probably identical with that obtained from 1-phenylindene by Mayer and Sieglitz (A., 1921, i, 554)]. All the experiments are carried out by distilling the glycols at 10—20 mm. or lower) through a tube packed with kieselguhr heated to the requisite temp. Ultra-violet absorption curves of many of the above compounds are given. H. B.

Dehydration of ditertiary acenaphthene glycols. N. MAXIM (Bull. Soc. chim., 1932, [iv], 51, 1147—1151).—3-Bromoacenaphthenequinone (I) and MgEtBr give 3-*bromo*-7 : 8-*dihydroxy*-7 : 8-*diethylacenaphthene*, m.p. 196°, dehydrated by conc. HCl in AcOH to 3-*bromo*-7 : 8-*diethylideneacenaphthene* (II), m.p. 159°, which is oxidised by $Na_2Cr_2O_7$–AcOH to (I) and 4-bromonaphthalic anhydride. The colour (orange-red) of (II) is deeper than that of the parent 7 : 8-diethylideneacenaphthene (A., 1928, 1137). H. B.

Mechanism of hydrolysis of phenyl benzoate in aqueous ethyl alcohol. C. W. GIBBY and W. A. WATERS (J.C.S., 1932, 2643—2646).—The sequence of reactions in the hydrolysis of BzOPh with NaOH in 95% EtOH at 30° is: (i) $EtOH+NaOH \rightleftharpoons NaOEt+H_2O$; (ii) $BzOPh+NaOEt \longrightarrow BzOEt+NaOPh$ (rapid); (iii) $BzOEt+NaOH \longrightarrow NaOBz+EtOH$ (slow). The presence of free PhOH in a mixture of BzOPh, NaOH, and EtOH can be detected (Br-H_2O; diazo-coupling) in <1 min.; BzOEt is isolated in almost quant. yield after 5 min. The rate of hydrolysis of BzOEt by NaOH is decreased greatly by the presence of free PhOH. Hydrolysis in the mixed solvent probably proceeds by ionic additive mechanisms involving OH′, OEt′, and OPh′. H. B.

Action of potassium pyrosulphite on aromatic acid chlorides. Preparation of aromatic anhydrides. I. GASOPOULOS (Praktika, 1931, 6, 347—353; Chem. Zentr., 1932, i, 3171—3172).—The aromatic acid chloride (1 mol.) is heated in C_6H_6 with a *tert.* base (1 mol.; C_5H_5N, NMe_2Ph, quinoline) in presence of excess of $K_2S_2O_5$; the corresponding acid anhydride is obtained in good yield. *p*-Nitrobenzoyl chloride affords the anhydride in 70% yield. A. A. E.

Action of ammonia and amines on the esters of unsaturated acids. II. Action of ammonia, methylamine, and diethylamine on ethyl cinnamate. K. MORSCH (Monatsh., 1932, 61, 299—308).—Interaction of Et cinnamate and EtOH–NH_3 at room temp. for 30 weeks gives unchanged ester (42·6%), Et β-amino-β-phenylpropionate (I) (13%), β-amino-β-phenylpropionamide [*H oxalate*, m.p. 171·5° (decomp.)] (12%), and cinnamamide [*oxalate*, m.p. 160·5—161° (decomp.)] (20·1%); reaction is slower than with liquid NH_3 at room temp. (Stosius and Philippi, A., 1925, i, 918). Liquid NH_3 at 100°/70 hr. gives unchanged ester (35%), (I) (35%), and a mixture of the amides (21·4%). Et cinnamate and EtOH–NH_2Me at room temp. for 14 days afford unchanged ester (32·5%), Et β-methylamino-β-phenylpropionate (32·5%), and β-methylamino-β-phenylpropionmethylamide (about 26%); at 100°/24 hr. the corresponding % are 17·3, 17·8, and about 46. Addition of $NHEt_2$ across the double linking does not occur; there is no reaction at room temp., but at higher temp., both in absence and presence of EtOH, cinnamdiethylamide results. H. B.

β-Thionaphthoic acid and di-β-naphthoyl disulphide. L. SZPERL [with U. DEBSKA] (Chem. Listy, 1932, 26, 444—446).—Na β-thionaphthoate, obtained from Na_2S and β-naphthoyl chloride, yields β-*thionaphthoic acid*, m.p. 44—45° (*K*, *Ba*, *Pb*, and *Ag* salts), when treated with HCl, and *di*-β-*naphthoyl disulphide*, m.p. 185—186°, when treated with I. R. T.

Phenanthrene-1-carboxylic acid. L. F. FIESER (J. Amer. Chem. Soc., 1932, 54, 4110).—K phenanthrene-1-sulphonate and $K_4Fe(CN)_6$ give 1-*cyanophenanthrene*, m.p. 128°, oxidised (CrO_3 at 90°) to 1-*cyanophenanthrenequinone*, m.p. 339°, and hydrolysed by EtOH–KOH to the *amide*, m.p. 284°, of *phenanthrene*-1-*carboxylic acid*, m.p. 232—233° (*Me ester*, m.p. 57°). C. J. W. (*b*)

Phenolic acids. I. Alkyl salicylates and their 3 : 5-dinitro-derivatives. P. P. T. SAH and S. MA (Sci. Rep. Nat. Tsing Hua Univ., 1932, 1, 201—204).—For the following esters of salicylic acid *d* and n_D at 20° and 25° are recorded, the figures in parentheses being the m.p. of the 3 : 5-$(NO_2)_2$-derivatives (prepared by fuming HNO_3 and oleum below 0°): Me; Et (92—93°); Pr^{α}, b.p. 249—251° (67—68°); Pr^{β}, b.p. 240—242° (101—102°); Bu^{α}, b.p. 270—272° (60—61°); Bu^{β}, b.p. 260—262° (72—73°); *iso*amyl, b.p. 276—278° (61—62°). The use of 3 : 5-dinitrosalicylic acid for identification of alcohols is suggested. R. S. C.

Configuration of the mandelic acid from amygdalin and of the active phenylaminoacetic acids. O. LUTZ (Ber., 1932, 65, [*B*], 1609—1613).—The activity graph of mandelic acid from amygdalin in 0·05*M* solution in presence of 0·05*M*-Na_2MoO_4 and varying amounts of NaOH and HCl, respectively (cf. this vol., 720), shows that it belongs to the *d*-series. The graph of *d*(−)-phenylglycine in presence of varying amounts of NaOH and HCl proves it to belong to the *d*-series; the *l*(+)-acid belongs to the *l*-series. H. W.

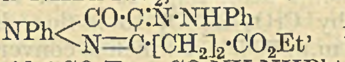
Action of hypochlorous acid on arylidene-cyanoacetic acids. J. A. McRae and C. Y. Hopkins (Canad. J. Res., 1932, 7, 248—257).—Aq. NaOCl and the Na salts of *o*- (I) and *p*- (II) -methoxybenzylidene-, piperonylidene- (III), and veratrylidene-cyanoacetic acids give the corresponding arylacetic acids. o-*Chlorobenzylidenecyanoacetic acid*, m.p. 53°, and NaOCl give *α-cyano*-β-o-*chlorophenylglycidic acid*, m.p. 159°, changed by alkaline H_2O_2 to *α-cyano*-β-o-*chlorophenylglyceric acid*, m.p. 186°. Indefinite results were obtained with the following cyanoacetic acids: benzylidene-, cinnamylidene-, furfurylidene-, 6-*nitropiperonylidene*- (m.p. 247°), *o*- (new m.p. 231—232°) and *m*- (m.p. 171°; *NH_4 H* salt, m.p. 214—215°) (IV) -nitrobenzylidene-, and 3-*nitroanisylidene*- (m.p. 240°). (I) has m.p. 208° (*Et* ester, m.p. 53°). (III) and NaOBr gave (in one experiment only) (?) *α-bromo*-β-*hydroxy*-β-*piperonylpropionitrile* (not obtained pure), m.p. 106°. 3-Nitroanisaldehyde and hippuric acid give the *azlactone*, m.p. 206°. (IV) and HCN give a substance, hydrolysed to *m*-nitrophenylsuccinic acid (over-all yield 37%). R. S. C.

Fluorinated amino-acids and their derivatives. III. Fluorotyrosine and fluorothyronine and nuclear fluorinated β-phenylethylamines. G. Schiemann and W. Winkelmüller (J. pr. Chem., 1932, [ii], **135**, 101—127).—3-*Fluoro*-4-*methoxybenzaldehyde*, prepared in a crude state by oxidation of 3-fluoro-4-methoxytoluene (I) with $CrOCl_2$ in CS_2, is condensed with hippuric acid in Ac_2O in presence of NaOAc to give 2-*phenyl*-4-(3′-*fluoro*-4′-*methoxybenzylidene*)-5-*oxazolone*, m.p. 206·5°. This is hydrolysed by NaOH in EtOH to 3-*fluoro*-4-*methoxy*-α-*benzamidocinnamic acid*, m.p. 214° (decomp.), which with HI and red P gives dl-*α-amino*-β-3-*fluoro*-4-*hydroxyphenylpropionic acid* [*fluorotyrosine*] (II), m.p. 276—277° (decomp., rapid heating). Interaction of *o*-fluorophenetole, $Zn(CN)_2$, and dry HCl in C_6H_6, and hydrolysis of the product gives 3-*fluoro*-4-*ethoxybenzaldehyde*, which with hippuric acid in Ac_2O gives 2-*phenyl*-4-(3′-*fluoro*-4′-*ethoxybenzylidene*)-5-*oxazolone*, m.p. 169°, reduced by HI and P to (II). Nitration of α-amino-β-*m*-fluorophenylpropionic acid, decomp. 262°, reduction of the 4-*NO_2*-compound, m.p. 209·5°, thus formed with Sn and HCl, and diazotisation and decomp. of the resulting 4-*NH_2*-compound, decomp. >300° (*hydrochloride*, decomp. >310°), also gives (II).

3-*Fluoro*-4′-*methoxydiphenyl ether*, b.p. 161·4—161·6°/14 mm., is prepared by treating quinol Me ether with *m*-C_6H_4BrF and K_2CO_3 in presence of C_5H_5N and Cu-bronze at 180°. It is converted by a modified Gattermann synthesis [$Zn(CN)_2$–HCl] into 2-*fluoro*-4-p-*anisoxybenzaldehyde*, the *azlactone*, m.p. 155°, from which and hippuric acid in Ac_2O is reduced and demethylated by HI and P in Ac_2O to dl-*α-amino*-β-2-*fluoro*-4-p-*hydroxyphenoxyphenylpropionic acid* [*fluorothyronine*], m.p. 264·5°.

Decarboxylation of (II) in fluorene at 280° gives β-3-*fluoro*-4-*hydroxyphenylethylamine* [*fluorotyramine*] [*picrate*, m.p. 194° (decomp.)]; *m*-fluorophenylalanine, similarly, gives β-m-*fluorophenylethylamine* (III), b.p. 87°/15 mm. [*hydrochloride*, m.p. 233°; *picrate*, m.p. 157°]. m-*Fluorocinnamic acid*, m.p. 166·5°, is prepared from *m*-$C_6H_4F{\cdot}CHO$ and $CH_2(CO_2Et)_2$, and is reduced by Na–Hg to β-m-*fluorophenylpropionic acid*, m.p. 46°, b.p. 119·2°/0·4 mm. (oxidised by CrO_3–H_2SO_4 to *m*-fluorobenzoic acid), the *amide*, m.p. 96·5°, of which is converted into (III) by NaOBr.

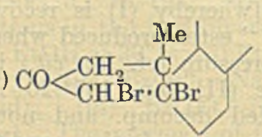
Oxidation of (I) with $Na_2Cr_2O_7$–H_2SO_4 gives 3-fluoro-*p*-anisic acid, m.p. 207·5° (lit. 204°). The *diazonium fluoborate*, decomp. 88°, from 2-methoxy-*m*-toluidine gives on decomp. 3-*fluoro*-o-*tolyl Me ether*, b.p. 58·6°/19 mm. 5(?)-*Nitro*-3-*fluoro*-p-*cresol*, m.p. 62·5°, b.p. 120—123°/13 mm., is prepared by nitration of 3-fluoro-*p*-tolyl Me ether. Oxidation with CrO_2Cl_2 in CS_2 of anisyl *p*-tolyl ether and hydrolysis of the product gives tarry materials only. 3-*Amino*-4-*methoxydiphenyl ether*, m.p. 71·5°, b.p. 205°/15 mm., prepared by reduction of the NO_2-compound, gives a *diazonium fluoborate*, decomp. 145°, from which only a trace of 3-fluoro-4-methoxydiphenyl ether was obtained. H. A. P.

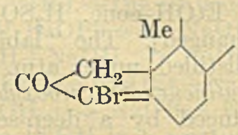
Structure of glutaconic acids and esters. VII. Derivatives of 3-methyl*cyclo*propene-1 : 2-dicarboxylic acid. G. A. R. Kon and H. R. Nanji (J.C.S., 1932, 2557—2568).—3-Methyl*cyclo*propene-1 : 2-dicarboxylic acid and its "normal" ester (Goss *et al.*, J.C.S., 1923, **123**, 327, 3342; A., 1925, i, 549) are the Δ^2-derivatives; ozonolysis of the Et ester (I) gives AcOH, $H_2C_2O_4$, and Et acetyloxaloacetate (*pyrazolone*, m.p. 230°, from $NHPh{\cdot}NH_2$), whilst reduction (H_2, colloidal Pd, aq. EtOH) and subsequent hydrolysis affords 3-methyl*cyclo*propane-1 : 2-dicarboxylic acid, m.p. 147° (cf. *loc. cit.*). Treatment of (I) with EtOH–NaOEt and subsequent dilution with H_2O gives *Et* 3-*ethoxy*-3-*methyl*cyclo*propane*-1 : 2-*dicarboxylate*, b.p. 145—146°/11 mm., a little of the ethoxy-acid, m.p. 156° (*anhydride*, m.p. 49°), and a little quasi-acid enolic *product*, b.p. 140°/11 mm., which is not isomeric with (I); the "labile" Et 3-methyl*cyclo*propane-1 : 2-dicarboxylate of Goss *et al.* (*loc. cit.*) could not be obtained by this method, or from Et 2 : 3-dibromo-3-methyl*cyclo*propane-1 : 2-dicarboxylate and "mol." K in xylene, or from (I) and EtOH–conc. H_2SO_4 [whereby (I) is recovered unchanged]. The "labile" ester produced when (I) is distilled under atm. pressure (cf. *loc. cit.*) is *Et* Δ^{α}-*butinene-αδ-dicarboxylate* (II), b.p. 137°/20 mm., produced by a deep-seated decomp. and not reconvertible into (I) under any of the conditions tried. Reduction (H_2, colloidal Pd, aq. EtOH) of (II) and subsequent hydrolysis gives adipic acid. Hydrolysis of (II) with 10% HCl affords lævulic acid, whilst aq. MeOH–KOH yields (mainly) β-*keto-adipic acid*, m.p. 124—125° (decomp.) (which with semicarbazide gives CO_2 and lævulic acid semicarbazone), and a little β-*methoxy*-Δ^{α}-*butene-αδ-dicarboxylic acid*, m.p. 186° (decomp.) (formed by addition of MeOH to the acetylenic acid). (II) treated with EtOH–NaOEt does not give a Na derivative (cf. *loc. cit.*); *Et* β-*ethoxy*-Δ^{α}-*butene-αδ-dicarboxylate*, b.p. 155°/15 mm. (free *acid*, m.p. 161°, hydrolysed by aq. HCl to lævulic acid) (ozonolysis products, $H_2C_2O_4$ and Et succinate), is formed by addition of EtOH. Ozonolysis of (II) gives much unchanged (II), syrupy acidic products, and some impure Et αβ-diketoadipate (the free acid could not be prepared by hydrolysis); the latter is oxidised by H_2O_2 to succinic acid and with $NHPh{\cdot}NH_2$,AcOH affords the *phenylhydrazone*,  $NPh<\begin{smallmatrix}CO{\cdot}C{:}N{\cdot}NHPh\\ N{=}C{\cdot}[CH_2]_2{\cdot}CO_2Et\end{smallmatrix}$, m.p. 120° [*phenylhydrazide* ($\cdot CO_2Et = \cdot CO{\cdot}NH{\cdot}NHPh$), m.p. 225—226°]. (II), unlike (I), reacts with EtOH–conc. H_2SO_4; addition of EtOH probably occurs, but the resulting product has not been characterised.

Me 3-methyl-Δ^2-*cyclo*propene-1 : 2-dicarboxylate (III) and MeOH–NaOMe give mainly Me 3-methoxy-3-methyl*cyclo*propane-1 : 2-dicarboxylate; a Na derivative is not formed. Distillation of (III) under atm. pressure causes very little decomp. H. B.

Constitution of bile acids. XL. *iso*Deoxybilianic acid, pyro*iso*deoxybilianic acid, and norcholoidanic acid. H. Wieland, E. Dane, and L. Maiweg. **XLI. Pyrocholoidanic acid.** H. Wieland, E. Dane, and W. Schönberger. **XLII. Chollepidanic acid.** H. Wieland and K. Kraft. **XLIII. Degradation of lithobilianic acid.** H. Wieland, E. Dane, and E. Scholz (Z. physiol. Chem., 1932, 211, 164—176, 177—186, 203—210, 261—274; cf. this vol., 1131).—XL. Bromination of *iso*deoxybilianic acid gives the *monobromo-acid* (I), m.p. 208° (decomp.). Hydrolysis of (I) with *N*-NaOH affords *hydroxy*iso*deoxybilianic acid* (II), m.p. 205°. Oxidation of (II) did not yield *iso*choloidanic acid, but with $Pb(OAc)_4$ the *aldehydotetracarboxylic acid*, $C_{24}H_{36}O_9$ ($+H_2O$), m.p. 195° (decomp.), was obtained. Bromination of pyro*iso*deoxybilianic acid yields the *monobromo-*, m.p. 198°, and the *dibromo-* (III), m.p. 123° (decomp.), -acids. Hydrolysis of (III) with aq. NaOH eliminates the Br, giving an unsaturated *hydroxydiketocarboxylic acid*, $C_{23}H_{32}O_5$ (IV), m.p. 246°. In boiling C_5H_5N the unsaturated *monobromo-acid* (V), m.p. 205°, is obtained. With NaOH (V) does not yield (IV) but a *keto–enol acid*, $C_{23}H_{32}O_5$, m.p. 190°. Oxidation of (V) with $KMnO_4$ eliminates one C atom, giving a saturated *diketocarboxylic acid*, $C_{22}H_{32}O_6$, m.p. 191° (decomp.). These changes suggest the constitution shown for (III) and (V):

(III.)

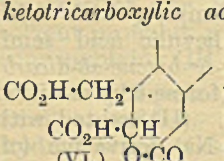




(V.)

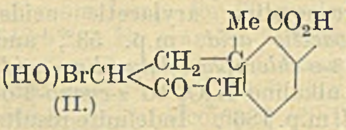
Oxidation of (IV) with alkaline $KMnO_4$ affords a *tribasic acid*, $C_{23}H_{32}O_9$ (VI), m.p. 224° (decomp.), probably as below.

Thermal decomp. of norcholoidanic acid gave a *ketotricarboxylic acid*, $C_{22}H_{32}O_7$ (VII), m.p. 165° (160°+H_2O) (*Ba* salt, m.p. about 290°), in the formation of which the CO_2H of the side-chain must be involved. With Br in AcOH, (VII) gives *monobromopyronorcholoidanic acid*, m.p. 235—240° (decomp.), which eliminates Br with C_5H_5N, giving *hydroxypyronorcholoidanic acid* (VIII), m.p. 210° (decomp.). Oxidation of (VIII) with CrO_3 in AcOH gives a *tetracarboxylic acid*, $C_{22}H_{32}O_6$ (?), m.p. 150—153° ($+2H_2O$).



(VI.)

XLI. In the closed pyrocholoidanic acid the CO_2H group of ring D must be lactonised with ring A. Bromination of the open acid gives a *monobromo-acid* (I), m.p. 219—220° (decomp.). NaOH replaces Br by OH giving a *hydroxyketotricarboxylic acid*, $C_{23}H_{34}O_8$ (II), m.p. 219° (decomp.), which readily yields the *lactone* (III), m.p. 236—238°. From the crude Et_2O filtrate of the lactone-dicarboxylic acid there was isolated an unsaturated *ketotricarboxylic acid*, $C_{23}H_{32}O_7$, m.p. 285—287°, which with NaOH yields (II). Bromination of (III) gives the *bromoketolactonedicarboxylic acid*, $C_{23}H_{31}O_7Br$ (IV), decomp. at 236°. Dil. aq. NaOH converts (IV) into the keto–enoltricarboxylic acid, $C_{23}H_{32}O_8$, m.p. 271° (slight decomp.), also obtained on oxidation of (II) with Fehling's solution or by hydrolysis of *dibromoketotricarboxylic acid*, decomp. at 229°. The closed pyrocholoidanic acid gives a *Br*-derivative, m.p. 223° (darkens).

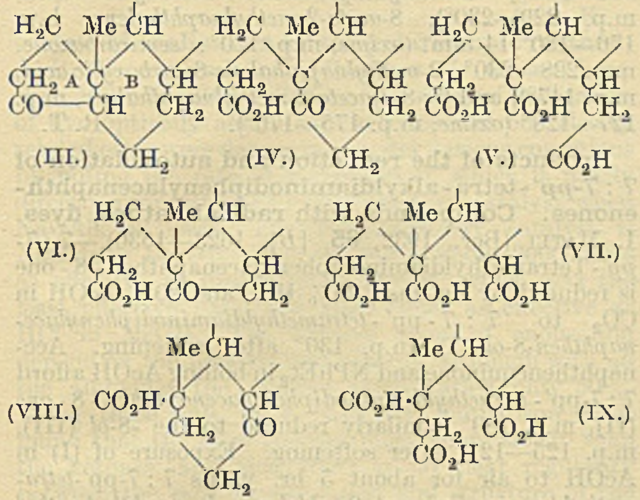


(II.)

Keto-β-deoxybilianic acid (A., 1931, 841) above its m.p. loses H_2O giving an unsaturated *tricarboxylic acid*, $C_{24}H_{32}O_7$, m.p. 248—250° (*Me* ester, m.p. 109°). Mono- or di-bromodeoxybilianic acid with KOH in MeOH affords an unsaturated *ketolactonedicarboxylic acid*, $C_{24}H_{32}O_7$ (V), m.p. 235—240° (decomp.) (*Me* ester, m.p. 195°). Reduction of (V) with Zn dust in AcOH and HCl gives a *ketotricarboxylic acid*, $C_{24}H_{36}O_7$, m.p. 210°, differing from ordinary α-deoxybilianic acid probably by epimerism at C_9.

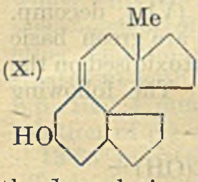
XLII. Chollepidanic acid (I), now formulated as a hexacarboxylic acid, $C_{24}H_{34}O_{12}$, $[\alpha]^{20}_{D}$ +38·8° in 50% aq. EtOH, is probably choloidanic acid with the Me group at C_{10} replaced by CO_2H. Pyrochollepidanic acid (*Me*$_3$ ester, m.p. 127°) gives on titration the open pyro-acid (*Me*$_4$ ester, m.p. 140°). Thermal decomp. of (I) gave as by-product in addition to Flaschenträger's acids a neutral *substance*, $C_{20}H_{26}O_2$(?), m.p. 205°.

XLIII. Deoxycholic acid yields an *Ac* derivative, m.p. 112—115° (decomp.), which on oxidation with CrO_3 in AcOH gives 12-*keto-3-acetoxycholanic acid*, m.p. 197° [*semicarbazone* (I), m.p. 194—195° (decomp.)]. With Na in EtOH at 170—180°, (I) gives the Na salt of lithocholic acid (II). Oxidation of (II) with HNO_3 gives lithobilianic acid (III) and iso*lithobilianic acid*, m.p. 262°. (III) together with the *allo*-isomeride was also obtained from deoxybilianic acid by the Kishner–Wolff method. β-Deoxybilianic acid similarly gives *allo*lithobilianic acid. Thermal decomp. of (III) at 280—295°/12 mm. affords the pyro-acid, which on oxidation with $KMnO_4$ in alkaline solution gives the *ketodicarboxylic acid* $C_{23}H_{36}O_5$ (IV), m.p. 187°. With NaOBr or HNO_3, (IV) yields the tetracarboxylic acid $C_{23}H_{36}O_8$ (V), (+EtOAc) m.p. 168—169° (decomp.). Thermal decomp. of (V) at 270—290°/vac. gives the *ketodicarboxylic acid* $C_{22}H_{34}O_5$ (VI), m.p. 167—168°, which then yields on oxidation with alkaline $KMnO_4$ the tetracarboxylic acid, $C_{22}H_{34}O_8$ (VII) (*Me*$_4$ ester, m.p. 75°), identical with the product obtained by Windaus from cholesterol (A., 1909, i, 920). Thermal decomp. of (VII) at 320° gives the ketodicarboxylic acid $C_{21}H_{32}O_5$ (VIII), m.p. 168°, which on oxidation with HNO_3 gives the tetracarboxylic acid (IX) (*Me*$_4$ ester, m.p. 84°), identical with Windaus' acid. These reactions are formulated as follows :


(III.) (IV.) (V.) (VI.) (VII.) (VIII.) (IX.)

To exclude the possibility of a cyclisation of the 1- and 8-CO_2H groups of (V) the acid $C_{22}H_{32}O_9$ (this vol., 614) was reduced by way of the semicarbazone to (VII).

The view that the ring in cholesterol adjoining the OH ring and containing the double linking is the same as that which was regarded as ring II in the bile acids must apparently be abandoned. The suggested form of cholesterol (X), although otherwise unexceptionable, does not explain the degradation of Diels' acid. J. H. B.

(X.)


Chemical constitution and rotatory power. Derivatives of chloro- and bromo-benzaldehydes. M. Betti and P. Pratesi (Atti R. Accad. Lincei, 1932, [vi], 15, 509—513).—The observation that, in the *o*-position, Br increases more than Cl the electronegative character of the Ph in BzOH (cf. Ostwald, A., 1889, 818) is paralleled by the $[M]_D$ vals. of the benzylidene compounds formed by condensing *d*-phenyl-2-hydroxy-1-naphthylmethylamine (I) (cf. A., 1901, i, 611; 1906, i, 950; 1907, ii, 661, 726; 1916, ii, 279; 1921, i, 107) with : PhCHO, +373·1°; *o*-C_6H_4Cl·CHO, −128·4°; *o*-C_6H_4Br·CHO, −308·7° (m.p. 157°). In the *m*- and *p*-positions, on the other hand, Cl increases the electronegative character of the Ph in BzOH more than Br does, the dissociation consts. being : BzOH, 0·006; *m*-C_6H_4Br·CO_2H, 0·0137; *m*-C_6H_4Cl·CO_2H, 0·0155; *p*-C_6H_4Br·CO_2H, 0·0065; *p*-C_6H_4Cl·CO_2H, 0·0093. The vals. of $[M]_D$ for the compounds formed by (I) with the *m*- and *p*-substituted aldehydes are : *m*-C_6H_4Br·CHO, +280·9° (m.p. 136°); *m*-C_6H_4Cl·CHO, +255·9°; *p*-C_6H_4Br·CHO, +348·1° (m.p. 155°); *p*-C_6H_4Cl·CHO, +282·2°. T. H. P.

Yield of aromatic substances when lignin hydrochloride is fused with potassium hydroxide. A. Winsvold (Cellulosechem., 1932, 13, 158—159).—In reply to Jonas and Freudenberg (cf. B., 1928, 363; A., 1928, 1227; 1929, 915) it is maintained that if requisite precautions are taken a yield of $>20\%$ of pure aromatic substances can be obtained by fusing lignin hydrochloride with KOH. A. G.

***cyclo*Propane series. *cyclo*Propanone.** P. Lipp, J. Buchkremer, and H. Seeles (Annalen, 1932, 449, 1—25).—γ-Chlorobutyronitrile and $NaNH_2$ give some cyclo*propanecarboxylamide*, m.p. 223·5—224·5°, which with Br and MeOH–NaOMe affords *Me* cyclo*propylcarbamate*, b.p. 84—85°/11 mm., m.p. 30—31°, hydrolysed by aq. KOH to *cyclo*propylamine. Treatment of this with HNO_2 under various conditions gives allyl alcohol. The Ag salt of *cyclo*propanecarboxylic acid (I) and an equiv. of I at 135° afford (I), its anhydride, and (mainly) slightly impure *glyceryl* cyclo*propanecarboxylate*, b.p. 144°/0·04 mm.; the latter is probably formed by way of the *cyclo*propyl, allyl, and βγ-di-iodopropyl esters of (I). *cyclo*Propyl Ph ketone and MgPhBr give cyclo*propyldiphenylcarbinol*, b.p. 150°/3 mm., m.p. 82—83° [*Me ether*, b.p. 140°/1·5 mm.; *bromide*, b.p. 138°/1·5 mm., converted by C_5H_5N into N-(cyclo*propyldiphenylmethyl*)*pyridinium bromide*, m.p. 128°, and by $NPhMe_2$ into (probably) a (cyclo*propyldiphenylmethyl*)*dimethylaniline*, b.p. 192°/0·3 mm. (*sulphate*)], which could be dehydrated only to an *ether*, $C_{32}H_{30}O$, b.p. 250°/0·09 mm., m.p. 112—113° (by $KHSO_4$ at 180—190°), or polymeric material; the *iodide*, m.p. 34°, and C_5H_5N give a *salt*, $C_{21}H_{20}NI$, m.p. 163°, converted by hot aq. NaOH into a little *diphenylmethylene*-cyclo*propane* (II), b.p. 110—114°/0·5 mm. (ozonolysis product $COPh_2$). A polymeric αα-*diphenylbutadiene* is prepared from diphenylallylcarbinol for comparison with (II). Excess of keten with diazomethane in Et_2O–MeOH gives a little *cyclo*butanone and (mainly) 1-*hydroxy*-1-*methoxy*cyclo*propane*, b.p. 45—46°/14 mm. (p-*nitrobenzoate*, m.p. 62—63°), converted by semicarbazide into β-*semicarbazidopropaldehydesemicarbazone* (III), m.p. 223° (decomp.); 1-hydroxy-1-ethoxy*cyclo*propane, obtained similarly using diazomethane in Et_2O–EtOH, is isomerised by dil. KOH to $EtCO_2Et$. Evaporation of the reaction mixture from keten and abs. Et_2O–diazomethane in air (not dried) gives 1 : 1-*dihydroxy*cyclo*propane* (cyclo*propanone hydrate*), m.p. 71—72°, which isomerises slowly (more rapidly by the action of hot H_2O or cold KOH) to $EtCO_2H$, and with semicarbazide gives (III). Evaporation in absence of moisture gives resinous polymeric material. Monomeric *cyclo*propanone thus appears to exist only in solution. An improved prep. of *cyclo*butanone (2 : 4-*dinitrophenylhydrazone*, m.p. 132—133°) is given (cf. this vol., 161).

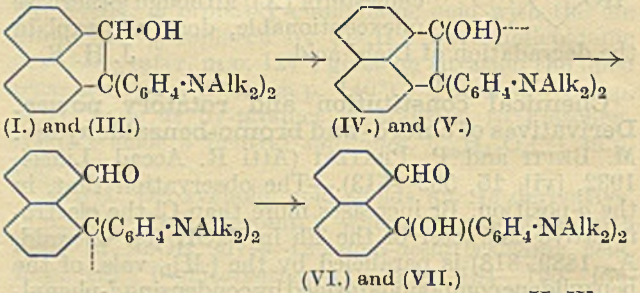
[With H. Verbeek.] Contrary to Dechamps (A., 1930, 585), distillation of Ca succinate gives COMeEt and a little $COEt_2$ [2 : 4-dinitrophenylhydrazone, m.p. 151·5° (lit. 156°)], and not $COMe_2$ and *cyclo*propanone. H. B.

Bromophenacyl esters of organic acids. H. Lund and T. Langvad (J. Amer. Chem. Soc., 1932, 54, 4107—4108).—p-*Bromophenacyl tiglate*, m.p. 67·9° (all m.p. are corr.), *adipate*, m.p. 152·6°, *chloroacetate*, m.p. 103·7°, m-*hydroxybenzoate*, m.p. 176·1—176·4°, p-*hydroxybenzoate*, m.p. 191·3—191·7°, m-*nitrobenzoate*, m.p. 135·4°, o-*chlorobenzoate*, m.p. 107°, m-*nitrocinnamate*, m.p. 178°, p-*nitrocinnamate*, m.p. 191°, o-*methoxycinnamate*, m.p. 145°, and o-*methoxy*allo-*cinnamate*, m.p. 97·5°, are described. C. J. W. (*b*)

Steric hindrance in mesitylenic ketones. E. P. Kohler and R. Baltzly (J. Amer. Chem. Soc., 1932, 54, 4015—4026).—Study of acetomesitylene (I), *dimesityl ketone* (II), and *dimesityl diketone* (III) shows that the two Me groups in the di-*o*-positions affect only those reactions which involve addition to the C atom in direct union with the mesityl group. These Me groups neither promote nor hinder the enolisation of (I), Et 2 : 4 : 6-trimethylbenzoylacetate, and similar substances; neither do they interfere with reactions which involve addition to the O of the CO group. In general, the hindrance is adequate to prevent all additive reactions that involve the α-C atom except reduction, but it may be overcome, in part, by another CO group in the α-position. The enolate of (I), prepared from (I) and MgEtBr in Et_2O, and AcCl give 2 : 4 : 6-*trimethylbenzoyldiacetylmethane*, m.p. 66—67°, isolated as the *Cu* salt. *Dibenzoyl*-2 : 4 : 6-*trimethylbenzoylmethane*, m.p. 192° (85% yield) (*Cu* salt), is similarly prepared. *p*-$C_6H_4Me\cdot SO_2Cl$ and the enolate give αβ-di-2 : 4 : 6-trimethylbenzoylethane, m.p. 138—139°, whilst $ClCO_2Et$ affords the *Mg* complex, m.p. 147°, of Et 2 : 4 : 6-trimethylbenzoylmalonate; the free ester could not be isolated [*Et* 2 : 4 : 6-*trimethylbenzoylacetate* (IV), b.p. 150°/11 mm., resulted from elimination of the Mg]. 2 : 4 : 6-Trimethylbenzoyl chloride and $CHNaAc\cdot CO_2Et$ give *Et mesitylcarbonate*, b.p. 139—141°/120 mm., and not (IV). (IV) and N_2H_4 in EtOH give 3-*mesityl*-5-*pyrazolone*, decomp. 290—300° (4-*benzylidene* derivative, decomp. 280°). The equilibrium mixture of (IV) contains 24·5% of enol; the EtOH solution contains 27·3%. The enolate of (I) and O_2 give (I); CO_2 apparently reacts, but a carbonated product could not be isolated. 2 : 4 : 6-Trimethylbenzoyl chloride and Mg mesityl bromide give (II), b.p. 200°/2 mm., m.p. 136—137°, which does not react with NH_2OH. Reduction of (II) with Na or Na–Hg and EtOH gives *dimesitylcarbinol* (V), m.p. 149—150° (*benzoate*, m.p. 154°), whilst reduction with HI and red P gives *dimesitylmethane*, m.p. 135°. (II) combines readily with Na in C_6H_6 to form a greenish-blue ketyl which, on hydrolysis, gives an equimol. mixture of (II) and (V); Mg+MgI_2 give a dark purple ketyl which, on hydrolysis, yields the same mixture. Mg mesityl bromide and Et mesitylglyoxylate give a small yield of (III), m.p. 122° (*oxime*, m.p. 209—210°), which is not reduced by Zn and AcOH, amalgamated Zn and conc. HCl, or by catalytic methods; Zn and EtOH–KOH slowly give *mesitylacetomesitylene* [2 : 4 : 6-*trimethylphenyl* 2 : 4 : 6-*trimethylbenzyl ketone*], m.p. 141°. Na_2O_2 and (III) in dil. MeOH give 2 : 4 : 6-$Me_3C_6H_2\cdot CO_2H$; (III) does not react with fused KOH or with *o*-$C_6H_4(NH_2)_2$, but combines with Na, forming a brown Na_2 compound, which with BzCl affords *hexamethyl*iso*benzil dibenzoate* [αβ-*dibenzoyloxy*-αβ-*dimesitylethylene*], m.p. 190°. C. J. W. (*b*)

Ketones of the naphthalene group. Synthesis of acetyl derivatives of 2-methylnaphthalene. K. Dziewoński and M. Brand (Rocz. Chem., 1932, 12, 693—701).—2-$C_{10}H_7Me$ reacts with AcCl in presence of $AlCl_3$ to yield 6-*aceto*-2-*methylnaphthalene*, m.p. 70—71° (*oxime*, m.p. 181°; *semicarbazone*, m.p. 240—242°; 2-*methylnaphthalene*-6-*carboxylic acid*, m.p. 229—230°), 8-*aceto*-2-*methylnaphthalene*, b.p. 176—180°/14 mm. (*oxime*, m.p. 120°; *semicarbazone*, m.p. 228—230°; 2-*methylnaphthalene*-8-*carboxylic acid*, m.p. 147°), and 6 : 8-*diaceto*-2-*methylnaphthalene*, m.p. 127—128° (*oxime*, m.p. 175—176°). R. T.

Products of the reduction and autoxidation of 7 : 7-*pp′*-tetra-alkyldiaminodiphenylacenaphthenones. Compounds with radical nature, dyes. I. I. Matei (Ber., 1932, 65, [*B*], 1623—1630).—7 : 7-*pp′*-Tetramethyldiaminodiphenylacenaphthen-8-one is reduced by Zn dust, 25% HCl, and 20% AcOH in CO_2 to 7 : 7-pp′-*tetramethyldiaminodiphenylacenaphthen*-8-*ol* (I), m.p. 130° after softening. Acenaphthenequinone and $NPhEt_2$ in boiling AcOH afford 7 : 7-pp′-*tetraethyldiaminodiphenylacenaphthen*-8-*one* (II), m.p. 189°, similarly reduced to the -8-*ol* (III), m.p. 125—127° after softening. Exposure of (I) in AcOH to air for about 5 hr. yields 7 : 7-pp′-*tetramethyldiaminodiphenyl*-8-*aldehydo*-1-*naphthylmethyl* (IV), the colour becoming deep blue, whilst (III) gives an analogous *product* (V). Much more protracted exposure of (I) or (IV) in AcOH to air leads to pp′-*tetramethyldiaminodiphenyl*-8-*aldehydo*-1-*naphthylcarbinol* (VI), m.p. 180° (decomp.), whilst (III) or (V) gives the *di*-p-*diethyl* compound (VII), decomp. above 160°. Salts of (VI) and (VII) are green basic dyes; (IV) and (V) also dye and are autoxidised on the fibre more rapidly than in solution. The following scheme is suggested:



H. W.

Reducing action of organomagnesium compounds. Action of magnesium *cyclo*hexyl bromide and iodide on benzophenone. A. E. Arbusov and I. A. Arbusova (J. Gen. Chem. Russ., 1932, 2, 388—396).—Mg *cyclo*hexyl bromide and $COPh_2$ give $COPh_2$ (30·7%), benzhydrol (5·9%), benzpinacone (13·4%), and *cyclo*hexylidenediphenylmethane (I). It is assumed that the first products of the reaction are the free radicals $Ph_2COMgBr$ · · · · (II) and C_6H_{11} · · · · (II). The union of these radicals, followed by dehydration of the *tert.*-alcohol formed, gives (I). The union of two radicals (II) gives benzpinacone, whilst reduction of (II) at the expense of (III) gives benzhydrol and *cyclo*hexene (not isolated). $COPh_2$ could be formed by the oxidation of (II).

With Mg *cyclo*hexyl iodide the products were $COPh_2$ (16·6%), benzpinacone (21·9%), di*cyclo*hexyl (7·7%), diphenyl*cyclo*hexylcarbinol (1·26%), (I) (5·1%), and tetraphenylethane (IV) (3·6%); no benzhydrol was isolated. The mutual oxidation and reduction of

(II) and (III) did not take place; hence the increased yield of benzpinacone and the formation of di*cyclo*hexyl. The formation of (IV) is difficult to explain.
G. A. R. K.

Rate of enolisation by the polariscopic method. J. B. Conant and G. H. Carlson (J. Amer. Chem. Soc., 1932, **54**, 4048—4059).—The rates of enolisation of five optically active aryl ketones and one closely related ester were determined under various conditions by noting the rate of racemisation, which is nearly directly proportional to the concn. of catalyst when NaOAlk is used. The most effective catalyst is NaOMe in $Bu^{\gamma}OH$; this catalyst is about 2000 times as effective as piperidine in MeOH, which was the least effective base, and 1000 times as effective as HCl in MeOH. The relative rates of enolisation depend on the catalyst and solvent, although with all the alkoxides the relative rates varied only 50%. Using these vals. as a basis for comparison, it is found that the ester enolises much more slowly than the ketones, and that there is no clear regularity between the rate of enolisation and structure of the ketone. The heat of activation of the enolisation is about 14±1 kg.-cal. The free energy of enolisation of the COPhMe derivatives is estimated to be between 5 and 14 kg.-cal. COPhMe and MgBuBr give *phenylmethylbutylcarbinol*, b.p. 129—130°/4 mm., which with MeOH and conc. H_2SO_4 affords *α-phenyl-α-methylamyl Me ether*, b.p. 105—106°/6 mm. This ether and liquid Na–K alloy in Et_2O give (after treatment with CO_2) *α-phenyl-α-methylhexoic acid* (I), b.p. 155°/4 mm. (*Me* ester, b.p. 115°/2 mm.). Resolution of (I) with quinine gives the *d*-form, $[\alpha]_{5461}$ +13·65° in EtOH, the chloride of which with MgPhBr affords *d-α-phenyl-α-methylhexophenone* [*Ph α-phenyl-α-methylamyl ketone*], b.p. 150—152°/0·5 mm., $[\alpha]_{5461}$ +30·78° in EtOH. d-*Ph β-phenyl-α-methylethyl ketone*, m.p. 42—43°, $[\alpha]_{5461}$ +87·5° in EtOH, is prepared from *d*-β-phenyl-α-methylpropionyl chloride and MgPhBr. *l*-$CH_2Ph{\cdot}CHPh{\cdot}COCl$ and Mg mesityl bromide give 1-2 : 4 : 6-*trimethylphenyl αβ-diphenylethyl ketone*, m.p. 113—114°, $[\alpha]_{5461}$ −8·06° in $COMe_2$. *d*-2 : 4 : 6-*Trimethylphenyl α-phenylethyl ketone*, m.p. 59—60·5°, $[\alpha]_{5461}$ +71·5° in MeOH, is prepared similarly. Tables give the results of the action of NaOBu in BuOH, NaOMe in MeOH, and piperidine in BuOH and in MeOH.
C. J. W. (*b*)

Fries rearrangement of α-naphthyl esters. H. Lederer (J. pr. Chem., 1932, [ii], **135**, 49—56).—By acting on α-naphthyl esters with $AlCl_3$ in $PhNO_2$ at 0—25° both the 2- and 4-ketones are formed; the proportion of the latter increases as the temp. is lowered, but below 0° the reaction is impracticably slow. The acidity of the latter is normal, but that of the former is low, and decreases rapidly as the series is ascended. The following are described: 1-hydroxy-4- and -2-naphthyl Me ketones; *α-naphthyl* n-*butyrate*, b.p. 182°/15—18 mm., and *phenylacetate*, m.p. 48°, b.p. 232°/15—18 mm.; 1-*hydroxy*-4-*naphthyl* Pr^a *ketone*, m.p. 167° (corr.); 1-*hydroxy-2-naphthyl* Pr^a *ketone*, m.p. 85° (corr.); 1-*hydroxy-2-naphthyl* CH_2Ph *ketone*, m.p. 94—95° (corr.). $CH_2Ph{\cdot}COCl$ has b.p. 202° (lit. 180—183°).
H. A. P.

Manufacture of substituted aromatic ketones. Soc. Chem. Ind. in Basle.—See B., 1932, 974.

Interconversion of mixed benzoins. E. M. Luis (J.C.S., 1932, 2547—2550).—*r*-4′-Methoxybenzoin (benzoyl-*p*-anisylcarbinol) and EtOH–KOH at room temp. for 3 days give *r*-4-methoxybenzoin (*p*-anisoylphenylcarbinol), which is unaffected by such treatment; interconversion probably proceeds by way of the αβ-dihydroxy-αβ-diarylethylene. *r*-4′-Dimethylaminobenzoin (I) is similarly converted into *r*-4-dimethylaminobenzoin (II); *p*-dimethylaminobenzil (III) is a by-product. (III) is also formed (to some extent) when (II) is treated with cold EtOH–KOH. (I) [or (II)] heated with EtOH–KOH gives (II), (III), BzOH, and *p*-$NMe_2{\cdot}C_6H_4{\cdot}CO_2H$. Determination of the structure of ketones by fission with EtOH–KOH is not applicable to mixed benzoins.
H. B.

Dehydration of the α-forms of *r*- and (+)-*p*-tolylhydrobenzoins. A. McKenzie, R. Roger, and W. B. McKay (J.C.S., 1932, 2597—2604).—*p*-Tolyl benzhydryl ketone, previously obtained (A., 1930, 778) by dehydration of *r*-*p*-tolylhydrobenzoin (α-form) (I) with conc. H_2SO_4 (cf. Koelsch, this vol., 746) and by semipinacolinic deamination of *r*- and (+)-β-amino-αβ-diphenyl-α-*p*-tolylethyl alcohol, is prepared from $CHPh_2{\cdot}CN$ and *p*-$C_6H_4Me{\cdot}MgBr$ with subsequent hydrolysis. Dehydration of (I) with $H_2C_2O_4$ gives r-p-*tolyldeoxybenzoin* (*Ph* p-*methylbenzhydryl ketone*) (II), m.p. 96—97°, synthesised by the following methods: (*a*) from MgPhBr and *p*-$C_6H_4Me{\cdot}CHPh{\cdot}CN$, m.p. 60—62° (lit. 59°), (*b*) from desyl chloride, PhMe, and $AlCl_3$ (cf. Koelsch, *loc. cit.*), (*c*) from *r*-benzoin, PhMe, $AlCl_3$, and HCl, (*d*) from *p*-$C_6H_4Me{\cdot}MgBr$ and desyl chloride. Dehydration of (I) with conc. H_2SO_4 now gives mainly (II), also formed (probably by way of α-hydroxy-αβ-diphenyl-β-*p*-tolylethylene) by dehydration of (+)-*p*-tolylhydrobenzoin with $H_2C_2O_4$ or dil. H_2SO_4.

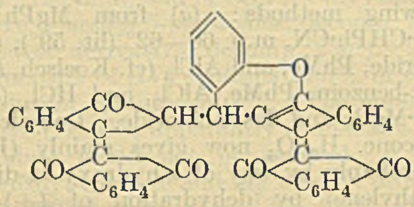
The *r*-*p*-tolyldeoxybenzoin, m.p. 159—160°, obtained by McKenzie and Widdows (J.C.S., 1915, **107**, 702) from *r*- or (+)-*p*-$C_6H_4Me{\cdot}CHPh{\cdot}COCl$, C_6H_6, and $AlCl_3$, is now shown to be $CPh_3{\cdot}OH$. The original reaction may have given $CPh_3{\cdot}CHPh{\cdot}C_6H_4Me(p)$, which then underwent scission to $\cdot CPh_3$, which is convertible into $CPh_3{\cdot}OH$ by way of the peroxide.
H. B.

Preparation of reduction products of benzoin. D. A. Ballard and W. M. Dehn (J. Amer. Chem. Soc., 1932, **54**, 3969—3971).—Reduction of benzoin with amalgamated Zn and conc. HCl–EtOH gives 50% of stilbene in 1—2 hr.; amalgamated Sn affords 88% of deoxybenzoin. KI, red P, and conc. HCl, boiled gently for 20 hr., give β-deoxybenzoin pinacone; Zn and NaOH afford deoxybenzoin, *iso*didesyl, didesyl, and an unknown compound, m.p. 208°. Details are given.
C. J. W. (*b*)

Fluorene series. IV. Preparation of 1 : 2-diacetylfluorene. K. Dziewoński and A. Kleszcz (Bull. Acad. Polonaise, 1932, **A**, 109—114; cf. A., 1931, 622).—Fluorene and AcCl with $AlCl_3$ in boiling CS_2 give (mainly) 1 : 2-*diacetylfluorene*, m.p. 188—190° [*diphenylhydrazone*, m.p. 250—252°; *dioxime*, m.p. 252°, which undergoes the Beckmann change (HCl in

Ac_2O–AcOH) yielding the Ac_2 derivative, m.p. 220° (decomp.), of 1 : 2-diaminofluorene], and small amounts of 2-acetyl- and 2 : 7-diacetyl-fluorenes. 1 : 2-*Diacetylfluorenone* [*triphenylhydrazone*, m.p. 252° (decomp.)] has m.p. 262°. H. B.

Derivatives of di-indone. Indandionedi-indones and bisdi-indones. M. V. Ionescu and H. Slusanschi (Bull. Soc. chim., 1932, [iv], **51**, 1109—1125).—Condensation of indandione (4 mols.) and RCHO (1 mol.) in boiling EtOH–piperidine gives mainly alkylidene- or arylidene-bisdi-indones (for constitution see A., 1928, 422); the following are prepared: *ethylidene-*, m.p. 263°; *propylidene-*, m.p. 265°; n-, m.p. 256°, and iso-, m.p. 234°, *-butylidene-*; iso*valerylidene-*, m.p. 263°; *heptylidene-*, m.p. 256°; β-*phenylpropylidene-*, m.p. 251°; *phenylethylidene*, m.p. 227°; *furfurylidene-*, m.p. 230°; o-, m.p. 295°, m-, m.p. 238°, and p-, m.p. 251°, *-chlorobenzylidene-*; o-, m.p. 289°, m-, m.p. 232°, and p-, m.p. 232°, *-nitrobenzylidene-*; o-, m.p. 256°, and m-, m.p. 231°, *-methoxybenzylidene-*; o-, m.p. 213°, m-, m.p. 272°, and p-, m.p. 228°, *-hydroxybenzylidene-*; *veratrylidene-*, m.p. 212°; 2-*hydroxy*-3-*methoxy-*, m.p. 227°; 2-*hydroxy*-4-*methoxy-*, m.p. 225°, and 4-*hydroxy*-3-*methoxy-*, m.p. 219°, *-benzylidene-*; *resorcylidene-*, m.p. 229°; *asarylidene-*, m.p. 253°; *cinnamylidene-*, m.p. 233°; p-*dimethylaminobenzylidene-*, m.p. 203°. When *o*-OH-aldehydes are used in the above condensation, the arylidenebisdi-indone is accompanied by its anhydro-derivative (as I); the *anhydro-salicylidene*, m.p. 309°, -2-*hydroxy*-3-*methoxybenzylidene-*, m.p. 296°, -2-*hydroxy*-4-*methoxybenzylidene-*, m.p. 304°, and *-resorcylidene-*, m.p. >380°, derivatives are thus obtained. By-products in some of the above condensations are the alkyl- or aryl-ideneindandionedi-indones (*loc. cit.*) and arylideneindandiones; the following are isolated: *ethylidene-*, m.p. 278°; o-, m.p. 283°, m-, m.p. 240°, and p-, m.p. 240°, *-nitrobenzylidene-*, and o-, m.p. 275°, and m-, m.p. 260°, *-methoxybenzylidene-indandionedi-indones*; m-*methoxybenzylidene-*, m.p. 143°, *veratrylidene-*, m.p. 205°, and *asarylidene-*, m.p. 206°, *-indandiones.* Ethylidenebisindandione, m.p. 254° (lit. 227°), is also a by-product when MeCHO is used. Indandione (3 mols.) and α-naphthylideneindandione (1 mol.) in EtOH–piperidine give α-naphthylidene-bisdi-indone (*loc. cit.*) and α-*naphthylideneindandionedi-indone*, m.p. 260°. H. B.

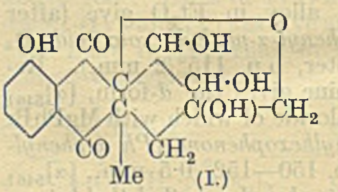

(I.)

Preparation of chloranil. M. Gallotti (Annali Chim. Appl., 1932, **22**, 602).—Benzoquinone (108 g.) is dissolved in small portions in 1080 g. of HCl (*d* 1·18). After 20 hr. stirring, 320 c.c. of H_2O_2 (120 vol.) are gradually added below 60°. The pasty mass is stirred for 12 hr., diluted with twice its wt. of H_2O, washed with H_2O on a vac. filter, and dried at 60—70°. Yield, 239 g, m.p. 289—290°. O. F. L.

Synthesis of aloe-emodin. P. C. Mitter and D. Banerjee (J. Indian Chem. Soc., 1932, **9**, 375—377).—The *chloride*, m.p. 190°, of 1 : 8-diacetoxy-anthraquinone-3-carboxylic acid (prepared by oxidation of diacetylchrysophanic acid) is converted by reduction (Rosenmund) and subsequent hydrolysis into 1 : 8-*dihydroxy*-3-*aldehydoanthraquinone*, m.p. 218°, reduced (H_2, PtO_2, $FeCl_2$, EtOH) to 1 : 8-*dihydroxy*-3-*hydroxymethylanthraquinone*, m.p. 219—220° (corr.), which is identical with natural aloe-emodin. Anthraquinone-2-carboxyl chloride is similarly reduced to the aldehyde and thence to 2-*hydroxymethylanthraquinone*, m.p. 183°. H. B.

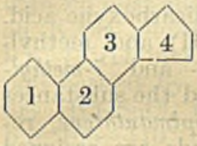
Synthesis of 1 : 2-benzanthraquinone by thermal dehydration of *o*-α-naphthoylbenzoic acid. M. Gallotti and P. Galimberti (Annali Chim. Appl., 1932, **22**, 598—600).—Dry *o*-α-naphthoylbenzoic acid (prep. described) is heated for 2 hr. at 130—140°, and then for a few sec. at 170°. The product has m.p. 168—169° after crystallising from AcOH; yield 80%. O. F. L.

Constitution of the aloins. III. R. S. Cahn and J. L. Simonsen (J.C.S., 1932, 2573—2582; cf. A., 1930, 609).—It is concluded from new and old analytical and chemical evidence that barbaloin is (I), $C_{16}H_{18}O_7$ (cf. J.C.S., 1877, **32**, 267). The halogenoaloins, previously (*loc. cit.*) designated halogenonorbarbaloins, are true derivatives of (I), and the tetrahalogenoaloe-emodins obtained on oxidation are *sec.* products. The constitution of the derivative, $C_{20}H_{15}O_9Br_3$, is uncertain. (I) gives by the Purdie method the *Me_5 ether*, m.p. 177—179° after sintering at 175° (2 : 4-*dinitrophenylhydrazone*, amorphous; *oxime*, a gum), $[\alpha]_{5461}$ −12·05° in $CHCl_3$, giving, with Br in $CHCl_3$, HCl and a gum, and oxidised by hot aq. $KMnO_4$ to rhein Me_2 ether. (I) and aq. borax give aloe-emodinanthranol (II) and MeOH (but not arabinose) (cf. Hauser, this vol., 370), and the yield is improved by addition of N_2H_4. Hydrogenation (Pd–C) of (II) in aq. KOH gives *dihydroaloe-emodinanthranol*, m.p. 180° (*K* salt). (II) with boroacetic anhydride in warm Ac_2O gives immediately a dark ppt., but (I) reacts much more slowly, owing probably to fission to (II). Hauser's formula for (II) is thus confirmed. (I) and aq. $FeCl_3$ at 110° give a 75% yield of aloe-emodin. Penta-acetyltribromobarbaloin ("nor" derivative) with CrO_3–AcOH–Ac_2O gives *tetrabromotriacetylaloe-emodin*, decomp. 291—292°, hydrolysed to tetrabromoaloe-emodin, m.p. 272° (lit. 264—266°). Tribromobarbaloin Me_5 ether ("nor" derivative) and hot piperidine give the phenolic *Me_3 ether*, dimorphic, decomp. 260° after sintering at 250°. R. S. C.


(I.)

Ramalic acid. G. Koller (Monatsh., 1932, **61**, 286—292).—The Et_2O extract of *Ramalina pollinaria* contains evernic (I) and ramalic acid (II), $C_{18}H_{18}O_7$, decomp. 209° (vac.) [Ac_2 derivative, m.p. (vac.) 175° (decomp.) (*Me* ester, m.p. 142°)]. (II) is hydrolysed by cold 30% NaOH in H_2 to orsenillic and rhizoninic acids and is probably identical with obtusatic acid (Asahina and Fuzikawa, this vol., 613). The ramalic acid of Hesse (A., 1898, i, 531) and Zopf (*ibid.*, 89) is either (I) or a mixture of (I) and (II). H. B.

Œstrin. VI. Ring structure of crystalline trihydroxy- and ketohydroxy-œstrin. G. F. Marrian and G. A. D. Haslewood (J.S.C.I., 1932, **51**, 277—283T).—The Me ethers of trihydroxy- (I) and ketohydroxy-œstrin (II) give " I vals." close to the theoretical for one double linking when treated with the Rosenmund–Kuhnhenn reagent; the *bromides* isolated from the reaction mixtures are $C_{19}H_{25}O_3Br$, m.p. 200—203°, and $C_{19}H_{23}O_2Br$, m.p. 191—193°, respectively, showing that the " I vals." are due to substitution and not addition of Br. Clemmensen reduction of (II) gives a phenolic *substance*, $C_{18}H_{24}O$, m.p. 133—134°, which is insol. in hot aq. NaOH (but forms a Na salt); the existence of the non-reactive " enolic " double linking of Butenandt *et al.* (this vol., 781) is no longer necessary. These results afford fairly conclusive evidence against the presence of a fourth double linking in (I) or (II) (which must be four- and not three-ring compounds). (II) is transformed by AcOH–conc. HCl into a more fusible and probably less acidic compound. Prolonged KOH-fusion of (I) gives a *phenoldicarboxylic acid*, $C_{18}H_{22}O_5$, m.p. 146—147° (turbid), 187—190° (clear), which yields an *Ac* derivative *anhydride*, m.p. 186—190°, and a *Me ether anhydride*, m.p. 172—174°. It is probable that (I) and (II) contain the annexed ring system. The CO group in (II) is probably in ring 4. Ring 1 or 2 is aromatic (and has a phenolic OH group) in both compounds.
H. B.



Amyrins. II. Products of selenium dehydrogenation. O. Brunner, H. Hofer, and R. Stein (Monatsh., 1932, **61**, 293—298; cf. A., 1929, 71; Ruzicka *et al.*, *ibid.*, 932; Dieterle, A., 1931, 624).—Dehydrogenation of α- or β-amyrin (or a mixture) with Se at 280—360° gives sapotalin (1 : 2 : 7-trimethylnaphthalene), a hydrocarbon, $C_{14}H_{16}$, m.p. 116° (*picrate*, m.p. 156—157°; *styphnate*, m.p. 166°) [probably identical with that obtained by Ruzicka *et al.* (this vol., 517) by dehydrogenation of betulin], a *hydrocarbon*, m.p. 304—305° (C 93·1, H 6·1%), and a *naphthol*, $C_{13}H_{14}O$, m.p. 156—157° (*benzoate*, m.p. 185°) [probably identical with that described by Ruzicka *et al.* (*loc cit.*)]. H. B.

α-Elemolic and elemonic acids. V. H. Lieb and M. Mladenović (Monatsh., 1932, **61**, 274—285).—Acetyl-α-elemolic acid (A., 1931, 960) is hydrolysed by EtOH–NaOEt to α-elemolic acid (I), m.p. 226°, $[\alpha]_{D}^{20}$ −29·56° in $COMe_2$, which analyses correctly as $C_{30}H_{48}O_3$. (I) is reduced (H_2, Pd–C, EtOH) to dihydro-α-elemolic acid (II), m.p. 238°, $[\alpha]_{D}^{20}$ −18·35° in EtOH, and converted by HBr in $CHCl_3$ into bromohydro-α-elemolic acid, m.p. 229°, $[\alpha]_{D}^{20}$ −15·6° in $COMe_2$, which with MeOH–KOH regenerates (I). The dibromide, m.p. 285°, $[\alpha]_{D}^{20}$ −8·16° in EtOH, of (I) and MeOH–KOH give bromo-α-elemolic acid, m.p. 283°. Analyses of all the above compounds support the C_{30} formula. Elemonic acid (III), m.p. 274—275°, $[\alpha]_{D}^{21}$ −66·85° in $CHCl_3$, affords an oxime, m.p. 236—237° (lit. 230—231°), $[\alpha]_{D}^{18}$ −112·8° in $CHCl_3$, which, contrary to Bauer and Dimokostoulos (A., 1931, 847), could not be reduced by Na–Hg (or catalytically). Oxidation of (II) with CrO_3 in AcOH gives *dihydroelemonic acid*, $C_{30}H_{48}O_3$, m.p. 293°, $[\alpha]_{D}^{20}$ −52·4° in $CHCl_3$ (*oxime*, m.p. 249°, $[\alpha]_{D}^{19}$ −6·16° in $CHCl_3$), identical with the acid (*oxime*, m.p. 231°, $[\alpha]_{D}^{20}$ −126·1° in $CHCl_3$) obtained by catalytic reduction of (III) [and previously described (this vol., 397) as tetrahydroelemonic acid] and isomeric with the dihydroelemonic acid of Ruzicka *et al.* (this vol., 749). H. B.

Stereochemical structure. V. Menthyl and bornyl esters of α-keto-acids. R. Roger and P. D. Ritchie (Biochem. Z., 1932, **253**, 239—265).—The mechanism of asymmetric induction is studied by comparison of the rotations of the menthyl and bornyl esters of α-keto-acids with those of the esters of the corresponding non-ketonic acids. Tables permit comparison of the rotations in different media ($COMe_2$, C_6H_6, $CHCl_3$, CS_2, EtOH, and EtOAc) for various wave-lengths (6708—4358 Å.) of such pairs of esters and the influence of temp. and concn. is investigated. P. W. C.

Oxidation of unsaturated compounds by selenium dioxide. E. Schenk and E. Borgwardt (Ber., 1932, **65**, [*B*], 1601—1602; cf. Riley and others, this vol., 833).—SeO_2 in EtOH is added slowly to a boiling mixture of technical α-pinene and EtOH, whereby verbenone, b.p. 97—99°/14 mm. (semicarbazone, m.p. 208—211°), is obtained.
H. W.

Synthesis of camphor. II. Saponification. M. Tomeo (Anal. Fís. Quím., 1932, **30**, 679—689).—Crude bornyl acetate gives a yield of borneol, m.p. 180—185°, of only 57·5%, as compared with 96—98·7% from the purified acetate. A 5—10% excess of NaOH is advisable, and refluxing should be continued for 2 hr. at 111°. The product obtained from purified acetate has m.p. 203°; this gives an 85% yield of camphor, compared with 95% from pure borneol. The results are discussed from the technical viewpoint. H. F. G.

Rotatory powers of substituted camphoranilic acids and *N*-phenylcamphorimides. M. Singh and R. C. Bhalla (J. Indian Chem. Soc., 1932, **9**, 363—369).—The following are prepared from camphoric anhydride, NH_2Ar, and NaOAc at 140—145°: 2′ : 4′-*dimethyl*-, m.p. 220—221°, 3′ : 5′-*dimethyl*-, m.p. 214—215°, 2′ : 4′-*dichloro*-, m.p. 200—201°, 2′ : 5′-*dimethoxy*-, m.p. 137—139°, 3′-*methoxy*-, m.p. 186·5°, and 3′-*ethoxy*-, m.p. 168°, -*camphoranilic acids*; 2′ : 4′-*dichloro*-, m.p. 62·5°, 2′ : 5′-*dimethoxy*-, m.p. 111—112°, 3′-*methoxy*-, m.p. 121—123°, 3′-*ethoxy*-, m.p. 93—95°, and 2′ : 6′-*dimethyl*-, m.p. 154—155°, -N-*phenylcamphorimides*. 4′-Nitro-2′-methoxy-, m.p. 182—184° (lit. 185—186°), 4′-*nitro*-2′-*ethoxy*-, m.p. 171—173°, 4′-nitro-2′-methyl-, m.p. 226—228° (lit. 229—230°), and 2′(or 6′)-*nitro*-3′-*methyl*-, m.p. 139—140°, -*camphoranilic acids* are obtained by nitration (fuming HNO_3–AcOH) of the appropriate acids. Vals. of $[M]_D$ for the above in various solvents are given. Introduction of a second Me in the *m*-position (with respect to the first Me) has little effect on the rotation; 4′-NO_2, 2′-OMe, and 2′-Cl groups cause depression (cf. A., 1931, 626).

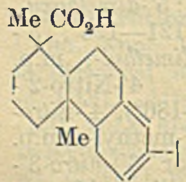
H. B.

Rotatory dispersive power of organic compounds. XX. Rotatory dispersion and circular dichroism of camphor-β-sulphonic acid in the region of absorption. T. M. Lowry and (Miss) H. S. French (J.C.S., 1932, 2654—2658; cf. A., 1930, 135).—The rotatory dispersion of camphor-β-sulphonic acid in H_2O rises rapidly to a max. (2000) at 3090 Å. and falls to a —max. (2450) at 2690 Å. with reversal of sign at 2950 Å. The ordinary absorption rises to a max., ε 35, at 2840 Å., and the circular dichroism to a max., $\varepsilon_r \sim \varepsilon_e$ 1·535, at 2900 Å. The ketonic band is thus shown to be composite.

R. S. C.

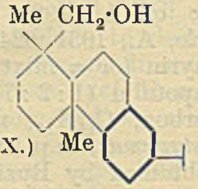
Polyterpenes. LXXII. Oxidations with perbenzoic acid and dehydrogenations with selenium in the amyrin series. L. Ruzicka, H. Silbermann, and P. Pieth. **LXXIII. Addition of maleic anhydride to abietic acid and *d*-pimaric acid.** L. Ruzicka, P. J. Ankersmit, and B. Frank. **LXXIV. Oxidation of methyl *d*-pimarate and dihydro-*d*-pimarate with perbenzoic acid.** L. Ruzicka and B. Frank. **LXXV. Carbon skeleton of abietic and *d*-pimaric acids.** L. Ruzicka, G. B. R. de Graaff, and H. J. Müller (Helv. Chim. Acta, 1932, **15**, 1285—1289, 1289—1294, 1294—1299, 1300—1303; cf. this vol., 948).—LXXII. Hydrogenation of β-amyrilene gives dihydro-β-amyrilene (I), m.p. 84—85°, new $[\alpha]_D$ +83° in C_6H_6, and an *isomeride*, m.p. 92—93°, $[\alpha]_D$ +77° in C_6H_6. Dihydro-α-amyrilene has new $[\alpha]_D$ +74° in C_6H_6. Use of EtOAc for purification led to isolation of purer, and some new, oxides produced by the action of BzO_2H on substances of the amyrin series. β-Amyrin oxide, $C_{30}H_{50}O_2$, has new m.p. 201—202°. β-Amyrilene gives a *dioxide*, $C_{30}H_{48}O_2$, m.p. 199—201° after sintering. (I) affords a *monoxide*, $C_{30}H_{50}O$, m.p. 126—127°. A mixture of α- and β-amyrin with Se under certain conditions affords the substituted naphthol, $C_{13}H_{14}O$, m.p. 153—154°, obtained from betulin (this vol., 517) and sapotalin.

LXXIII. Me abietate and maleic anhydride at 160° give an additive *compound* (II), $C_{25}H_{34}O_5$, m.p. 214—215°, $[\alpha]_D$ —26° in $CHCl_3$, hydrolysed by KOH–EtOH to the *anhydride-carboxylic acid* (III), $C_{24}H_{32}O_5$, m.p. 227—228°, $[\alpha]_D$ —25° in $CHCl_3$, the *Me_3* ester, m.p. 113° after sintering, of which is shown by its *R* to contain one ethylenic linking. (II) gives an impure *Me_2 Et* ester, b.p. 220°/0·35 mm. Et abietate (IV) gives a similar additive *compound*, which affords a *Me_2 Et* ester, b.p. 212°/0·3 mm.; the portion of (IV) which did not react yielded an *Et abietate*, (V), +2EtOH, m.p. 62—63°, and anhyd., m.p. 66—67°. American colophony and maleic anhydride afford (III) directly, $[\alpha]_D$ —28°. *d*-Pimaric acid reacts abnormally. The above reactions indicate the annexed formula for abietic acid, although isolation of (V) shows the natural acid to be a mixture of isomerides.

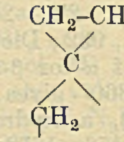


LXXIV. Previous results (A., 1928, 425) with *d*-pimaric acid and BzO_2H (VI) are confirmed. (VI) adds on about 1·6 atoms of O to Me *d*-pimarate, m.p. 69—70°, in $CHCl_3$ at 12° to yield a *dioxide*, amorphous, b.p. 199—205°/2 mm. Me dihydro-*d*-pimarate (VII), m.p. 79—80°, $[\alpha]_D$ +18·7° in C_6H_6 (modified prep.), reacts with 2 mols. of (VI) at 12° in $CHCl_3$ to give a mixture, b.p. 170—175°/0·15 mm., of mono- and di-oxide, from which on distillation a 50% yield of an *isomeride*, m.p. 54—55°, $[\alpha]_D$ +52° in C_6H_6, of Me *d*-pimarate was obtained. This yields an *isomeride*, m.p. 215—216, $[\alpha]_D$ about +60° in EtOH, of *d*-pimaric acid, and, when hydrogenated (PtO_2) in AcOH, an ester, hydrolysis of which gives a new *dihydropimaric acid*, m.p. about 189—192°, which is still unsaturated [$C(NO_2)_4$]. (VII) reacts, however, with only 1 mol. of (VI) at —10° to give in one experiment an unstable *oxide*, m.p. 103—104°, and in a second experiment an isomeric, stable *oxide*, m.p. 118—119°, which with AcOH and a drop of H_2SO_4 is dehydrated to yield *d*-pimaric acid, m.p. 186—188°. The dehydrogenation of (VII) at 12° and the formation of two oxides at —10° are abnormal and cast doubt on the utility of (VI) as a reagent in the polyterpene series.

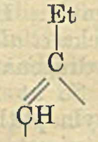
LXXV. Methylpimanthrenequinone (from *d*-pimarol) or methylretenequinone (from abietinol) with $KMnO_4$ gives hemimellitic and diphenyl-2 : 3 : 2′ : 4′-tetracarboxylic acids. Methylretene (VIII) and $K_3Fe(CN)_6$ give phenanthrene-1 : 7-dicarboxylic acid. These reactions indicate that (VIII) and methylpimanthrene are 1-*ethyl*-7-iso*propyl*- and 7-*methyl*-1-*ethyl-phenanthrene*, respectively, and the substances are re-named *homoretene* and *homopimanthrene*, respectively. The following compounds are assigned new formulæ: abietinol (IX); methylabietin (renamed homoabietin) (XI), formed from (IX) by a pinacolin change by way of (X); the tricarboxylic acids, $C_{11}H_{16}O_6$ and $C_{12}H_{18}O_6$, from abietic acid and *d*-pimaric acid, (XII) and (XIII), respectively;



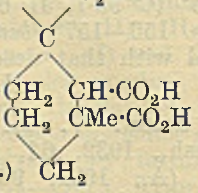
(IX.)



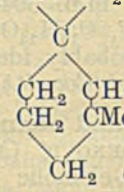
(X.)



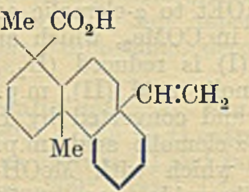
(XI.)



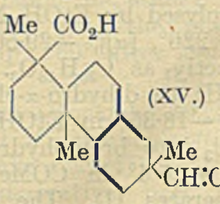
(XII.)



(XIII.)



(XIV.)



(XV.)

d-pimaric acid (XIV) or (XV), of which (XIV) is more probable, since tetrahydro-*d*-pimaric acid and

Se give only pimanthrene, whereas (XV) would be expected to yield also 4-methyl-7-ethylphenanthrene. (XIV) and (XV) can be built up from an irregular chain of isoprene units. The lines in heavy type indicate the possible positions of the ethylenic linkings. R. S. C.

2-Chloro-5-methylfuran and 5-nitro-2-methylfuran. H. Gilman and G. F. Wright (J. Amer. Chem. Soc., 1932, 54, 4108—4110).—N_2H_4–NaOEt reduction of 5-chlorofurfuraldehyde gives 36% of 2-chloro-5-methylfuran, identical with the decarboxylation product of 5-chloro-2-methyl-3-furoic acid; it does not react with Mg. Reduction of 5-nitrofurfuraldehyde gives 5-nitro-2-methylfuran. C. J. W. (*b*)

Allylic systems in furan. H. Gilman and R. A. Franz (Rec. trav. chim., 1932, 51, 991—995).—Mg 2-furyl iodide gives furfuryl alcohol, Et furoate, and furfuraldehyde with CH_2O, $ClCO_2Et$, and HCO_2Et, respectively. J. W. B.

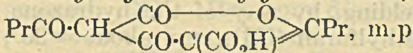
2 : 4-Dimethylfuran-3-aldehyde. T. Reichstein and H. Zschokke (Helv. Chim. Acta, 1932, 15, 1105—1110).—2 : 4-Dimethylfuran-3-carboxylic acid (I) (modified prep.), m.p. 125—126°, b.p. 131°/12 mm., and $SOCl_2$ give the *acid chloride*, b.p. 78—79°, yielding with HCN and C_5H_5N in Et_2O at −15° 2 : 4-*dimethylfuran*-3-*carboxylocyanide* (II), b.p. 91°/11 mm., which with Zn dust and AcOH gives the OH-nitrile, whence aq. K_2CO_3 affords 2 : 4-*dimethylfuran*-3-*aldehyde* (III), b.p. 73°/11 mm. (*semicarbazone*, m.p. 168°). (II) is polymerised by cold, conc. HCl and unchanged by dry HCl–$SnCl_2$ in Et_2O. The *oxime*, m.p. 74—76°, b.p. 105—110°/11 mm., with Ac_2O gives the *nitrile*, b.p. 66°/11 mm., hydrolysed by KOH–EtOH to (I). The acid chloride of (I) and NH_2Ph in Et_2O give the *anilide* (IV), m.p. 135—136°, which with PCl_5 (1 mol.) in warm PhMe yields the *chloroimide*, b.p. 132°/0·7 mm., changed by anhyd. $SnCl_2$ and dry HCl in Et_2O into the oily anil, which with $2N$-H_2SO_4 rapidly affords (III). When (IV) is heated with a large excess of PCl_5 and reduced, it yields an aldehyde, $C_7H_7O_2Cl$, m.p. 42°, which may be 5-*chloro*-2 : 4-*dimethylfuran*-3-*aldehyde*, since it gives a stable *semicarbazone*, m.p. 189°, or 2-*chloromethyl*-4-*methylfuran*-3-*aldehyde*, since with boiling $AgNO_3$ it ppts. AgCl. (III) is unstable to NaOH and differs from furan-α-aldehydes in forming a normal anil with NH_2Ph,AcOH. All m.p. are corrected. R. S. C.

Synthesis of two trimethylfurans and of trimethylfurfuraldehyde. T. Reichstein, H. Zschokke, and W. Syz (Helv. Chim. Acta, 1932, 15, 1112—1118).—Et αβ-diacetyl-*n*-butyrate and boiling 10% H_2SO_4 give *Et* 2 : 4 : 5-*trimethylfuran*-3-*carboxylate*, b.p. 100—105°/12 mm. (94·5% yield), and a little of the corresponding *acid* (I), m.p. 131—132°, which with Cu chromite and boiling quinoline affords 2 : 4 : 5-*trimethylfuran* (II), b.p. 114°/720 mm., 51·5°/12 mm. Et acetonedicarboxylate, Me α-chloroethyl ketone, and NH_3 in Et_2O give a 10·7% yield of *Et*$_2$ 2 : 3-*dimethylfuran*-4-*carboxylate*-5-*acetate*, b.p. about 110—115°/0·2 mm., hydrolysed by KOH–MeOH to the corresponding dicarboxylic *acid*, m.p. 211° (decomp.), which at 220—250° gives CO_2 and (I). The *hydrazone*, m.p. (crude) 52° (changed by warm AcOH to an azine), of 2 : 4-dimethylfuran-3-aldehyde with NaOMe at 200° affords 2 : 3 : 4-*trimethylfuran*, b.p. about 54—55°/57 mm., which with HCN and HCl in Et_2O at −15° gives 3 : 4 : 5-*trimethylfurfuraldehyde*, m.p. 31—32°, b.p. 68°/0·3 mm., oxidised (Ag_2O–NaOH) to 3 : 4 : 5-*trimethyl*-2-*furoic acid*, m.p. 185° (decomp.), and yielding, by way of the hydrazone, 2 : 3 : 4 : 5-tetramethylfuran (III), m.p. about −30°, b.p. 44°/12 mm. (III) prepared by Willstätter's method (A., 1914, i, 286) is not pure. "Dimethylketopentene" is probably 5-*methyl*-2-*ethylfuran*, and not (II) (cf. *loc. cit.*); similarly, "methyluvinic acid" is probably 2-*methyl*-5-*ethylfuran*-3-*carboxylic acid*, not (I), and "methylmethronic acid" is 2-*methylfuran*-3-*carboxylic acid*-5-α-*propionic acid*. R. S. C.

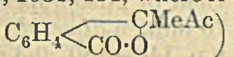
Synthesis of 2-*iso*propylfuran and 5-*iso*propylfurfuraldehyde. T. Reichstein, H. Zschokke, and G. Rona (Helv. Chim. Acta, 1932, 15, 1118—1124).—2-Furyl Me ketone or Et furoate and MgMeI give 2-*furyldimethylcarbinol*, m.p. about 11—12°, b.p. 62°/11 mm., dehydrated by boiling Ac_2O to give a poor yield of 2-iso*propenylfuran* (I), b.p. below about 30°/70 mm., a *dimeride*, b.p. 75°/0·3 mm., and a *substance*, b.p. 140—180°/0·3 mm. Hydrogenation (PtO_2) of (I) in Et_2O affords 2-iso*propylfuran* (II), b.p. about 40°/60 mm., yielding 5-iso*propylfurfuraldehyde*, b.p. 86—87°/11 mm. (*semicarbazone*, m.p. 167°), oxidised by Ag_2O to 5-iso*propyl*-2-*furoic acid*, m.p. 66—67°. Et β-keto-γ-methylvalerate and αβ-dichloroethyl ether in Et_2O and aq. NaOH give in poor yield *Et* 2-iso*propylfuran*-3-*carboxylate*, b.p. 92°/12 mm., and Et β-*iso*butyroxycrotonate. The former ester yields the corresponding *acid*, m.p. 79°, which with Cu chromite and boiling quinoline gives (II). Et sodiomalonate and Et β-2-furylacrylate give *Et*$_3$ β-2-*furylpropane*-αγγ-*tricarboxylate*, b.p. 162—165°/0·7 mm., hydrolysed to the corresponding *acid*, which at the m.p. (158°) or when distilled yields β-2-furylglutaric acid, decarboxylated to (II) best with Cu chromite and boiling β-naphthoquinoline. R. S. C.

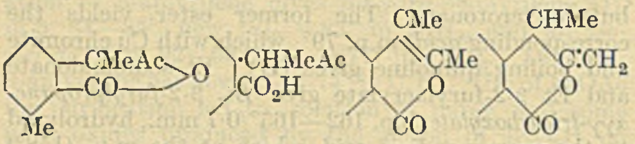
Abnormal reaction of furfuryl halides with potassium cyanide. T. Reichstein and H. Zschokke (Helv. Chim. Acta, 1932, 15, 1124—1127).—2-Furylmethylcarbinol (I), b.p. 65·5—66·5°/11 mm., PBr_3, and C_5H_5N in pentane at −15° give an unstable solution of the corresponding chloride, which with aq. KCN yields 5-*ethyl*-2-*furonitrile*, b.p. about 68—70°, hydrolysed by KOH–MeOH to 5-*ethyl*-2-*furoic acid* (II), m.p. 94—95°, also prepared from 5-ethylfurfuraldehyde and Ag_2O–NaOH. (I), C_5H_5N, and $SOCl_2$ give a similar unstable solution, whence (II) was obtained. 2-Furyldimethylcarbinol, PBr_3, and C_5H_5N in C_5H_{12} at −20° give a very unstable solution, giving with KCN a very poor yield of a neutral *oil*, b.p. about 80°/12 mm. The halides could not be isolated. R. S. C.

Synthesis of 2 : 6-diethyl- and 2 : 6-di-*n*-propyl-γ-pyrones. S. S. Deshapande (J. Indian Chem. Soc., 1932, 9, 303—308).—Dehydropropionylacetic acid (improved prep. given; cf. von Pechmann and Neger, A., 1893, i, 398) and boiling HCl (*d* 1·19) give 2 : 6-*diethyl*-γ-*pyrone*, b.p. 126°/7 mm., m.p. 10° [*hydrochloride*, m.p. 77—78°; *chloroplatinate*, m.p. 188° (decomp.); *picrate*, m.p. 110°; *mercuri-*

chloride, m.p. 72° (decomp.)], converted by conc. aq. NH_3 at 130° into 2 : 6-*diethyl-4-pyridone* (+H_2O), m.p. 65—66° [*hydrochloride* (+H_2O), m.p. 76—78°; *chloroplatinate*, m.p. 203° (decomp.)]. Acetonedicarboxylic acid, PrCOCl, and a little conc. H_2SO_4 give *carboxydehydro*-n-*butyrylacetic acid*,  $\mathrm{PrCO{\cdot}CH}<\begin{matrix}\mathrm{CO}\text{————}\mathrm{O}\\ \mathrm{CO{\cdot}C(CO_2H)}\end{matrix}\geqslant\mathrm{CPr}$, m.p. 80°, the *K* salt, m.p. 164°, of which when heated with H_2O and then acidified (AcOH) affords *dehydro*-n-*butyrylacetic acid*, b.p. 140—144°/4 mm., m.p. 16°. This is converted (as above) into 2 : 6-*di*-n-*propyl-γ-pyrone*, b.p. 136°/5 mm. [*picrate*, m.p. 61°; *chloroplatinate*, m.p. 162—164°; *mercurichloride*, m.p. 88—89° (decomp.)]. 2 : 6-*Di*-n-*propyl-4-pyridone* [*monohydrate*, m.p. 62°; *hydrochloride* (+H_2O), m.p. 96—98°; *chloroplatinate*, m.p. 204°] has b.p. 210—215°/12 mm., m.p. 85—88°.

H. B.

Congo copal oil. 3-Acetyl-3 : 7-dimethylphthalide. L. Westenberg and J. P. Wibaut (Rec. trav. chim., 1932, **51**, 1004—1007).—The lactone of the methyl ketone (I) (A., 1931, 484, where it is erroneously given the structure  $\left(\mathrm{C_6H_4}<\begin{matrix}\text{——}\mathrm{CMeAc}\\ \mathrm{CO{\cdot}O}\end{matrix}\right)$ obtained by oxidation of 1 : 2 : 5-trimethylnaphthalene, is converted by HI (*d* 2·0) and red P into the iso*coumarin* derivative (III) or (III*a*), m.p. 135°, converted by NaOH–MeOH and subsequent acidification with HCl into the *keto-acid* (II), m.p. 108° (*oxime*, m.p. 150°), which by treatment with HI (*d* 2·0), gives H_2O and (III).



(I.) (II.) (III.) (III*a*.)

Determination of Br addition to (III) gives only 1·37 atoms Br per mol. lactone instead of the calc. 2.

J. W. B.

Pæonol derivatives : a case of bromine displacement. J. Shinoda, D. Sato, and M. Kawagoye (J. Pharm. Soc. Japan, 1932, 52, 91—94).—Nitration of pæonol gives the 5-NO_2-derivative (cf. Adams, A., 1919, i, 160), converted by standard methods into the 5-NH_2-, m.p. 113—114°, 5-OH-, m.p. 166—167°, 5-Cl-, m.p. 154—155°, and 5-Br-, m.p. 172—173° (I) (cf. A., 1897, i, 221), -derivatives; the last-named is converted by Ac_2O at 180° into 6-*bromo-7-methoxy-3-acetyl-2-methyl*-1 : 4-*benzopyrone*, m.p. 190—191°, and under milder conditions into the acetate, m.p. 90—91°. Oxidation of the Me ether of (I) with $KMnO_4$ gives 5-*bromo*-2 : 4-*dimethoxybenzoylformic acid*, m.p. 170—171° (*oxime*, m.p. 164—166°), further oxidised by H_2O_2 to 5-bromo-2 : 4-dimethoxybenzoic acid, m.p. 198—200°. Nitration of (I) (cf. Adams, *loc. cit.*) gives a mixture of the 3-*NO_2*-derivative, m.p. 125—126° {3-*NH_2*-compound, m.p. 109—110° [*hydrochloride*, m.p. 215° (decomp.)]}, and 6-*bromo-5-nitropæonol* (II), m.p. 125—126°, the Br having been displaced by the NO_2 group. The 5-*NH_2*-derivative, m.p. 135° (*hydrochloride*, m.p. 205—206°), corresponding with (II), gave 6-*bromopæonol*, m.p. 133—134° (III) [*phenylhydrazone*, m.p. 192—193° (decomp.); *Me ether*, m.p. 52—53°; *acetate*, m.p. 125°; 5-*bromo* 7-*methoxy-3-acetyl-2-methyl*-1 : 4-*benzopyrone*, m.p. 178—179°], when replacement of its NH_2 group by OH was attempted. Oxidation of (III) with $K_2S_2O_8$ gives a *bromohydroxypæonol*, m.p. 164—166°. H. A. P.

***O*-Methylation of quercetin.** J. A. Anderson (Canad. J. Res., 1932, 7, 283—284).—Freudenberg's method gives penta- (I) and tetra-methylquercetin in the proportions 2 : 1 (cf. this vol., 167). Modification of the method gives an 84% yield of (I). R. S. C.

Yellow colouring matter of Khapli wheat, *Triticum dicocci*. II. Constitution of tricetin. J. A. Anderson (Canad. J. Res., 1932, 7, 285—292; cf. A., 1931, 1426).—Khapli wheat contains H_2O-sol. substances (also present in six other varieties), possibly glucosides of tricetin (I), and small amounts of (I) (modified prep.), m.p. 288° after softening at 278° (also obtained from Marquis wheat leaves in smaller yield). The Ac_3 derivative of (I) by Freudenberg's method gives the *Me_3 ether* (II), m.p. 192—193°, hydrolysed by KOH–EtOH to *O*-trimethylgallic acid (III) and 2-hydroxy-4 : 6-dimethoxyacetophenone. Phloroglucinol Me_3 ether (modified prep.) is converted into 2-acetoxy-4 : 6-dimethoxyacetophenone. Phloroacetophenone, 3 : 4 : 5-trimethoxybenzoic anhydride, and the Na salt of (III) at 175° yield a little 5 : 7-*dihydroxy*-3′ : 4′ : 5′-*trimethoxyflavone* (IV), m.p. 269—270°, and much 3-(3″ : 4″ : 5″-*trimethoxybenzoyl*)-5 : 7-*dihydroxy*-3′ : 4′ : 5′-*trimethoxyflavone*, m.p. 203—204·5° (*Ac_2* derivative, m.p. 189—191°) [hydrolysed by aq. KOH to (IV)]. The *Ac_2* derivative, m.p. 160—162°, of (IV) gives by Freudenberg's method the Me_5 ether, identical with (I), whilst HI and AcOH demethylate (IV) to 5 : 7 : 3′ : 4′ : 5′-*pentahydroxyflavone* (V), decomp. above 330°, the Ac_5 derivative of which is identical with that of (I). (I) is thus proved to be (IV). Many of the data of Badhwar *et al.* (this vol., 621) regarding (IV) and its derivatives are corrected.

R. S. C.

Dye from acacia wood. K. Brass and H. Kranz (Naturwiss., 1932, 20, 672—673).—The dye (I) from *Gleditschia monosperma* is identical with that from *Robinia pseudacacia* (II) (cf. B., 1932, 760), since both yield *Ac_5* and *$(MeO)_5$*- (III) derivatives, m.p. 224° and 148°, respectively. (I), $C_{15}H_{10}O_7$, +1 or $2H_2O$ and anhyd., is 3 : 3′ : 4′ : 5′-*tetrahydroxyflavonol*, since (*a*) (III) with KOH–MeOH gives gallic acid Me_3 ether and fisetol Me_2 ether, and (*b*) gallaldehyde Me_3 ether and pæonol give 3 : 3′ : 4′ : 5′-*tetramethoxyflavonol*, m.p. 194°, yielding (III) when methylated. (II) contains also a substance, which gives an *Ac* derivative, m.p. 141°. R. S. C.

Plant dyes. XLII. Isomeric carotenes and their relations to vitamin-*A*. P. Karrer, K. Schöpp, and R. Morf. **XLIII. Carotenoids of flowers.** P. Karrer and A. Notthafft. **XLIV. Reactions of gossypol.** P. Karrer and E. Tobler. **XLV. Constitution of diglucosidic anthocyanins.** P. Karrer and G. de Meuron (Helv. Chim. Acta, 1932, **15**, 1158—1165, 1195—1204, 1204—1212, 1212—1217; cf. this vol., 976).—XLII. The mother-liquors (A) from α- and β-carotene contain a third *carotenoid* (not obtained pure), an oil, adsorbed by Al_2O_3 and desorbed therefrom by 90% MeOH (not by ligroin), with absorption max. in CS_2 at 482 and 453 mμ; it has no vitamin activity. (A) contained also α-carotene, m.p. 172°, absorption max. at 510 and 476 mμ; since it has $[\alpha]^{24}_{644}$ +130°, carrots must contain also inactive α-carotene, and the rotation is, therefore, no measure of the carotene content of a prep. *iso*Carotene (I) (modified prep.), $C_{40}H_{56}$, m.p. 192—193° (corr.), with cold alkaline $KMnO_4$ gives αα-dimethylglutaric (II), αα-dimethylsuccinic, and (probably) succinic acids, with hot $KMnO_4$ and CrO_3 3·8 and 6 mols. of AcOH, respectively, with O_3 in CCl_4–AcOH (I) but not $COMe_2$, geronic or *iso*geronic acid, and is hydrogenated (PtO_2) in AcOH to $C_{40}H_{80}$. (I) thus probably contains only one ring, which differs from the β-ionone ring in the position of the ethylenic linking. The β-ionone ring is considered to be essential for vitamin-*A* activity.

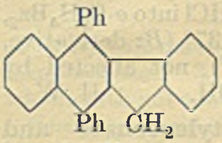
XLIII. The following carotenoids, occurring mainly as esters, were isolated from the flowers named: xanthophyll from *Caltha palustris*, *Trollius europæus*, *Ranunculus arvensis*, and *Tragopogon pratensis* (I); violaxanthin from (I), *Laburnum*, and *Sinapis officinalis*; zeaxanthin (II) from *Senecio Doronicum*; and lycopene from *Dimorpheteca aurantica*. Carotenoids are not confined to yellow flowers. The name "phytoxanthin" is proposed for carotenoids containing O and 40 C atoms, whilst the name xanthophyll is retained for the substance, $C_{40}H_{56}O_2$, obtained from green leaves. The following *esters* of (II) were prepared: $(EtCO_2)_2$, m.p. 142°; $(Pr^{\alpha}CO_2)_2$, m.p. 132°; $(Bu^{\alpha}CO_2)_2$, m.p. 125°; *di*-n-*hexoate*, m.p. 117—118°; and *di*-n-*heptoate*, m.p. 107°.

XLIV. Gossypol (I) (modified prep. from cottonseeds), m.p. 199°, gives a *quinoxaline* derivative, m.p. 298° after sintering and decomp., and is, therefore, an α-diketone or, more probably, an *o*-quinone. It is phenolic, gives an Ac_6 derivative (II), but two of the OH groups titrate as acids and two are characterised by resistance to hydrolysis when esterified. With 40% NaOH at 100° (I) gives HCO_2H (2 mols.) and *apo*gossypolic acid, $C_{28}H_{30}O_6$ (Ac_6 derivative; no CO group). With O_3 under certain conditions (I) gives *gossypolic acid*, $(C_{12}H_{14}O_4)_x$ (x=probably 2), m.p. 241°, shown by colour reactions to be an α-OH-acid, yielding with CH_2N_2 in Et_2O *Me methylgossypolate*, $[C_{12}H_{12}O_2(OMe)_2]_x$, m.p. 142°, which is hydrolysed by 2*N*-KOH–MeOH to *methylgossypolic acid*, m.p. 225°. The *dihydrazone*, m.p. about 285°, of (I) with NaOEt at 180° gives a *substance*, $C_{30}H_{34}O_6N_2$, decomp. from 170°, containing the grouping $CH_2{\cdot}C{:}N{\cdot}NH_2$. (I) is not a glucoside and does not give MeCl or EtCl with conc. acids.

XLV. When an anthocyanin is treated with H_2O_2, the excess of H_2O_2 destroyed by Pt-black, and the glucoside-ester hydrolysed either by $NHPh{\cdot}NH_2$, or by NH_3, the sugar from position 3 is liberated and can be identified as osazone. Subsequent treatment with HCl hydrolyses the glucoside at position 7 and allows this sugar component to be identified. Results with pæonin, cyanin, monardin, and hirsutone are in agreement with the conclusions of Robinson (this vol., 1140). Violanin, however, gives the osazone of a polysaccharide in the first stage. R. S. C.

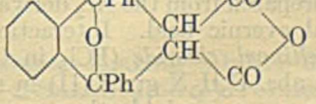
Synthesis of chromones. III. Condensation of β-naphthol with ethyl alkylacetoacetates. D. CHAKRAVARTI (J. Indian Chem. Soc., 1932, 9, 389—392; cf. this vol., 519).—β-$C_{10}H_7{\cdot}OH$, $CHAcMe{\cdot}CO_2Et$, and conc. H_2SO_4 give a little 3 : 4-*dimethyl*-1 : 2-βα-*naphthapyrone*, m.p. 127°; with P_2O_5 as the condensing agent, 2 : 3-*dimethyl*-1 : 4-βα-*naphthapyrone*, m.p. 130°, results. β-$C_{10}H_7{\cdot}OH$ does not condense with Et α-ethyl- and -*n*- and -*iso*-propyl-acetoacetates in presence of H_2SO_4; the use of P_2O_5 gives 2-*methyl*-3-*ethyl*-, m.p. 117°, 2-*methyl*-3-*propyl*-, m.p. 95°, and 2-*methyl*-3-iso*propyl*-, m.p. 131°, -1 : 4-βα-*naphthapyrone*, respectively. These results agree with the generalisation previously made (*loc. cit.*). The course of the Pechmann and Simonis reactions depends on both the phenol and the ester. 2-*Styryl*-3-*methyl*-, m.p. 186°, -3-*ethyl*-, m.p. 183°, -3-*propyl*-, m.p. 168°, and -3-iso*propyl*-, m.p. 187°, -1 : 4-βα-*naphthapyrones* have been prepared. H. B.

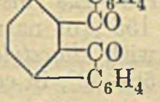
Condensation of 2 : 5-diphenyl-3 : 4-benzfuran with unsaturated compounds. I. R. WEISS and A. BELLER. **II. 1 : 4-Diphenylnaphthalene and derivatives.** R. WEISS and A. ABELES [with E. KNAPP] (Monatsh., 1932, 61, 143—146, 162—168).—I. Addition of 2 : 5-diphenyl-3 : 4-benzfuran (I) to Et cinnamate occurs readily in EtOH, best under the influence of HCl, and gives *Et* 1 : 2 : 4-*triphenylnaphthalene*-3-*carboxylate*, m.p. 138—140°. This was not hydrolysable by ordinary methods, and with HI and PhOH gives 1 : 4-*diphenyl*-2 : 3-*benzfluorene* (II), m.p. 199°, or, with conc. H_2SO_4, 1 : 4-*diphenyl*-2 : 3-*benzofluorenone* (III), m.p. 208°. (II) is identified by synthesis by addition of (I) to indene, and is oxidised by CrO_3 in AcOH to (III).



(II.)

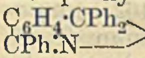
II. Interaction of (I) with maleic anhydride in xylene gives 1 : 4-*diphenyl*-1 : 4-*oxido*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-2 : 3-*dicarboxylic anhydride* (IV), m.p. 270—274°, converted by HCl in AcOH (with loss of H_2O) into 1 : 4-*diphenylnaphthalene*-2 : 3-*dicarboxylic anhydride* (V), m.p. 275°, and by cold conc. H_2SO_4 into 1 : 2 : 3 : 4-*dibenzoylenenaphthalene* (VI), m.p. 295—297°. The anhydride ring of (V) resisted all other attempts at disruption or substitution. Addition of (I) to acraldehyde occurs under the influence of HCl in the cold to give 1 : 4-*diphenyl*-2-*naphthaldehyde*, m.p. 146—148° (*oxime*, m.p. 187—191°), at higher temp. a *substance*, $C_{23}H_{16}O_2$, m.p. 163—166° [not (VII)], is formed. The aldehyde is oxidised by $KMnO_4$ in aq. $COMe_2$ to 1 : 4-*diphenyl*-2-*naphthoic acid* (VII), m.p. 223—225° (*Me* ester, m.p. 163—165°), and a little 1 : 4-*diphenylnaphthalene* (VIII), m.p. 135—137° (*NO_2*-derivative, m.p. 163—165°) (definitely different from the substance described as such by Franssen, A., 1925, i, 1146). Distillation of the Na salt of (VII) with KOH in N_2 gives (VIII) and a little 2-*phenyl*-3 : 4-*benzfluorenone*,

(IV.)


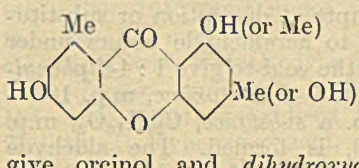


(VI.)

m.p. 189°, the latter of which was synthesised for comparison from the chloride of (VII) ($SOCl_2$) by action of $AlCl_3$ in CS_2. H. A. P.

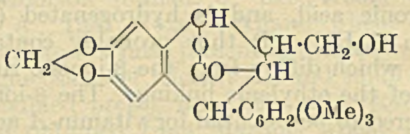
αα′-Substituted ββ′-benzo-αα′-dihydrofurans. II. F. Seidel and O. Bezner (Ber., 1932, **65**, [*B*], 1566—1574; cf. A., 1929, 73).—*o*-Cyanotriphenylmethane in Et_2O is converted by MgPhBr at room temp. into *o*-benzoyltriphenylmethane (I), m.p. 88°, which does not react with $NHPh{\cdot}NH_2$ in AcOH or with molten p-$NO_2{\cdot}C_6H_4{\cdot}NH_2$. It is oxidised to diphenylphthalide (II) and yields a 2 : 4-*dinitrophenylhydrazone*, m.p. 218—220° after softening at 200°. It differs completely from 2 : 2 : 5-triphenyl-3 : 4-benzodihydrofuran, m.p. 120°, which does not react with 2 : 4-dinitrophenylhydrazine, and evidence of mutual interconvertibility is not obtained. The prep. of 5-hydroxy-2 : 2 : 5-triphenyl-3 : 4-benzo-2 : 5-dihydrofuran (III), m.p. 121°, from (II) and MgPhBr, from *o*-dibenzoylbenzene, and from (I) and Br is recorded. (I) and *o*-benzoyltriphenylcarbinol (IV) are related as ring–chain tautomerides. Reduction of (I) from each source by HCO_2H affords 2 : 2 : 5-triphenyl-3 : 4-benzo-2 : 5-dihydrofuran. With 2 : 4-dinitrophenylhydrazine (I) affords the *diazine*  $\begin{matrix}C_6H_4{\cdot}CPh_2\\CPh{:}N\text{——}\end{matrix}\!\!>\!N{\cdot}C_6H_3(NO_2)_2$, m.p. 245—247° (or $+1C_6H_6$, m.p. 77°, and $+1EtOH$, m.p. 160—163°). Attempts to synthesise (IV) from o-*cyanobenzophenone*, m.p. 86·5°, and MgPhBr lead to 1-*hydroxy*-1 : 3-*diphenyl*iso*indole*, converted by conc. HCl into o-$C_6H_4Bz_2$, and the *imine* of (IV), m.p. 135—137° (*Bz* derivative, m.p. 240° after softening at 225°), not affected by boiling 2*N*-HCl or 2*N*-NaOH–EtOH. H. W.

Synthesis of methyl diacetylevernate and tetra-acetylgyrophorate. G. Koller (Monatsh., 1932, **61**, 147—161).—Gyrophoric acid (I) readily gives an Ac_4 derivative, decomp. 231°, converted by CH_2N_2 into its *Me* ester (II), m.p. 202°, energetic alkaline hydrolysis of which gives only orcinol. Hydrolysis of (I) with cold 30% NaOH gives lekanoric (III) and orsellinic acids. The *Me* ester, m.p. 157° (CH_2N_2), of *triacetyl-lecanoric acid* (Ac_2O and C_5H_5N), readily gives the corresponding Ac_2 (IV), m.p. 149—150°, and *Ac*, m.p. 167°, derivatives on incomplete hydrolysis by alkali. Methylation of the free OH group in (IV) with CH_2N_2 gives *Me diacetylevernate*, m.p. 128—129°, also prepared from the Ac_2 derivative, m.p. 155°, of natural evernic acid. Interaction of (IV) with *diacetylorsellinoyl chloride* (PCl_5 in CCl_4), m.p. 56—58°, in cold abs. C_5H_5N gives (II) in small yield, thus confirming the structure assigned to (I) by Asahina (this vol., 851). Thermal decomp. of (I) or (III) give orcinol and *dihydroxydimethylxanthone*, m.p. 260° (annexed formula), also formed by distillation of (III) with Ac_2O. H. A. P.

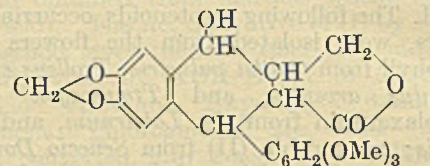


Eosin *B*. W. C. Holmes, C. G. Melin, and A. R. Peterson (Stain Tech., 1932, **7**, 121—127).—The absorption spectra of the two known dibromodinitrofluoresceins have been determined. Commercial eosin *B* is impure. H. W. D.

Podophyllin. W. Borsche and J. Niemann (Ber., 1932, **65**, [*B*], 1633—1634).—In reply to Späth and others (this vol., 1137) it is stated that podophyllomeronic acid is 6 : 7-methylenedioxy-2-methylnaphthalene-3-carboxylic acid, since it can be converted through phyllomeronic acid (6 : 7-dihydroxy-2-methylnaphthalene-3-carboxylic acid) and phyllomerol (6 : 7-dihydroxy-2-methylnaphthalene) into 2-methylnaphthalene. These observations and the isolation of 4 : 5-methylenedioxy-ω-3′ : 4′ : 5′-trimethoxyphenylphthalide by the oxidative degradation of podophyllic acid establish the constitutions (I) and (II) for podophyllotoxin and picropodophyllin respectively.



(I.)



(II.)

H. W.

Podophyllin. II. W. Borsche and J. Niemann (Annalen, 1932, **499**, 59—76).—Oxidation of podophyllomeronic acid (I) (this vol., 618) [Br_2-derivative, m.p. 359° (*Me* ester, m.p. 233—234°)] with HNO_3 (*d* 1·4) gives 6-*nitrotoluene*-2 : 4 : 5-*tricarboxylic acid* (II), m.p. 232—233° (*Me*₃ ester, m.p. 95—96°), whilst oxidation with alkaline $KMnO_4$ at 100° (bath) affords *toluene*-2 : 4 : 5-*tricarboxylic acid*, m.p. 212—215° (*Me*₃ ester), which is nitrated to (II). Boiling $KMnO_4$ converts (I) into pyromellitic acid. (I) heated with quinoline and Cu-bronze gives *podophyllomerol* (6 : 7-*methylenedioxy*-2-*methylnaphthalene*), m.p. 129—129·5° (*picrate*, m.p. 133—134°), whilst fusion with KOH and a little Zn dust at 280—325° affords *phyllomeronic acid* (III) (6 : 7-*dihydroxy*-2-*methylnaphthalene*-3-*carboxylic acid*), m.p. 243—244° [*Me* ester, m.p. 186—187°; *Me*₂ *ether* (IV), m.p. 223—225° (*Me* ester, m.p. 125—126°); Ac_2 derivative, m.p. 220° (previous sintering); Br_2-derivative, m.p. 265° (decomp.) (previous darkening) (*Me*₂ *ether Me* ester, m.p. 127—129°)], which when heated with $Ba(OH)_2$ gives *phyllomerol* (6 : 7 - *dihydroxy* - 2 - *methylnaphthalene*), m.p. 161—162° [*Me*₂ *ether*, m.p. 98—100° (*picrate*, m.p. 120—121°), obtained similarly from (IV)]. Zn dust distillation of (III) gives 2-$C_{10}H_7Me$. (I) is 6 : 7 - methylenedioxy - 2 - methylnaphthalene - 3 - carboxylic acid. Oxidation of podophyllic acid with cold alkaline $KMnO_4$ gives $H_2C_2O_4$, picropodophyllin, a *lactone*, $C_{18}H_{16}O_7$, m.p. 218—221°, and substances, m.p. 195—200° and 210—213°; the last is methylated (CH_2N_2) to a *compound*, $C_{20}H_{18}O_7$, m.p. 166—167°. Oxidation at 100° (bath) gives 3 : 4 : 5-$(OMe)_3{\cdot}C_6H_2{\cdot}CO_2H$, $H_2C_2O_4$, and two aldehydo- or keto-acids, $C_{12}H_{14}O_6$ (2 : 4-*dinitrophenylhydrazones*, m.p. 200—201° and 176—177°). Picropodophyllin and podophyllotoxin (see preceding abstract), heated with $MeOH$–N_2H_4,H_2O give *podophyllhydrazide*, m.p. 155—160° (decomp.). H. B.

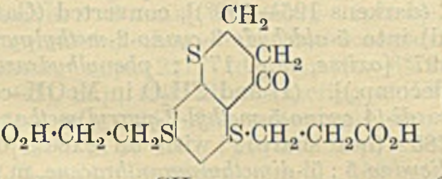
Synthesis of aldehydes in the furan series. III. Dicyclic furan substances, difuryl and difurylmethane. T. Reichstein, A. Grüssner, and H. Zschokke (Helv. Chim. Acta, 1932, 15, 1066—1074; cf. this vol., 166).—Furoylacetic acid and di-β-chloroethyl ether in Et$_2$O and aq. NaOH give 2 : 2′-difuryl-3-carboxylate (I), b.p. 86—98°/0·5 mm. (21% yield), and sometimes a neutral *substance*, b.p. 52°/0·5 mm.; the latter gives a *Na* salt and is possibly a lactone. The acid obtained by hydrolysing (I) with quinoline and Cu chromite at 160—200° gives difuryl (66·6% yield), b.p. 63—64°/11 mm., which with HCN and HCl in dry Et$_2$O at −15° gives 2 : 2′-*difuryl*-5-*aldehyde*, b.p. 91—94°/0·4 mm., m.p. 54° (*semicarbazone*, m.p. 221°), oxidised by Ag$_2$O to 2 : 2′-*difuryl*-5-*carboxylic acid*, m.p. 154°. A dialdehyde could not be obtained, activity of the second furan ring being decreased by the negatively substituted ring attached directly to it. 2-Bromofuran and activated Cu–Mg (modified prep.) in Et$_2$O give the Grignard reagent, which with furonitrile gives 2 : 2′-*difuryl ketone*, m.p. 34°, b.p. about 110°/0·5 mm. (decomposed by N$_2$H$_4$ in EtOH at 180° and unchanged at 150°), reduced by Na and EtOH to 2 : 2′-*difurylmethane* (II), m.p. about −30°, b.p. 78°/12 mm., also obtained in poor yield from Mg 2-furyl bromide and furfuryl chloride. (II) with HCN and HCl in Et$_2$O at −15° gives 2 : 2′-*difurylmethane*-5 : 5′-*dialdehyde*, m.p. 118—119°, b.p. about 165°/0·5 mm. [*disemicarbazone*, decomp. about 260°; *dioxime*, m.p. about 185—187° (decomp.)], decomposed by dil. alkali with colour changes. All m.p. are corrected. R. S. C.

Stereoisomeride of 2 : 3 : 5 : 6-tetrachlorodioxan. W. Baker (J.C.S., 1932, 2666—2667).—Chlorination of dioxan gives, besides "2 : 3-dichlorodioxan," a new 2 : 3 : 5 : 6-*tetrachlorodioxan*, m.p. 101°, nearly quantitatively hydrolysed to glyoxal.
R. S. C.

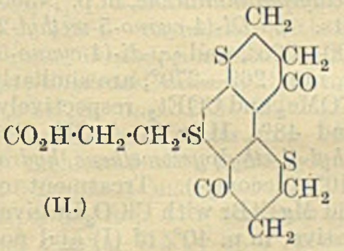
Synthesis of difuryl- and dithienyl-acryloylmethane. W. Lampe, S. Rozenblumówna, and A. Kessel (Chem. Listy, 1932, 26, 454—458).—β-Furylacryloyl chloride (I) condenses with Et sodioacetoacetate to yield *Et* β-*furylacryloylacetoacetate*, m.p. 50—52°, which on heating eliminates CO to give β-*furylacryloylacetone* (II), m.p. 62—64°. The Na salt of (II) condenses with (I) to yield *di*-β-*furylacryloylacetone*, m.p. 98—100°, which on hydrolysis eliminates AcOH to yield *di*-β-*furylacryloylmethane* (III), m.p. 128—130°. The corresponding thienyl compounds, prepared analogously, are: β-*thienylacryloyl chloride*, m.p. 128—129°, *Et* β-*thienylacryloylacetoacetate*, m.p. 65°, β-*thienylacryloylacetone*, m.p. 86—87°, *di*-β-*thienylacryloylacetone*, m.p. 107—108°, and *di*-β-*thienylacryloylmethane* (IV), m.p. 182—184°. (III) and (IV) are substantive yellow dyes for cotton. Solutions of (III) give max. absorption for λ 4128 Å., of (IV) for λ 4228 Å., as compared with 3780 Å. for the corresponding Ph derivative. R. T.

New synthesis of diphenylene sulphide. H. W. Schwechten (Ber., 1932, 65, [*B*], 1608—1609).—The tetrazotised solution of 2 : 2′-diaminodiphenyl is treated with K hexathiocyanochromiate. The pptd. complex salt is dried with MeOH and Et$_2$O. When heated with twice its wt. of KCl it yields a mixture of diphenylene sulphide and disulphide, from which the former is isolated by distillation over Cu-bronze or the latter by crystallisation from MeOH.
H. W.

Thiophenols. Thiochromanone and thioxanthone [derivatives]. V. Bellavita (Gazzetta, 1932, 62, 655—663).—The *Na* salt of *s*-C$_6$H$_3$(SH)$_3$ (A., 1909, i, 791) reacts with CH$_2$Cl·CH$_2$·CO$_2$Na to form *benzene*-1 : 3 : 5-*tri*-β-*thiopropionic acid*, m.p. 171—172°, which with warm conc. H$_2$SO$_4$ yields *thiochromanone*-5 : 7-*di*-β-*thiopropionic acid* (I), m.p. 216°, 5 : 6-*thiopyranonothiochromanone*-7-β-*thiopropionic acid* (II), m.p. 224–225°, and 5 : 6 : 7 : 8-*bisthiopyranonothiochromanone* (III), m.p. above 320°. The same Na salt reacts with diazotised anthranilic acid to form *benzene*-1 : 3 : 5-*tri*-o-*thiobenzoic acid*, m.p. 300°, which with hot conc. H$_2$SO$_4$ yields *thioxanthone*-1 : 3-*di*-o-*thiobenzoic acid* (IV), m.p. above 320°, and 1 : 2 : 3 : 4-*bis*-(2′ : 3′)-*thiochromononothioxanthone* (V), m.p. above 320°.



(I.)



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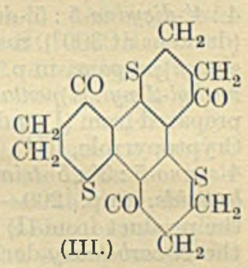

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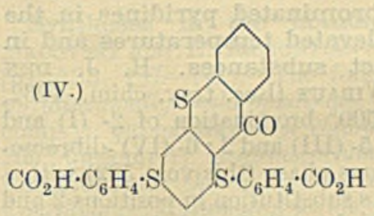

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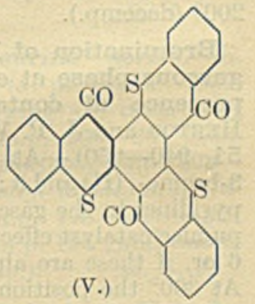


(V.)

E. W. W.

Electron-sharing ability of organic radicals. VI. 2-Substituted pyrrolines and pyrrolidines. D. F. Starr, H. Bulbrook, and R. M. Hixon (J. Amer. Chem. Soc., 1932, 54, 3971—3976; cf. this vol., 167).—The general method (A., 1931, 849) of prep. of 2-substituted pyrrolines is improved. 2-p-*Tolylpyrroline*, b.p. 125—132°/6—8 mm., m.p. 60—61° (*picrate*, m.p. 185—186°), reduced to 2-*p*-tolylpyrrolidine, b.p. 128—130°/8—10 mm., 141—144°/23—25 mm. [picrate, m.p. 173° (lit. 150°)]; 2-cyclo*hexylpyrroline*, b.p. 114—116°/22—24 mm. (*picrate*, m.p. 117°), reduced to 2-*cyclo*hexylpyrrolidine, b.p. 84—87°/7—9 mm., 214—221° [*chloroaurate*, m.p. 105—106°; the m.p. (153°) of the picrate reported by De Jong and Wibaut (A., 1930, 479) could not be confirmed], and 2-*benzylpyrrolidine*, b.p. 129—

131°/17—19 mm., 150—153°/44—46 mm. (*picrate*, m.p. 136—137°), are described. Dissociation consts. are reported as follows : 2-ethyl-, 6·09 ($-\log K_B$) ; 2-benzyl-, 6·92 ; 2-*p*-tolyl-, 6·41 ; 2-phenyl-, 7·12—7·27, and 2-*cyclo*hexyl-pyrroline, 6·05 ; 2-*p*-tolyl-, 4·00 ; 2-benzyl-, 3·64, and 2-*cyclo*hexyl-pyrrolidine, 3·20. If the criteria for measuring chemical affinity are observed, the polar properties of any group may be expressed as a mathematical function of the electron-sharing ability of the attached radical. C. J. W. (*b*)

3-Cyano-2-methylpyrrole. W. H. Strain (Annalen, 1932, **499**, 40—46).—Et αβ-dichloroethyl ether and diacetonitrile in aq. NH_3 give 3-*cyano-2-methylpyrrole* (I), m.p. 133° [4 : 5-*Br*$_2$-derivative, decomp. >200° (darkens 195—200°)], converted (Gattermann method) into 5-*aldehydo*-3-*cyano*-2-*methylpyrrole* (II), m.p. 197° [*oxime*, m.p. 177° ; *phenylhydrazone*, m.p. 177° (decomp.)]. (I) and CH_2O in MeOH–conc. HCl afford *di*-(4-*cyano*-5-*methyl*-2-*pyrryl*)*methane*, m.p. 280—285° (not sharp) ; with an excess of CH_2O, 4 : 4′-*dicyano*-5 : 5′-*dimethylpyranthracene*, m.p. >360° (darkens at 300°), results. ββ-*Di*-(4-*cyano*-5-*methyl*-2-*pyrryl*)*propane*, m.p. 300—305°, and γγ-*di*-(4-*cyano*-5-*methyl*-2-*pyrryl*)*pentane*, m.p. 269—270°, are similarly prepared from (I) and $COMe_2$ and $COEt_2$, respectively. Cryptopyrrole, (II), and 48% HBr in AcOH give 4-*cyano*-5 : 3′ : 5′-*trimethyl*-4′-*ethylpyrromethene hydrobromide*, m.p. 209—210° (decomp.). Treatment of the product from (I) and MgEtBr with $ClCO_2Et$ gives the N-*carbethoxy*-derivative, m.p. 40°, of (I) and not *Et* 3-*cyano*-2-*methylpyrrole*-5-*carboxylate*, m.p. 127°, which is obtained by dehydration of the *oxime*, m.p. 178° (not sharp), of Et 3-aldehydo-2-methylpyrrole-5-carboxylate with Ac_2O–KOAc. Hydrolysis of the product from (I) and SO_2Cl_2 in Et_2O with H_2O gives some 4 : 5-dichloro-2-aldehydo-3-cyanopyrrole, m.p. 200° (decomp.). H. B.

Bromination of brominated pyridines in the gaseous phase at elevated temperatures and in presence of contact substances. H. J. den Hertog and J. P. Wibaut (Rec. trav. chim., 1932, **51**, 940—950).—At 500° bromination of 2- (I) and 3-bromo-, (II) and 3 : 5- (III) and 2 : 6- (IV) -dibromopyridines in the gaseous phase (this vol., 522) with a pumice catalyst effects substitution in positions 2 and 6 or, if these are already substituted, in position 4. At 300° the position of substitution varies with the catalyst (given in parentheses), being 3- and 5- with $FeBr_2$ and 2- and 6- with Cu_2Br_2. Thus at 500°, (II) gives 2 : 5-di- (25%) and 2 : 3 : 6-*tri*-, m.p. 82° (25% ; also from 2 : 6-Br_2-compound) (36% unchanged) ; (III) affords 2 : 3 : 5-tri- and 2 : 3 : 5 : 6-*tetra*-, m.p. 102—103° (also from 2 : 6-compound) (50% unchanged) ; whilst (IV) gives 2 : 4 : 6-*tri*-, m.p. 107° (28%) (60% unchanged), -*bromopyridine*. At 300° (I) gives 2 : 5-di- and 2 : 3 : 5-tri- ($FeBr_2$) or 2 : 6-di- (27%) and *penta*-, m.p. 209·5—210° (Cu_2Br_2 ; 66% unchanged) ; (IV) gives 2 : 3 : 6-tri- (30%) and 2 : 3 : 5 : 6-tetra- (5%) ($FeBr_2$; 42% unchanged) ; whilst (III) gives 2 : 3 : 5-tri- (22%) (Cu_2Br_2 ; 53% unchanged) -bromopyridine. No differential contact action is observed when C_5H_5N itself is brominated at 300° [(II) and (III) formed], probably owing to the much greater formation of carbonaceous matter which coats the catalyst and destroys its sp. action. Interaction of C_5H_5N and Br at 250° without a contact substance gives, in addition to (III), 3 : 5-*dibromo*-4-*aminopyridine*, m.p. 168—169°, identical with the compound obtained by Fischer and Riemerschmied (A., 1883, 923) from pyridine-3-sulphonic acid and erroneously described as a dibromopyridine. With Cu_2Br_2 at 350° is obtained, also, a *dibromopyridine*, m.p. 88—88·5° (not 2 : 5-derivative), whilst from the product previously obtained by bromination of C_5H_5N (*loc. cit.*) is isolated 3 : 4 : 5-*tribromopyridine*, m.p. 100—102°. The various bromination products and their physical properties are summarised. J. W. B.

2-Methylhexamethyleneimine. A. Müller and P. Krauss (Monatsh., 1932, **61**, 212—218).—The 2-methylhexamethyleneimine (*Bz* derivative, b.p. 185—187°/13 mm.) of Gabriel (A., 1909, i, 493) is proved by direct comparison to be different from 2-ethylpiperidine, and identical with the product of reduction of ε-amino-*n*-heptolactam (this vol., 1239) with Na and EtOH. Its $PhSO_2$ derivative is oxidised by aq. $KMnO_4$ to ε-benzenesulphonamido-*n*-heptoic acid (*loc. cit.*). The ready formation of the 7-membered ring seems to be favoured by the α-Me group. The reduction product of phenyl ε-amino-*n*-amyl ketone (Gabriel) differs markedly from α-benzylpiperidine, thus confirming the cyclic structure (2-phenylhexamethyleneimine) originally assigned. H. A. P.

Electrolytic preparation of *iso*indolines. E. W. Cook and W. G. France (J. Physical Chem., 1932, **36**, 2383—2389).—*iso*Indolines are prepared by electrolytic reduction of methylphthalimidine, phthalimidine, methylphthalimide, and phthalimide. *N*-Amino*iso*indoline is prepared similarly from *N*-nitroso*iso*indoline. Variations in the yields obtained with different electrodes are attributed to the H_2 overvoltages and probable differences in selective activation of the depolariser by the metals. R. H. C. (*b*)

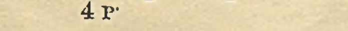
Indolenines. V. Addition of acyl halides to indolenines. H. Leuchs, G. Wulkow, and H. Gerland (Ber., 1932, **65**, [*B*], 1586—1593 ; cf. A., 1929, 704).—The additive nature of the reaction between indolenines and acyl chlorides is established by experiments in the absence of H_2O and alkali. 3 : 3-Dimethylindolenine, $(C_{10}H_{11}N)_3$ (I), and BzCl quantitatively yield the non-isolated 2-chloro-1-benzoyl-3 : 3-dimethylindoline, transformed by H_2O into 2-hydroxy-, m.p. 202—204° (yield 93%), by NaOMe into 2-methoxy-, m.p. 71—72° (74%), by NH_3–MeOH into 2-amino-, m.p. 116°, and by AgOBz into 2-benzoyloxy-, m.p. 147—148°, -1-benzoyl-3 : 3-dimethyl indoline ; with AgOAc it gives the 2-*OAc*-derivative, m.p. 156—157°. (I) and AcCl yield a resinous product identified by transformation into 2-hydroxy-, m.p. 118°, and 2-amino-, m.p. 78—80°, -1-acetyl-3 : 3-dimethylindoline. With *p*-NO_2·C_6H_4·COCl (I) yields 2-*chloro*-1-p-*nitrobenzoyl*-3 : 3-*dimethylindoline*, m.p. 147—148° (or $+C_6H_6$, m.p. about 143° after softening at 105°), converted by boiling H_2O into the corresponding 2-*OH*-compound, m.p. 167—169° (or $+C_6H_6$, m.p. 165—167° after softening), and by $ClCO_2Et$ into the resinous 2-*chloro*-1-*carbethoxy*-3 : 3-

dimethylindoline, whence 2-*hydroxy*-1-*carbethoxy*-3 : 3-*dimethylindoline*, m.p. 84°. 2-*Bromo*-1-m-*bromobenzoyl*-3 : 3-*dimethylindoline*, m.p. 114—115° (vac.), is obtained from m-*bromobenzoyl bromide*, b.p. 156°/38 mm. β-Phenyl-α-benzylpropionamide, m.p. 129°, is transformed by MgPhBr in Et_2O into Ph β-phenyl-α-benzylethyl ketone, m.p. 78°: the *phenylhydrazone*, m.p. 92—94°, is transformed by $ZnCl_2$ in EtOH at 105° into 2-*phenyl*-3 : 3-*dibenzylindolenine*, m.p. 123—125°, in poor yield. 2-Methyl-1-hydrindonephenylhydrazone is converted by boiling 12*N*-HCl into the non-cryst. 3 : 2 : o-*benzylene*-3-*methylindolenine* (II) (non-cryst. *hydrochloride*; *picrate*, m.p. 146°), transformed by Ac_2O and NaOAc at 100° into 2-*acetoxy*-1-*acetyl*-3 : 2 : o-*benzylene*-3-*methylindoline*, m.p. 122°, from which the corresponding 2-*OH*-, m.p. 199°, and 2-NH_2-, m.p. 137°, compounds are derived. 2-*Chloro*-1-*benzoyl*- (corresponding 2-*OH*-derivative, m.p. 177°) and 2-*chloro*-1-p-*nitrobenzoyl*- (corresponding 2-*OH*-compound, m.p. 197°) -3 : 2 : o-*benzylene*-3-*methylindoline* are described. The product derived from BzCl and 3 : 2-*o*-benzylene-3-ethylindolenine (III) is converted into the corresponding 2-hydroxy-1-benzoyl-, m.p. 145—146°, and 2-benzoyloxy-1-benzoyl-, m.p. 179°, -3 : 2-*o*-benzylene-3-ethylindolines. 2-*Hydroxy*-1-p-*nitrobenzoyl*-, m.p. 156—157°, and -1-*benzenesulphonyl*-3 : 2-o-*benzylene*-3-*ethylindoline*, m.p. about 120°, or $+C_6H_6$, m.p. 83—87° (decomp.) after softening at 77°, are derived from the non-cryst. additive compounds of (III) and *p*-$NO_2 \cdot C_6H_4 \cdot COCl$ and $PhSO_2Cl$, respectively. (III) and AcCl give a non-cryst. substance identified by conversion into 2-hydroxy-, m.p. 160°, 2-acetoxy-, m.p. 125°, 2-amino-, m.p. 138°, -1-acetyl-3 : 2-*o*-benzylene-3-ethylindoline.

2-Phenyl-1-hydrindone is best obtained by rapid dissolution of αβ-diphenylpropionic acid in H_2SO_4 and treatment of the mixture with ice. The acid monohydrate is transformed by PCl_5 (1·2 mols.) or $SOCl_2$ into the anhydride and a *compound*, $C_{30}H_{24}O_2$, m.p. 238°, converted by MeOH–NH_3 at 100° into αβ-diphenylpropionamide and regarded as a derivative of 1 : 3-*cyclo*butanedione.

2-*Chloro*-1-*benzoyl*-3 : 2-o-*benzylene*-3-*phenylindoline*, m.p. 169—170° (corresponding 2-*OH*-compound, m.p. 192—193°), is derived from 3 : 2-*o*-benzylene-3-phenylindolenine (IV) and BzCl. Similarly from (IV) are derived 2-*chloro*-, m.p. 185—186°, and 2-*hydroxy*-, m.p. 198—200°, -1-p-*nitrobenzoyl*-3 : 2-o-*benzylene*-3-*phenylindoline*. 3-Phenylindolenine appears to react with difficulty or not at all with $PhSO_2Cl$; the non-cryst. additive product with AcCl is hydrolysed to 2-hydroxy-1-acetyl-3 : 2-*o*-benzylene-3-phenylindoline, m.p. 184°. H. W.

Syntheses of pyrrolic and indolic alcohols. Q. Mingoia (Gazzetta, 1932, 62, 844—854).—Trioxymethylene, or better gaseous CH_2O, in Et_2O converts Mg indole into 3-*indolylcarbinol*, m.p. 158° (*Ac* derivative, m.p. 95°), together with *bis*-3-*indolylmethyl ether*; Mg 2-methylindole yields 2-*methyl*-3-*indolylcarbinol*, m.p. 205—206° (*Ac* derivative, m.p. 140—142°), and *bis*-(2-*methyl*-3-*indolylmethyl*) *ether*. Mg pyrrole yields the *di-ether*,


$$C_4H_3N{<}\begin{matrix}CH_2 \cdot O \cdot CH_2\\ CH_2 \cdot O \cdot CH_2\end{matrix}{>}C_4H_3N.$$

E. W. W.

Action of nitrous acid on amines of the indole series. N. I. Putochin and N. P. Davydova (J. Gen. Chem. Russ., 1932, 2, 290—296; cf. A., 1931, 629).—3-Indolylmethylamine sulphate (I) when treated with $Ba(NO_2)_2$ gives quinoline, whilst 2-methyl-3-indolylmethylamine (II), which cannot form the intermediate cyclic complex, affords di-(2-methylindolyl)-ethane. Indolealdoxime and Ac_2O give the *acetate*, m.p. 154°, reduced (H_2 and PtO_2) to the amine, isolated as (I); (II) is similarly prepared from 2-methylindolealdoxime (*acetate*, m.p. 149—150°).

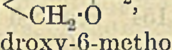
G. A. R. K.

Aminotetrahydroquinolines. I. E. Balaban (J.C.S., 1932, 2624—2626).—Reduction of the corresponding NO_2-compounds gives the following *quinoline* derivatives: 5-*amino*-6-*methoxy*- (*picrate*, m.p. 225°); 8-amino-6-methoxy- (I) [*hydrochloride*, m.p. 228°; *picrate*, m.p. 221° (decomp.)]; 6-amino-8-methoxy- (II), m.p. 169° after sintering at 165° (lit. 168°) (*picrate*, m.p. 224° after softening); 8-*amino*-7-*methoxy*- (III), m.p. 108° [*picrate*, m.p. 226° (decomp.)]; 5-*amino*-8-*methoxy*-, m.p. 156° (*picrate*, m.p. 126°). Reduction with Sn–HCl–EtOH affords 5-*amino*-6- and -8-*methoxy*-1 : 2 : 3 : 4-*tetrahydroquinoline* [*dihydrochlorides*, $+H_2O$, m.p. 247° (decomp.) and $+0{\cdot}5H_2O$, m.p. 258—260° (decomp.), respectively; *dipicrate* of the former, m.p. 147°). Similar reduction of 2-chloro-6-nitro-4-methylquinoline gives a little *dl*-6-amino-4-methyl-1 : 2 : 3 : 4-tetrahydroquinoline [*dipicrate*, m.p. 173° (decomp.)]. 8-Methoxyquinoline and fuming HNO_3 at 0° give the 5-NO_2-compound [*nitrate*, $+H_2O$, m.p. 177° (effervescence)], whilst 7-methoxyquinoline gives the 8-NO_2-compound, m.p. 178° [*nitrate*, m.p. 155—156° (effervescence)], and a little ?-NO_2-compound, m.p. 200°. Reduction of (I), (II), and (III) gives coloured solutions, but no tetrahydro-base. The free tetrahydroquinolines are unstable in air. R. S. C.

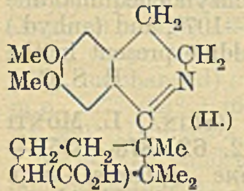
Syntheses in the homoneurine series. E. Macovski and E. Ramontianu (J. pr. Chem., 1932, [ii], 135, 137—141).—The following are described: *pyridiniumallyl chloroplatinate*, m.p. 200—201° (decomp.); *quinoliniumallyl chloroplatinate*, m.p. 208—209° (decomp.); iso*quinoliniumallyl iodide*, m.p. 78° (impure), and *chloroplatinate*, m.p. 175° (decomp.); 2-*methylquinoliniumallyl iodide*, m.p. 196°, and *chloroplatinate*, m.p. 194—195° (decomp.). H. A. P.

Reaction of quinoline and benzaldehyde. W. M. Cumming and J. G. Gillan (J.C.S., 1932, 2666).—The base, m.p. 99—100°, obtained by Cumming *et al.* (this vol., 155) is benzylidenequinaldine [*hydrochloride*, m.p. ($+H_2O$) 106—107°, and (anhyd.) 221—221·5°], formed from quinaldine present in the quinoline. R. S. C.

Quinoline derivatives. II. (Signa) L. Monti and G. Verona (Gazzetta, 1932, 62, 878—885).—8-*Hydroxy*-5(?)-*quinolylmethylamine* [*picrate*, m.p. 195° (decomp.)] is obtained as the *hydrochloride* by the action of HCl on its Bz derivative (A., 1905, i, 247), which with NaOH gives a green *polymeride*, also obtainable from 8 : 8′-dihydroxy-5 : 5′-diquinolylmethane (A., 1913, i, 990). The *hydrochloride* and *picrate*, m.p. 185—187° (decomp.), of 6-*hydroxy*-?-

quinolylmethylamine are similarly prepared from its *Bz* derivative, m.p. 231—232° (from $C_9H_6N·OH$ and $OH·CH_2·NHBz$), which with KOH gives 6′ : 6-*dihydroxy-? ?-diquinolylmethane*, m.p. >300° (*hydrochloride*; *Ac*$_2$ derivative, m.p. 203—204°). The latter is not obtained by the action of CH_2O on 6-hydroxyquinoline in H_2SO_4, which gives 6 : ω-*methylenedioxy-?-methylquinoline*,  $C_9H_5N{<}\begin{smallmatrix}O—CH_2\\CH_2·O\end{smallmatrix}$, m.p. 119° (*picrate*, m.p. 216°). 2-Hydroxy-6-methoxy-4-methylquinoline (this vol., 402) with $OH·CH_2·NHBz$ yields 2-*hydroxy*-6-*methoxy*-4-*methyl-?-quinolylmethylbenzamide*, m.p. 280—282°. E. W. W.

Synthesis of *iso*quinoline derivatives. II. K. S. Narang, J. N. Rây, and S. S. Silooja (J.C.S., 1932, 2510—2513; cf. A., 1931, 1168).—1-Methylnorhydrastinine (I), o-$NO_2·C_6H_4·CHO$, and NaOEt in EtOH give 1-*o-nitrostyrylnorhydrastinine*, m.p. 132°, but other aldehydes do not condense. (I) and MeI give 1-methylhydrastinium iodide, m.p. 257°, which with Al–Hg, hot H_2O, and a little HCl affords 1-methyldihydrohydrastinine (hydrochloride, m.p. 221°; *picrate*, m.p. 192—193°). β-3 : 4-Dimethoxyphenylpropiono-β-piperonylethylamine, m.p. 146°, and $POCl_3$ in PhMe at 110° afford 1-β-3′ : 4′-*dimethoxyphenylethylnorhydrastinine*, m.p. 90°, the *methiodide*, m.p. 196°, of which is reduced by Al–Hg to 1-β-3′ : 4′-*dimethoxyphenylethyldihydrohydrastinine*, m.p. 101°. β-*Piperonylpropiono*-β-3′ : 4′-*dimethoxyphenylethylamide*, m.p. 149°, with PCl_5 in $CHCl_3$ gives 6 : 7-*dimethoxy*-1-β-*piperonylethyl*-3 : 4-*dihydro*iso*quinoline*, m.p. 75·5° (*hydrochloride*, m.p. 187—188°), the *methiodide*, m.p. 175°, of which is reduced to the *tetrahydro*iso*quinoline* derivative, m.p. 101° (*picrate*, m.p. 137°). The following were prepared by similar methods: β-*piperonylpropiono*-β-*piperonylethylamide*, m.p. 135°; 1-β-*piperonylethylnorhydrastinine* (best by $POCl_3$), m.p. 105° (*methiodide*, m.p. 229°); 1-β-*piperonylethyldihydrohydrastinine*, an oil (*picrate*, m.p. 102°); 6 : 7 : 3′ : 4′-*tetramethoxy*-1-β-*phenylethyl*-3 : 4-*dihydro*iso*quinoline*, m.p. 94° (*picrate*, m.p. 129°; *methiodide*); 6 : 7 : 3′ : 4′-*tetramethoxy*-1-β-*phenylethyl-2-methyl*-1 : 2 : 3 : 4-*tetrahydro*iso*quinoline*, an oil (*picrate*, m.p. 166°). β-Piperonylethylamine, phthalic anhydride, and a little NaOAc at 150—160° give *phthalo*-β-*piperonylethylimide*, m.p. 140°, and β-*piperonylethylphthalamic acid*, m.p. 143°; the acid with PCl_5 in hot $CHCl_3$ yields 6 : 7-*methylenedioxy*-1-*phenyl*-3 : 4-*dihydro*iso*quinoline-2′-carboxylic acid*, m.p. 175°. β-3 : 4-*Dimethoxyphenylethylcamphoramic acid* and $POCl_3$ in PhMe at 110° give 6 : 7-*dimethoxy*-1-(3′-*carboxy*-1′ : 2′ : 2′-*trimethyl*cyclo*pentyl*)-3 : 4-*dihydro*iso*quinoline* (II), m.p. 65° (evolution of CO_2 at 85°). The methiodide, m.p. 259°, of veratrylidene-β-piperonylethylamine, m.p. 78°, with Ag_2O in aq. EtOH gives an oily *base* (*picrate*, m.p. 179°), not identical with 1-3′ : 4′-dimethoxyphenyldihydrohydrastinine. R. S. C.



(II.)

Formation of heterocyclic nuclei containing iodine, nitrogen, and oxygen. L. Mascarelli (Mem. Accad. Italia, 1932, 3, Chim., No. 2, 5—15).—A review of the reactions by which diphenyleneiodonium, carbazole, and diphenylene oxide derivatives are formed from 2 : 2′-disubstituted Ph_2 derivatives with elimination of one of the substituents. R. K. C.

Naphthenic acids from petroleum. S. von Pilat and J. Reyman [with H. Morawski, F. Rosenkranz, and C. Zembal] (Annalen, 1932, 499, 76—83; cf. von Braun, A., 1931, 1396).—The naphthenic acids from Potok petroleum are esterified (EtOH–HCl), fractionated, and the fractions (*a*) b.p. 95—170°/3 mm. and (*b*) 170—220°/3 mm. reduced (Na–EtOH) to the corresponding alcohols (*a*) b.p. 100—168°/2 mm. (composition $C_{11}H_{22}O$) and (*b*) 168—200°/3 mm. ($C_{17}H_{31}O$). Condensation of the corresponding bromides with $CHNa(CO_2Et)_2$ and treatment of the resulting esters with $CO(NH_2)_2$ and EtOH–NaOEt gives (*a*) *barbituric acids*, $C_{15}H_{24}O_3N_2$, m.p. 208—211°, and $C_{16}H_{26}O_3N_2$, m.p. 218—220°, and (*b*) a *barbituric acid*, $C_{22}H_{38}O_3N_2$, m.p. 173—177°. The naphthenic acids from the illuminating oil fraction of the above petroleum similarly afford a *barbituric acid*, $C_{15}H_{24}O_3N_2$, m.p. 187—188°; an *isomeride*, m.p. 194—195°, and an *analogue*, $C_{18}H_{30}O_3N_2$, m.p. 201—202°, are similarly obtained from the same fraction of a Czechoslovakian oil. When Et naphthenates are reduced with Na and 96% EtOH in "benzine," a preponderance of glycols results. H. B.

Variation with p_H of ultra-violet spectra of some six-membered heterocyclic compounds. G. Florence, J. Enselme, and M. Pozzi (Compt. rend., 1932, 195, 614—615).—The increase in the absorption of diethyl-, ethylbutyl-, and diallyl-malonylcarbamide in passing from p_H 2 to p_H 6 and 9 is ascribed to enolisation. Uric acid probably has an enolic structure, and its strong absorption increases only slightly with p_H. The increased absorption of phenylethylmalonylcarbamide is related to electropositive nuclei. The decrease of absorption of diketopiperazine with increasing p_H is probably due to hydrolysis. A. C.

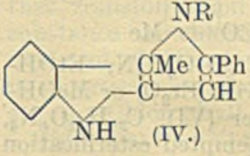
Thermal decomposition of azines. L. B. Howard and G. E. Hilbert. **Thermal decomposition of benzaldazine under 1000 atmospheres pressure of nitrogen, hydrogen, and ammonia** [with R. Wiebe and V. L. Gaddy] (J. Amer. Chem. Soc., 1932, 54, 3628—3641).—The products of the pyrolysis of benzaldazine (I), anisaldazine, o-chlorobenzaldazine, p-tolualdazine (II), hydroanisamide, tri-o-chlorohydrobenzamide (III), and benzoinhydrazone (IV) are given. Lophine [2 : 4 : 5-triphenylglyoxaline] (V) or its corresponding derivative is obtained from (I), (II), (III), and (IV). (V) is probably derived from (I) by way of benzaldimine, the intermediate existence of which is supported by the fact that pyrolysis of the mixed azine of PhCHO and fluorenone gives 9-iminofluorene. $CH_2Ph·NH_2$ or $(CH_2Ph)_2NH$ when heated at 300° yields (V) and tetraphenylpyrrole (VI), but in presence of stilbene only (VI) is obtained. The azines of $COPh_2$ and COPhMe and the mixed azine of $COPh_2$ and fluorenone are more stable to heat than the above aldazines and tend to eliminate PhCN rather than N. The pyrolysis of (I) is little affected by 1000 atm. of H_2 or N_2; with NH_3 the reaction is complex. H. A. B. (*b*)

Condensation products of pyrroles with acetaldehyde, acetone, and phorone. H. Fischer, A. Schormüller, and R. E. Windecker (Annalen, 1932, **498**, 284—296).—αα-Di-(4-carbethoxy-3 : 5-dimethyl-2-pyrryl)ethane and Br (1 or 2 mols.) in the cold give 4 : 4′-dicarbethoxy-3 : 5 : 3′ : 5′-tetramethylpyrromethene hydrobromide; with 3 mols. of Br, 5-bromo-3 : 4′-dicarbethoxy-4 : 3′ : 5′-trimethylpyrromethene results (probably by fission of the intermediate methine linking and formation of Et 5-bromo-2 : 4-dimethylpyrrole-3-carboxylate). MeCHO reacts with 3-propionyl-2 : 4-dimethyl- and 3-acetyl-2-methyl-4-ethyl-pyrroles in EtOH–conc. HCl to give *αα-di-*(4-*propionyl*-3 : 5-*dimethyl-2-pyrryl*)*ethane*, m.p. 180°, and *αα-di*-(4-*acetyl*-5-*methyl*-3-*ethyl*-2-*pyrryl*)-*ethane*, m.p. 248°, respectively. Cryptopyrrole and hæmopyrrolecarboxylic acid with hot Ac_2O and AcOH afford *acetylcryptopyrrole*, m.p. 112°, and *acetylhæmopyrrolecarboxylic acid*, m.p. 171°, respectively; all attempts to condense these with 2-unsubstituted pyrroles failed. Cryptopyrrole, $COMe_2$, and conc. HCl give *δδ-di*-(3 : 5-*dimethyl*-4-*ethyl-2-pyrryl*)-βζ-*dimethyl*-$\Delta^{\beta\epsilon}$-*heptadiene*, m.p. 148°, also obtained using mesityl oxide or, better, phorone in place of $COMe_2$; opsopyrrole similarly gives an O-containing *product*, m.p. 110°. Cryptopyrrolecarboxylic acid similarly affords *δδ-di*-(3 : 5-*dimethyl*-4-β-*carboxyethyl-2-pyrryl*)-βζ-*dimethyl*-$\Delta^{\beta\epsilon}$-*heptadiene*, m.p. 177°; the 4 : 5-*dimethyl*-3-β-*carboxyethyl* isomeride (*Me*$_2$ ester, m.p. 110°) has m.p. 280°. Hæmopyrrolecarboxylic acid, paracetaldehyde, and HBr–AcOH give a *compound*, $C_{32}H_{48}O_5N_3$, m.p. 283° (decomp.) (darkens at 280°), whilst Et 2 : 4-dimethylpyrrole-3-carboxylate, EtCHO, and EtOH–conc. HCl afford *αα-di*-(4-*carbethoxy*-3 : 5-*dimethyl-2-pyrryl*)*propane*, m.p. 139°.

Fusion of 5 : 5′-dibromo-4 : 4′-dimethyl-3 : 3′-di-β-carboxyethylpyrromethene hydrobromide (I) and 5-bromo-3 : 4′-dicarbethoxy-4 : 3′ : 5′-trimethylpyrromethene give coproporphyrin (spectrum) and traces of (probably) deuteroporphyrin and dicarbethoxydi-β-carboxyethylporphin. 4 : 4′-Dicarbethoxy-3 : 5 : 3′ : 5′-tetramethylpyrromethene hydrobromide and (I) fused with succinic–methylsuccinic acids afford 5 : 8-*dicarbethoxy*-1 : 4 : 6 : 7-*tetramethyl*-2 : 3-*di*-β-*carboxyethylporphin* (corresponding *Me*$_4$ ester, m.p. 282°). 5-Carboxy-3 : 3′-dimethyl-4-ethyl-4′ : 5′-di-β-carboxyethylpyrromethene hydrobromide, m.p. 145° (from 3-methyl-4 : 5-di-β-carboxyethylpyrrole-2-carboxylic acid, 2-formyl-3-methyl-4-ethylpyrrole-5-carboxylic acid, and 40% HBr in AcOH), and Br in AcOH give 5-*bromo*-3 : 3′-*dimethyl*-4-*ethyl*-4′ : 5′-*di*-β-*carboxyethylpyrromethene hydrobromide* (II), m.p. 203° (decomp.), which when fused with 5-bromo-4-carbethoxy-3 : 4′ : 5′-trimethyl-3′-ethylpyrromethene hydrobromide (III) affords a little mesoporphyrin [formed by self-condensation of (II)] and a dicarbethoxyporphin [from (III)].

Di-(5-carboxy-4-methyl-3-ethyl-2-pyrryl)methane, $COMe_2$, and 40% HBr give a *compound*, m.p. 120—122° (darkens at 105°), brominated to a *substance*, darkens from 170° and decomp. slowly, which with EtOH–NH_3 affords a *base*, $C_{28}H_{34}N_3Br_4$, m.p. 115°, converted by 10% MeOH–KOH into a *compound*, $C_{19}H_{24}O_6N_2$, m.p. 106°. H. B.

Chemotherapy. Attempts to find antimalarials. II. Pyrrylindoles. J. S. Aggarwal, A. U. Qureshi, and J. N. Ray (J. Amer. Chem. Soc., 1932, **54**, 3988—3992; cf. A., 1931, 743).—α-Benzoyl-ββ-diacetylethane (I), prepared by a modification of March's method (A., 1901, i, 596), is accompanied by a little *αγ-dibenzoyl*-ββ-*diacetylpropane* (II), m.p. 125°. The following *N*-aryl derivatives of 3-acetyl-5-phenyl-2-methylpyrrole are obtained from (I) and the requisite NH_2Ar: *Ph*, m.p. 101° {*phenylhydrazone*, m.p. 162°; *piperonylidene*, m.p. 164°, and *salicylidene*, m.p. 192° [*hydrochloride*, m.p. 135° (decomp.)], derivatives}; o-, m.p. 95°, m-, m.p. 142°, and p-*tolyl* (III), m.p. 150° [corresponding *phenylhydrazones*, m.p. 126° (decomp.), 156°, and 167—168°, respectively]; o-, m.p. 152°, and p-*anisyl*, m.p. 124° (*phenylhydrazones*, m.p. 174° and 185°, respectively); o-*ethoxyphenyl*, m.p. 100°; α-, m.p. 128°, and β-*naphthyl*, m.p. 140° [*phenylhydrazone*, m.p. 152° (decomp.)]; o-, m.p. 170° (*phenylhydrazone*, m.p. 182°), m-, m.p. 136° (*phenylhydrazone*, m.p. 158°), and p-*nitrophenyl*, m.p. 115°. Of the above phenylhydrazones, only those from the Ph, *m*- and *p*-tolyl, and *p*-anisyl derivatives are converted (by heating with $ZnCl_2$) into *pyrrylindoles* (IV), m.p. 221°, 220—221°, 224°, and 228°, respectively. (III) and piperonal in EtOH–KOH give a *compound*, $C_{28}H_{23}O_3N$, m.p. 132°.



(IV.)

αβ-Dibenzoyl-α-acetylethane (V) and CH_2BzBr give (II), which with NH_2Ph affords 4 : 4-*diacetyl*-1 : 2 : 6-*triphenyl*-1 : 4-*dihydropyridine*, m.p. 130°, oxidised by NaOBr to $CHBr_3$. (V) and NH_2Ph give a *pyrrole*, m.p. 134° (*phenylhydrazone*, m.p. 174°), analogous to the above; *o*-, *m*-, and *p*-$C_6H_4Me{\cdot}NH_2$ similarly afford *pyrroles*, m.p. 150°, 156°, and 142°, respectively. Some of the above compounds have antipyretic properties and are toxic to paramecium.

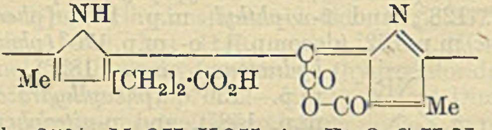
C. J. W. (*b*)

The cyanines. E. Princevalle (L'Ind. Chimica, 1932, 7, 1350—1357).—A review.

2-α- and 2-β-Pyridylbenziminazole. A. Leko and G. Vlajinatz (Bull. Soc. Chim. Yougoslav, 1932, **3**, 85—89).—The *Ag* salts of 2-α- (*A*) and 2-β-pyridylbenziminazole (*B*), and the double *salts* *A*,$CuCl_2$ and *B*,$CuCl_2$,$2H_2O$ are described. R. T.

Chlorophyll. XXIV. Phæopurpurin 18 and its identification with phyllopurpurin; chlorin p_6 and preparation of chlorin *e* trimethyl ester. H. Fischer, W. Gottschaldt, and G. Klebs. **XXV. Chlorophyll *b*. I.** H. Fischer, F. Broich, S. Breitner, and L. Nüssler. **XXVI. Complex iron salts of chlorophyll-porphyrins and -purpurins.** H. Fischer and H. K. Weichmann. **XXVII. Phæophorbide *a*, chlorin *e*, and chlorophyll *a*.** H. Fischer and H. Siebel (Annalen, 1932, **498**, 194—227, 228—267, 268—283; **499**, 84—108).—XXIV. Phæopurpurin 18 (I), prepared essentially by Conant and Moyer's method (A., 1930, 1299), is $C_{33}H_{34}O_5N_4$ (cf. *loc. cit.*), m.p. 270—280° (decomp.), and is esterified (CH_2N_2 in Et_2O–C_5H_5N)

to a Me ester (II), $C_{34}H_{36}O_5N_4$, m.p. 260° (previous sintering). When the Et_2O solution obtained during the prep. of (I) is treated with CH_2N_2, a *Me_3* ester, $C_{36}H_{42}O_6N_4$, m.p. 264—267° (not sharp) (not depressed by phyllopurpurin Me ester), is obtained: the isolation of (I) (as crystals) involves anhydride formation. The conversion of phæophorbide *a* into (I) by PrOH–KOH in Et_2O–C_5H_5N is accompanied by loss of 1 C atom as HCO_2H. (I) is degraded by hot HCO_2H to pyrroporphyrin, by HI–AcOH at 55° or HBr–AcOH at 150° to rhodoporphyrin (III), by HBr–AcOH at 50° to rhodoporphyrin-γ-carboxylic acid anhydride (IV), and by hot AcOH to (IV). (II) and HBr–AcOH at 50° give (III) (mainly) and (IV). (IV) is also formed when (I) or (II) is heated to 265—275°. (I) heated with Na_2CO_3–C_5H_5N gives rhodoporphyrin-γ-carboxylic acid (V), indicating that (I) contains the partial structure (*A*); (V) is formed by way of (IV) (which also contains structure *A*). Hydrolysis of (I) with 25% MeOH–KOH in Et_2O–C_5H_5N, EtOH–$Ba(OH)_2$, conc. HCl saturated with Et_2O, or MeOH–HCl gives *chlorin* p_6 [*Me_3* ester (VI), $C_{36}H_{42}O_6N_4$, m.p. 236°, also obtained on attempted esterification (MeOH–HCl, Me_2SO_4–alkali) of (II) and by the action of excess of CH_2N_2 on (I) in MeOH–C_5H_5N], which is degraded by HI to (III), by Na_2CO_3–C_5H_5N to a small amount of a porphyrin (Me ester, m.p. 256°) similar to (V), and by hot HCO_2H to pyrroporphyrin, (III), a chlorin, and (I). (VI) is converted by HI into (V), by HBr–AcOH into (III) and (IV), and by conc. H_2SO_4 into a little (II). Treatment of (I) with piperidine in C_5H_5N gives an unstable chlorin, whilst phæoporphyrin a_5 similarly affords an additive *compound*, $C_{36}H_{38}O_5N_4,C_5H_{11}N$ (*Me* ester, m.p. 263°, formed by esterification with CH_2N_2).



(*A*.)

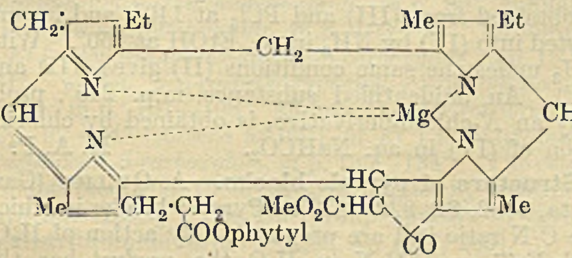
Phæophorbide *a* warmed with 1% NaOH in a current of air gives the unstable ψ-chlorin p_6 [when the residue from its Et_2O solution is heated at 100° for some time (I) results] [*Me_3* ester, $C_{36}H_{42}O_6N_4$, m.p. 225°, degraded (HI–AcOH) to an *ester*, $C_{36}H_{40}O_6N_4$, m.p. 240°, similar to but not identical with the Me ester of (V)] and a mixture of phæophorbide *a* and decarboxylated phæophorbide *a*, which is degraded (HI–AcOH) to (III), phylloerythrin, and phæoporphyrin a_5; similar results are obtained using Na_2CO_3, $NaHCO_3$, or aq. NH_3 in place of NaOH. Phæophorbide *a* warmed with 1% NaOH in N_2 gives a substance [degraded (HI–AcOH) to phylloerythrin] spectroscopically identical with it; other products formed are chlorin e_7 (degraded to chloroporphyrin e_5) and a small amount of a purpurin (converted by Na_2CO_3–C_5H_5N into a chlorin which is degraded by HI–AcOH to phylloerythrin). Phæophorbide *a* (or methylphæophorbide *a*) treated with Et_2O–CH_2N_2 in MeOH–C_5H_5N gives a good yield of chlorin *e* Me_3 ester.

[With E. Plötz.] The purpurin obtained from methylchlorophyllide and PrOH–KOH is identical with (I) [spectrum; conversion (as above) into (IV) and (V)].

XXV. An improved method of separating phæophorbide *a* and *b* (I) from the hydrolysis products of phæophytin is described. Hydrolysis of (I) with aq. $Ba(OH)_2$ gives rhodin *g* (II), which contains 3 CO_2H groups, gives Me_3 esters, $C_{37}H_{40}O_7N_4$, m.p. 265° (MeOH–HCl) and 253° (Me_2SO_4) [neither of which depresses the m.p. (251°) of the Me_3 ester (CH_2N_2) prepared by Treibs and Wiedemann (A., 1929, 941)], affords a condensation *product*, $C_{74}H_{78}O_{12}N_{10}$, with o-$C_6H_4(NH_2)_2$, is converted by fusion with succinic acid into phyllo- and pyrro-porphyrins, and is degraded by HBr–AcOH at 180° to rhodo- and phylloporphyrins and deoxophylloerythrin [the last two compounds are also formed similarly from (I)]. (II) heated with N_2H_4,H_2O in $NPhMe_2$ gives small amounts of two chlorins; in EtOH, a *chlorin*, $C_{31}H_{35}O_4N_4$, and an uncharacterised rhodin result. (II) and hot HCO_2H give rhodo- and phyllo-porphyrins and *rhodinporphyrin* g_3, $C_{32}H_{34}O_3N_4$ [*Me* ester, m.p. 231° (*semicarbazone*; *hæmin*), converted by MgMeI into a *compound*, $C_{35}H_{42(44)}O_2N_4$, m.p. 212°, spectroscopically identical with phylloporphyrin]; the latter is converted by HBr–AcOH at 140° into phylloporphyrin, by MeOH–KOH and MgO in C_5H_5N into a rhodin and phyllo- and pyrro-porphyrins, and by oleum (15% SO_3) into a rhodin. Methylphæophorbide *b* and (I) [which is a (mono) Me ester] are degraded by HI–AcOH to *phæoporphyrin* b_7 (III), $C_{35}H_{38}O_7N_4$ [*oxime*; *hæmin*; *Me* ester (CH_2N_2), m.p. 262°; *Me_2* ester (MeOH–HCl), m.p. 245°], which contains a CO_2Me group, is degraded by HBr–AcOH or by MeOH–KOH in C_5H_5N–MgI_2 to rhodoporphyrin, and with MgMeI gives a *compound*, $C_{40(41)}H_{50(52)}O_4N_4$, m.p. 248°, and a porphyrin, m.p. 268° (spectroscopically identical with phæoporphyrin a_5). (III) is converted by boiling HCO_2H into the *Me* ester (*oxime*) of *phæoporphyrin* b_5 [formed from (III) and 40% MeOH–KOH] (*oxime*; *hæmin*; *Me_2* ester, $C_{34}H_{36}O_5N_4$, m.p. 235°, which with MgMeI gives a porphyrin, m.p. 234°, spectroscopically identical with the compound from rhodoporphyrin Me_2 ester and MgMeI), which is degraded by 5% NaOMe in C_5H_5N at 160° to pyrro- and rhodo-porphyrins [also formed with phylloporphyrin by similar treatment of (III)]. Oxidation of (I) with CrO_3–H_2SO_4 gives methylethylmaleimide and $H_2C_2O_4$, indicating the presence of a CO group in the $·CH_2·CH_2·CO_2H$ side-chain, whilst reduction affords small amounts of hæmopyrrole and its carboxylic acid. (I) and MgMeI give (after decomp. and treatment with CH_2N_2) a *compound*, $C_{38}H_{45}O_6N_4$. (I) heated at 240—250° in N_2 eliminates approx. 1 mol. of CO_2; (II) at 290—300° similarly affords CO_2 (approx. 2 mols.) and pyrroporphyrin. (I) is hydrolysed by 10% MeOH–KOH in C_5H_5N to (II); with Na and PrOH in N_2, a substance, m.p. 228°, results (in one case only). (II) and 25% PrOH–KOH in C_5H_5N give a substance [*Me* ester, $C_{37}H_{42}O_7N_4$, m.p. 245°, spectroscopically identical with (II)]; with 40% MeOH–KOH and O_2, a substance (*Me* ester, $C_{35}H_{36}O_5N_4$, m.p. 277°) similar to ψ-verdoporphyrin is formed. Methylphæophorbide *b* and EtOH–NH_3 at 130° give a *compound*, $C_{35}H_{40}O_6N_6$, the *methiodide* of which when heated with KOH affords NH_2Me. Alternative structures are suggested for (I) and (II).

XXVI. Complex *Fe* salts (*hæmins*) (m.p. quoted in brackets) of the following are prepared: chloroporphyrin e_6 and its Me_3 ester [260°]; phæoporphyrin a_5 [decomp. 300°] and its Me_2 ester [305—306° (decomp.)]; phæoporphyrin a_5 oxime [above 300°]; phylloerythrin oxime (also formed by oximation of phylloerythrin hæmin); phæoporphyrin a_7 Me_3 ester [291° (decomp.)]; dimethylphæopurpurin a_7 [210° (decomp.)]; phæopurpurin 18 Me ester. The effect of N_2H_4,H_2O on the spectra of these hæmins in C_5H_5N and other solvents is recorded. Short treatment of phylloerythrin hæmin with MeOH–KOH–C_5H_5N gives a chlorin-like compound and a substance, which when freed from Fe by the $Fe(OAc)_2$–HCl method, affords phylloerythrin and rhodoporphyrin-γ-carboxylic acid (I); more prolonged treatment gives (after removal of Fe) a little (I), some rhodoporphyrin, and (mainly) the green anhydride of (I).

XXVII. Chlorin e_7 and cold MeOH–HCl give a *Me_2* ester (I), probably $C_{36}H_{40}O_7N_4$, m.p. 214° (corr.) (*Cu* salt), reduced (HI–AcOH) to chloroporphyrin e_5 and converted slowly by cold MeOH–HCl into chlorin *e* Me_3 ester (II), also obtained from (I) and chlorin e_7 by esterification with CH_2N_2 or Me_2SO_4–alkali. All the specimens of (II) are $C_{37}H_{42}O_6N_4$ and are all reduced (HI–AcOH) to chloroporphyrin e_6. Chlorin e_7 and diazoethane in Et_2O–C_5H_5N give *chlorin* e *Et_3* ester, $C_{40}H_{48}O_6N_4$, m.p. 149°, also reduced to chloroporphyrin e_6. Short hot alkaline hydrolysis of (II) gives chlorin *e*, $C_{34}H_{36}O_6N_4$, which has the same spectrum and HCl no. as chlorin e_7 but is reduced (HI–AcOH) to chloroporphyrin e_5. Similar hydrolysis of phæophorbide *a* gives chlorin *e*, verdoporphyrin, and a phæophorbide-chlorin mixture (reduced by HI to phylloerythrin and rhodoporphyrin), whilst hydrolysis with aq. $Ba(OH)_2$ in air or N_2 gives chlorin *e*, deoxypyrrophæophorbide *a* (formed as the main product by hydrolysis with 5% KOH), and a chlorin-like substance (reduced by HI to mainly rhodoporphyrin). These substances and some purpurin are obtained by hydrolysis of methylphæophorbide *a* with 8% $Ba(OH)_2$, whilst ethylchlorophyllide is hydrolysed by 33% MeOH–KOH to chlorin *e* and rhodin *g*. The structures of (II), chloroporphyrin e_6 Me_3 ester, phæophorbide *a*, and chlorophyllide *a* are discussed. Chlorophyll *a* is best represented as:

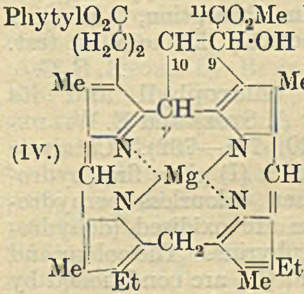


H. B.

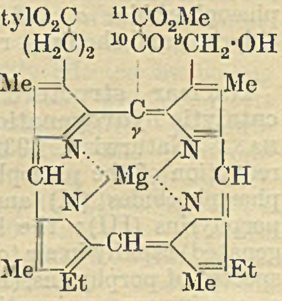
Mechanism of the phase test and the constitution of chlorophyll *a* and *b*. A. Stoll and E. Wiedemann (Helv. Chim. Acta, 1932, 15, 1128—1136).—Allomerisation of chlorophyll consists solely in oxidation at C9, CH·OH to CO or CH_2·OH to CHO with chlorophyll *a* and *b*, respectively (cf. this vol., 174, 756), and takes place in the alkaline medium of the phase test. Phæophorbide *a* (I) is rapidly allomerised by I in AcOH at room temp.; the product (II) gives a negative phase test, but has almost the same absorption as (I). (I) readily gives a characteristic *Bz* derivative in the cold, but no oxime; (II) gives an *oxime* in the cold, but no Bz derivative. Oximation of methylchlorophyllide and phæophytin (this vol., 756) is preceded by allomerisation. Phæoporphyrin *a* and phylloerythrin, which have a CO group at C9, are derivatives of allomerised chlorophyll *a*. Careful treatment of (I) with HI–AcOH yields *protophæoporphyrin* a (III), cryst., which is autoxidisable, gives a yellow phase test, and has an absorption almost identical with that of phæoporphyrin a_5; it is supposed that a perhydro-compound is first formed, which is then dehydrogenated both in the nucleus (thus destroying the chlorin nature of the product) and at C9 by the liberated I. (III), solid or in solution, oxidises (with loss of phase) to phæoporphyrin a_5, which yields an *oxime*, and in the phase test gives chloroporphyrin e_6 smoothly. Careful allomerisation of (I) with alkali gives solutions of a substance with the properties of a chlorin *e* Me ester, no hydrolysis taking place. The generalisation is made that transformation of chlorophyll derivatives into substance of chlorin nature by alkali consists in oxidation of C9 and subsequent ring-opening, followed in vigorous treatment by hydrolysis of the Me ester group. Chlorophyll *a* is, therefore, (IV).

Chlorophyll *b* (V) readily gives a *Bz* derivative and an *oxime* in the cold. The CO group is responsible for the rhodin nature of (V) and its derivatives. (V) and rhodins contain the grouping $\dot{:}C(\gamma)\cdot\dot{C}(10)\cdot C$; thus, phæophorbides of the *b* series with RMgAlk pass into the *a* series by conversion of the CO group into $C(OH)Alk_2$ and reduction of the nucleus. Phæophorbide *b* (VI) is allomerised by I in AcOH. Both (V) and its allomerisation product give rhodin *g* Me ester when cautiously treated with alkali. The formation of feebly basic products with 6 or 7 O atoms in the *a* and *b* series, respectively, is caused by addition of O. (V) with HI–AcOH gives *protophæoporphyrin* b (VII), which gives a yellow phase-test and does not give an oxime, and is therefore formed by wandering of a H atom from C9 to C10 and change of CO to C·OH. (V), therefore, does not contain the *iso*cyclic "side-ring." (VII) with alkali gives *rhodinporphyrin* g_7. Allomerised (V) is changed back to (V) by reduction; the spontaneous reaction, CH·OH(9) ⟶ CO, is thus reversible and may play a part in plant metabolism. Treatment of chlorophyll with alkali causes first dehydrogenation at C9,

(IV.)

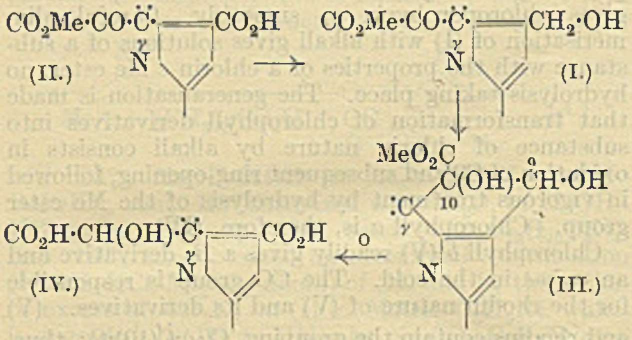


(V.)



rearrangement of the conjugated ethylenic linkings, and fission of Mg·N auxiliary valencies, thus causing the " brown phase," followed by further reaction of the CO group and return of the valencies to the original condition, thus restoring the chlorophyll spectrum. (V) is given the formula shown. R. S. C.

Constitution of chlorophyll and the formation from it of the fundamental dicarboxylic acids. A. Stoll and E. Wiedemann (Helv. Chim. Acta, 1932, 15, 1280—1285; cf. preceding abstract).—Benzoylphæophorbide *a* is stable to dehydrating agents, *e.g.*, I–EtOH. Phæophorbide *b* oxime (I) with MgMeBr gives a green Mg complex *salt*, changed to (I) by dil. acids. Rhodin *g* (II) readily gives an *oxime*, the absorption of which closely resembles that of phæophorbide *b* oxime (II). Change of phæophorbide *b* to (II) by alkali and to protophæoporphyrin *b* (III) by acid is represented by the partial formulæ :

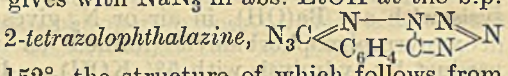


(III) gives no oxime and a yellow phase test, and has an absorption almost identical with that of protophæoporphyrin *a*, from which it differs only in having an OH group at C10. The change of (I) to (III) is the first transformation of series *b* into series *a*. Rhodinporphyrin g_7 is phæoporphyrin a_7 and is allotted formula (IV). Fischer's formula for this substance is incorrect [since (IV) does not give an oxime] and is now assigned to rhodin *g*. In agreement with the hypothesis of reduction of the CHO group, phæophorbides *a* and *b* with KOH–MeOH in the presence of a little aq. $Na_2S_2O_4$ are hydrolysed, but not oxidised at C9, and unchanged chlorophyllides or phæophorbides can be recovered after a considerable time by dilution and extraction with Et_2O, whereas without $Na_2S_2O_4$ such recovery is possible only within a few seconds. The alcoholic dicarboxylic acids thus obtained are named *norphæophorbide* a and b; they give yellow and red phases, have acid nos. 9 and 13, closely resemble phæophorbides *a* and *b* in absorption, and give chlorin *e* and rhodin *g*, respectively, in the phase test. R. S. C.

Nuclear structure of chlorophyll and its catalytic hydrogenation. A. Stoll and E. Wiedemann (Naturwiss., 1932, 20, 791—792).—Catalytic reduction of the phæophorbides (I) gives first hydrophæophorbides (II) and then colourless perhydroporphyrins (III); the latter are oxidised (dehydrogenated) rapidly in air to porphyrins. The colour and spectra of porphyrins, (I), and (II) are conditioned by a continuous conjugation of double linkings. All known porphyrins contain two superfluous double linkings; one of these (nuclear) disappears during the change porphyrins ⟶ (I), the other during (I) ⟶ (II). The conjugation is abolished during the production of (III). Formulæ are assigned to chlorophyll *a* and *b* which are supported by the above results; that of *a* contains one O less than that of *b* and has an additional ring (between C_9 and C_{10}). H. B.

Bilirubinoid colouring matters. IV. Dehydrobilirubin. R. Lemberg (Annalen, 1932, 499, 25—40).—Mild reduction of uteroverdin Me ester (I), most probably $C_{35}H_{38}O_6N_4$, m.p. 209° (all m.p. are corr.) (cf. this vol., 627), with HI–AcOH gives bilirubic acid, showing that uteroverdin is dehydrobilirubin. The EtOH mother-liquors from the prep. of bilirubin (from gallstones) contain dehydrobilirubin Me_2 ester (II), m.p. 214—215°, which is identical with (I); (II) is also formed (by dehydrogenation) when gallstones are heated with AcOH. Whilst methylethylmaleimide is obtained by HNO_3-oxidation of dehydromesobilirubin (glaucobilin) ester (Fischer *et al.*, this vol., 627) (also prepared by oxidation of mesobilirubin with $FeCl_3$ in AcOH, subsequent removal of Fe with alkali, and esterification), it is not produced by similar oxidation of (I) or (II). (II) is also prepared by oxidation of bilirubin with $FeCl_3$ in AcOH (or MeOH–HCl) (as above). The constitution of (I) is discussed (cf. A., 1930, 488; *loc. cit.*). H. B.

Reaction of 1 : 4-dichlorophthalazine with sodium azide. R. Stollé and H. Storch (J. pr. Chem., 1932, [ii], 135, 128—136).—1 : 4-*Dibromo-* (I), m.p. 162°, and 1-*bromo-4-hydroxy-phthalazine*, m.p. 273°, are prepared from 1 : 4-dihydroxyphthalazine and PBr_5 at 95—160°. (I) or the corresponding Cl_2-compound gives with NaN_3 in abs. EtOH at the b.p. 4-*azido*-1 : 2-*tetrazolophthalazine*,



$N_3C{<}\genfrac{}{}{0pt}{}{N\text{——}N\text{-}N}{C_6H_4\text{-}C{=}N}{>}N$

(II), m.p. 152°, the structure of which follows from the removal of one N_3 group only by NaOH with formation of 4-*hydroxy*-1 : 2-*tetrazolophthalazine* (III), m.p. 258° (decomp.) (*Ag* salt; *Ac* derivative, m.p. 165°; O-*Me ether*, m.p. 211°; *Et ether*, m.p. 187°), and its conversion into 4-*amino*-1 : 2-*tetrazolophthalazine*, m.p. 305° (IV) (Ac_2 derivative, decomp. 260°), by heating at 200° in tetrahydronaphthalene. The corresponding 4-*Cl*-compound, m.p. 195° (decomp.), is obtained from (III) and PCl_5 at 140°, and is converted into (IV) by NH_3 in aq. EtOH at 150°. With NH_3 under the same conditions (II) gives (III) and (IV). An unidentified substance, m.p. 249°, probably an *N*-chloro-derivative, is obtained by chlorination of (IV) in aq. $NaHCO_3$. H. A. P.

Structure of pyrrole blacks. A. Quilico (Gazzetta, 1932, 62, 822—839).—Pyrrole blacks in which the C/N ratio is 4 are prepared. By action of H_2O_2 and $Fe^{\cdots}$ on C_4H_4N in H_2O the *product* has the formula $C_{40}H_{44}O_{20}N_{10}$, and loses H_2O and CO_2 when heated. In presence of AcOH the *product* has the formula $C_{40}H_{40}O_{13}N_{10}$; with CH_2N_2 this gives a *product* $C_{50}H_{56}O_{14}N_{10}$. In alkali the blacks are sol. before methylation, insol. after. Action of Br on $C_{42}H_{34}O_{15}N_{10}$ yields a *product* $C_{44}H_{30}O_{26}N_{10}Br_{10}$, and NH_4 tetroxalate. E. W. W.

Dioximes. XCIII, XCIV. G. Ponzio. **XCV.** M. Milone. **XCVI.** G. Longo (Gazzetta, 1932,

62, 854—859, 860—868, 868—873, 873—877).—XCIII. Action of $POCl_3$ on the β form of amino-phenyl- and -*p*-tolyl-glyoximes yields 5-*amino*-3-*phenyl*-1 : 2 : 4-*oxadiazole*, m.p. 153—154° [*hydrochloride*, m.p. 165° (decomp.); *Ac* derivative, m.p. 183—184°], which is hydrolysed to the 5-OH-compound, and converted by HI into NH_2·CPh:NH, and -3-p-*tolyl*-1 : 2 : 4-*oxadiazole*, m.p. 221—222° (*Ac* derivative, m.p. 173—174°). The α forms of the above, and the α or β forms of HON:CPh·C(NHPh):NOH and HON:CBz·C(NH_2):NOH give only 1 : 2 : 5-oxadiazoles.

XCIV. 4-Benzamido-3-benzoyl-1 : 2 : 5-oxadiazole treated with KOH–EtOH loses the 3-Bz grouping, and then isomerises into *cyano*-N-*benzoylformamid oxime*, m.p. 138—140° (*Ac* derivative, m.p. 140°), which is converted by boiling H_2O into 3-cyano- and 3-carbamido-5-phenyl-1 : 2 : 4-oxadiazole. 4-*Benzamido*-3-p-*toluoyl*-1 : 2 : 5-*oxadiazole*, m.p. 149—150°, gives the same products.

XCV. The velocity of hydrolysis of Ac_2 and Bz_2 derivatives of glyoxime and its Me, Me_2, and MeEt derivatives is studied. *Dibenzoylglyoxime* has m.p. 139°.

XCVI. The β (but not the α) forms of chloroglyoxime react with KCN in Et_2O, giving β-*cyanoglyoxime*, m.p. 131° (decomp.) [*Ni* salt; Ac_2, m.p. 145—146°, and Bz_2, m.p. 185—186° (decomp.), derivatives]. This is converted by NH_2OH in MeOH into *aminotrioxime* (α-*amino*-αβγ-*trioximinopropane*), m.p. 147—148° (decomp.), which with Ac_2O gives 4-*amino*-3-*acetoximinomethyl*-1 : 2 : 5-*oxadiazole*, m.p. 157—158°, hydrolysed (NaOH) to the 3-*oximinomethyl* compound, m.p. 187—188°. E. W. W.

Interaction of α-*p*-carbethoxyphenyl-γ-alkylthiocarbamides with bromine: effect of the *iso*butyl group on hydrotribromide formation in 1-alkylaminobenzthiazoles. R. F. Hunter and E. R. Parken (J. Indian Chem. Soc., 1932, **9**, 357—361).—α-p-*Carbethoxyphenyl*-γ-*methylthiocarbamide*, m.p. 147—148°, from *p*-$CO_2Et\cdot C_6H_4\cdot NCS$ and NH_2Me in EtOH, and Br in $CHCl_3$ give the *hydrotribromide*, m.p. 137—138° (decomp.), of *Et* 1-*methylaminobenzthiazole*-5-*carboxylate*, m.p. 169° (free *acid*, m.p. 298°; *Ac* derivative, m.p. 174°). α-p-*Carbethoxyphenyl*-γ-*ethylthiocarbamide*, m.p. 89°, similarly gives the *hydrotribromide*, m.p. 103—104° (decomp.), of *Et* 1-*ethylaminobenzthiazole*-5-*carboxylate*, m.p. 150—151°, whilst α-p-*carbethoxyphenyl*-γ-iso*butylthiocarbamide*, m.p. 107—108°, affords the *hydrotribromide*, m.p. 92—94° (softens at 90°), of *Et* 1-iso*butylaminobenzthiazole*-5-*carboxylate*, m.p. 133—134°. The esters are obtained from the hydrotribromides by treatment with aq. H_2SO_3. The $Bu^β$ group appears to favour hydrotribromide formation (cf. A., 1927, 263).

H. B.

Echitamine in *Alstonia* barks. J. A. Goodson (J.C.S., 1932, 2626—2630).—The following percentages of total alkaloids and echitamine (I), respectively, occur in the species of *Alstonia* bark named; *angustiloba* (II) (Malaya), 0·17, 0·04; *congensis* (III) (Gold Coast), 0·38—0·56, 0·18—0·34, (Nigeria) 0·11—0·12, 0·03—0·04, (Cameroons) 0·18, 0·09; *constricta* (Australia) 0·40, 0; *Gilletii* (Belgian Congo), —, 0·21; *macrophylla* (Philippines) 0·99, 0; *scholaris* (IV) (Belgian Congo) —, 0·04, (India) 0·16—0·27, 0·08—0·10, (Philippines) 0·28—0·40, 0·20—0·31; *spathulata* (Malaya) 0·06, 0·03; and *villosa* (Australia) 1·61, 0. (III) and (IV) yield also small amounts of *echitamidine*, $C_{20}H_{26}O_3N_2$, m.p. (+H_2O) 135° after softening at 127° and (anhyd.) 244° (decomp.), $[\alpha]_D^{16}$ −515° in EtOH [*picrate*, m.p. 226—227° (decomp.); *hydrochloride*, m.p. (+$4H_2O$) 105° after softening at 75° and (anhyd.) 179° (decomp.), $[\alpha]_D^{16}$ −473° in H_2O; *hydrobromide*, m.p. (+$2H_2O$) 114° after softening at 105° and (anhyd.) 181° (decomp.), $[\alpha]_D^{15}$ −422° in H_2O; *hydriodide*, m.p. (+$3H_2O$) 110° and (anhyd.) 182° (decomp.), $[\alpha]_D^{16}$ −389° in H_2O; *sulphate*, m.p. (+$11H_2O$) 87° after softening at 73°, and (anhyd.) 169° (decomp.), $[\alpha]_D^{17}$ −362° in H_2O]; abnormal OMe and NMe analyses indicate the presence of a NMe but not a OMe group. (II) and (IV) contain a lactone, now named *C*, obtained previously (A., 1925, i, 1166) from (III), whilst (IV) contains also an isomeric *lactone S*, $C_9H_{14}O_3$, m.p. (+H_2O) 80—84° and (anhyd.) 107° (*Ac* derivative, m.p. 86—90°), $[\alpha]_D$ +142·5° in *N*-H_2SO_4, 143·3° in H_2O, 97·9° in *N*-NH_3, and 60·1° in *N*-NaOH. Lactone *C* has $[\alpha]_D$ +50·6°, 50·6°, 65·3°, and 94·1°, respectively, in these solvents. Both lactones contain one fully reduced ring and a saturated side chain or chains. (I) and hot aq. NaOH (1 equiv.) give MeOH and demethylechitamine, reconverted into the hydriodide and *Me sulphate*, m.p. 253° (decomp.), of (I) by hot MeI and cold Me_2SO_4, respectively; the ester nature of (I) is thus confirmed. The HCl salt of (I) and MeOH form an additive *compound* (1 : 1), m.p. 277° (decomp.), $[\alpha]_D^{16}$ −52° in H_2O. R. S. C.

Demethylation of narcotine and vitamin-*C*. J. Brüggemann (Z. physiol. Chem., 1932, **211**, 231—240).—Narcotine was demethylated in stages in order to obtain methylnornarcotine. This was not obtained cryst. and the products were antiscorbutically inactive (cf. Rygh *et al.*, this vol., 310). J. H. B.

Microchemical identification of alkaloids. F. Amelink (Pharm. Weekblad, 1932, **69**, 1121—1123).—Prostigmine (dimethylcarbamic ester of *m*-hydroxyphenyltrimethylammonium methosulphate) does not react visibly with $PtCl_4$, but when NaI is added a characteristic cryst. ppt. forms; the sensitivity is 0·1%. $K_4Fe(CN)_6$, picric acid, and $HgCl_2$ also yield ppts., but the first reaction is the most useful. Various other reactions of the alkaloid are described.

H. F. G.

Use of hydrobromic acid in the characterisation of arylarsinic acids. G. Schuster (Compt. rend., 1932, **195**, 611—614).—Replacement of the ·AsO_3H_2 group by Br is readily effected by boiling HBr (*d* "1·75") (cf. A., 1931, 105), which converts *o*- and *p*-nitrophenyl-, *p*-aminophenyl-, *p*-chlorophenyl-, phenyl-, *o*-tolyl-, *p*-tolyl-, and 2-nitro-3-hydroxyphenyl-arsinic acids into *o*-$C_6H_4Br\cdot NO_2$ (86%), *p*-$C_6H_4Br\cdot NO_2$ (88%), *p*-$C_6H_4Br\cdot NH_2$ (72%), *p*-C_6H_4ClBr (91%), PhBr (40—42%), *o*-C_6H_4MeBr (45%), *p*-C_6H_4MeBr (52%), and 5 : 6-dibromo-2-nitrophenol (?) (83%), respectively. Poor yields resulting from similar treatment of phenyl- and 4-nitrophenyl-dichloroarsines are greatly improved by using the corresponding arsinoxides. A. C.

Trypanocidal action and chemical constitution. XIII. Arylthioarsinites from cysteine and glutathione. A. COHEN, H. KING, and W. I. STRANGEWAYS (J.C.S., 1932, 2505—2510; cf. this vol., 408).—Reduction of Me phenylglycine-*p*-arsinite (SO_2 method) gives N-*phenylglycine*-p-*arsinoxide Me ester*, solid, which with conc. aq. NH_3 at −10° gives N-*phenylglycineamide*-p-*arsinoxide* (I), cryst., changed by warm 3% AcOH into *tri(phenylglycineamide)arsine*, m.p. about 225° (decomp.), which with I yields the *oxide*, effervescence at about 160°. (I) and aq. cysteine hydrochloride (II) afford *di*-(β-*amino*-β-*carboxyethyl*) N-*phenylglycineamide*-p-*thioarsinite* (III), $+1{\cdot}5H_2O$, cryst., $[\alpha]_{5461}$ +9·3° in *N*-HCl, whilst glutathione (IV) yields similarly *di(glutathionyl)* N-*phenylglycineamide*-p-*thioarsinite*, amorphous. Tryparsamide and (II) give an inseparable mixture of cystine and (III), changed by cold, conc. 16% HCl to cystine and tricysteinylarsine. *N*-Phenylglycine-*p*-dichloroarsine and MeOH–HCl give phenylglycine Me ester, whilst reduction [also of (I)] in acid solution similarly removes As. Reduction of 4-acetamido-2-hydroxyphenylarsinic acid gives the corresponding *arsinoxide*, cryst., $+0{\cdot}5H_2O$, which with (II) yields *di*-(β-*amino*-β-*carboxyethyl*) 4-*acetamido*-2-*hydroxyphenylthioarsinite*, $+2{\cdot}25H_2O$, gelatinous, and with (IV) the corresponding *di(glutathionyl)* compound (V), amorphous. 4-Amino-2-hydroxyphenylarsinic acid, however, loses As when reduced in acid solution, and with (II) (4 mols.) gives tricysteinylarsine. 3-Amino-4-hydroxyphenylarsinic acid, when reduced, yields 3-*amino*-4-*hydroxyphenyldichloroarsine hydrochloride*, cryst., which with (II) gives di-(β-amino-β-carboxyethyl) 3-amino-4-hydroxyphenylthioarsinite, m.p. 237—238° (decomp.) [lit. 225—227° (uncorr.)]; the arsinoxide with (IV) gives the *di(glutathionyl)* compound, a syrup. Dithioacetic acid, when reduced with Zn dust and 3*N*-HCl at 35—40° and then condensed with tryparsamide, affords di(carboxymethyl) phenylglycineamide-*p*-thioarsinite. The above condensation products are toxic to *Trypanosoma equiperdum*, (V) being extremely effective. R. S. C.

Organo-arsenic compounds. I, II. H. N. DAS-GUPTA (J. Indian Chem. Soc., 1932, 9, 371—373, 393—401).—I. The following are prepared by alkaline coupling of the diazotised aminocoumarins with (?)-sulpho-α-naphthylarsinic acid (Hill and Balls, A., 1922, i, 1080): *coumarin*-6-, m.p. 185° (decomp.), 7-*methylcoumarin*-6-, decomp. 235° (shrinks at 168°), 4 : 7-*dimethylcoumarin*-6-, m.p. 204° (decomp.), 1 : 2-α-*naphthapyrone*-6-, shrinks at 170°, and 4-*methyl*-1 : 2-α-*naphthapyrone*-6-, m.p. 162° (decomp.), -*azo*-(?)-*sulpho*-α-*naphthylarsinic acids*.

II. The following are prepared by the Bart method: *xanthone*-3-*arsinic acid*, m.p. > 335°; 8-*nitroxanthone*-1-*arsinic acid*, m.p. > 330° (from 8-*nitro*-1-*aminoxanthone*, m.p. 205—207°, prepared by reduction of 1 : 8-dinitroxanthone with $SnCl_2$ and EtOH–conc. HCl); 7-*nitroxanthone*-2-*arsinic acid* (I), m.p. > 340° (from 7-nitro-2-aminoxanthone, m.p. 264—265°); *bromonitroxanthonearsinic acid*, m.p. 258—260° (decomp.) [from the *bromonitroaminoxanthone*, m.p. 143—145°, obtained by reduction ($EtOH–NH_4HS$) of bromodinitroxanthone]; ψ-1 : 8-iso*naphthoxazone*-3-*arsinic acid*, m.p. 225—227° (decomp.) [from 3-*amino*-ψ-1 : 8-iso*naphthoxazone*, m.p. 270°, obtained by reduction ($EtOH–NH_4HS$) of the 3-NO_2-derivative, m.p. 228—230°, which is prepared from 3 : 6-dinitrocoumarin, glycerol, and conc. H_2SO_4 at 135—170°]; *xanthoquinoline*-β-*arsinic acid*, m.p. > 345° (shrinks at 315°) [from β-*aminoxanthoquinoline*, m.p. 276—278°, prepared by reduction ($EtOH–NH_4HS$) of the NO_2-compound]. (I) is reduced by $FeSO_4$ and aq. NaOH to 7-*aminoxanthone*-2-*arsinic acid*, m.p. > 347° (*Ac* derivative, m.p. > 340°). H. B.

Arsenic derivatives of indazole. E. PŁAŻEK and E. NEYMANÓWNA (Rocz. Chem., 1932, 12, 706—714).—*Indazole*-6-*arsinic acid*, m.p. 206—208°, produced, together with other unidentified products, by adding Na_3AsO_3 to diazotised 6-aminoindazole, yields *indazole*-6-*arsinoxide* (I), decomp. > 170°, on treatment with SO_2, *bis*-6-*arsenoindazole*, decomp. > 240°, on reduction, and *indazole*-6-*arsenious disulphide* on treatment with H_2S; *indazole*-6-*thioarsinoxide*, m.p. 170°, is obtained from H_2S and (I). *Indazole*-7-, m.p. 222—225°, -5-, solid at 340°, and -4-*arsinic acid*, m.p. 242°, 7-, decomp. 170°, 5-, m.p. 286°, and 4-*arsenoindazole oxide*, decomp. 250°, *bis*-7-, m.p. 216°, and *bis*-5-*arsenoindazole*, unstable, are prepared analogously to the above compounds. Indazole-6- and -4-arsinic acids are much stronger acids than are the -7- and -5-compounds. R. T.

Ring fission of heterocyclic arsenic derivatives. G. A. RAZUVAIEV and M. M. KOTON (J. Gen. Chem. Russ., 1932, 2, 529—533).—The fission of various As derivatives with HCl in CCl_4 under pressure, with or without addition of $AsCl_3$, has been examined. 10-Chloro-, 10-chloro-2 : 7-dimethyl-, 10-chloro-1 : 2-benzo-, and 10-chloro-3 : 4-benzo-9 : 10-dihydrophenarsazines are the most easily decomposed, then chlorophenoxarsine, and finally diphenylenechloroarsine. The fission of arsinic acids proceeds most readily in acid solution, whilst alkalis retard the change. Phenarsazinic acid is the most easily decomposed, then diphenylenearsinic acid, phenoxarsinic acid being the most stable but less so than acyclic acids (diphenylarsinic acid). G. A. R. K.

Phosphonium compounds with an asymmetric phosphorus atom. G. KAMAY (J. Gen. Chem. Russ., 1932, 2, 524—528).—$PPhEt_2$ when heated with CH_2PhCl in CO_2 gives $CH_2Ph{\cdot}PPhEt_2Cl$, m.p. 194—195°, which decomposes when heated in CO_2 to $PPhEt_2$, $CH_2Ph{\cdot}PPhEt$ (I), and $PPh(CH_2Ph)_2$ (II). (I) with $Ac{\cdot}CH_2Cl$ in CO_2 gives *phenylbenzylethylacetonylphosphonium chloride*, syrupy, and with phenacyl bromide *phenylbenzylethylphenacylphosphonium bromide*, m.p. 166—169° decomposed by boiling H_2O into COPhMe and phenylbenzylethylphosphine oxide. (II) with EtBr gives *phenyldibenzylethylphosphonium bromide*, m.p. 170—171°. The first two salts yielded only irresolvable bromocamphorsulphonates. G. A. R. K.

Elimination of metallic tin from tin tetraphenyl. M. M. KOTON (J. Gen. Chem. Russ., 1932, 2, 345—347).—$SnPh_4$ heated at 250° with H_2 at 50 atm. does not decompose; at 275° 6·3% decomposes to yield Sn and C_6H_6, whilst at 350° 71·4% decomposes. With $Pr^{\beta}OH$, $CH_2Ph\cdot OH$, or tetralin the products are similarly C_6H_6 and Sn. R. T.

Application of thallium in organic chemistry. VII. Chelate rings. R. C. MENZIES and E. R. WILTSHIRE (J.C.S., 1932, 2604—2606; cf. A., 1931, 1280).—Dialkylthallium halides and TlOEt in C_6H_6 give solutions of the corresponding dialkylthallium ethoxides, from which the appropriate diketones ppt. the following compounds: *dipropyl-* (m.p. 181°) and *dibutyl-* (m.p. 138—139°) *-thallium acetylacetone*; *Tl dipropionylmethane*, m.p. 70°, *dimethyl-* (m.p. 121°), *diethyl-* (m.p. 116°), and *dipropyl-dipropionylmethane*, m.p. 89°; *dimethyl-* (m.p. 162°) and *diethyl-propionylacetone*, m.p. 147°. These compounds form a graduated series, the stability and insolubility in H_2O falling from the $TlBu_2$ compound, which resembles Cu or Be compounds, to Tl acetylacetone, which approaches the Na and K compounds. The m.p. of the Me compounds are abnormal. R. S. C.

Racemisation. XI. Action of alkali on polypeptides. P. A. LEVENE and R. E. STEIGER (J. Biol. Chem., 1932, 98, 321—332).—Glycine anhydride, NaOH, and *l*-α-bromo*iso*hexoyl chloride afford l-α-*bromo*iso*hexoylglycylglycine*, m.p. 130—132°, $[\alpha]_D^{30}$ −36·4° in H_2O, which with aq. NH_3 gives d-*leucylglycylglycine* (I), $[\alpha]_D^{30}$ −49·4° in H_2O. (I) is similarly converted successively into l-α-*bromo*iso*hexoyl*-d-*leucylglycylglycine*, m.p. 190° (corr.) (decomp.), $[\alpha]_D^{30}$ −5·64° in EtOH, d-*leucyl*-d-*leucylglycylglycine* (II), $[\alpha]_D^{30}$ −8·6° in $C_5H_5N{-}H_2O$; *chloroacetyl*-d-*leucyl*-d-*leucyl*-d-*leucine*, m.p. 198—199° (decomp.), $[\alpha]_D^{27}$ +71·2° in EtOH (from $CH_2Cl\cdot COCl$ and the tripeptide), gives *glycyl*-d-*leucyl*-d-*leucyl*-d-*leucine* (III), $[\alpha]_D^{30}$ +82·3° in *N*-NaOH. The hydrolysis and racemisation of (II) and (III) by *N*-NaOH for 8 days at 25° were quantitatively studied, the loss of optical activity under these conditions being 19 and 23%, respectively, *i.e.*, considerably > that observed (4%) with the parent tripeptide *d*-leucyl-*d*-leucyl-*d*-leucine (A., 1931, 1430). Hydrolysis of (II) and (III) with 20% HCl at 100° was also studied. J. W. B.

Union of bio-colloids. VIII. M. Z. GRYNBERG and S. KISIEL (Biochem. Z., 1932, 253, 146—151).—If the aggregation of the colloid (gelatin) is prevented by heating, no binding of uric acid occurs. The amount of binding varies greatly with the substance (egg protein, ovalbumin, birch charcoal) used and with the [H˙]. Between p_H 6·5 and 7·5 the degree of binding increases, but it is only partly dependent on the degree of dissociation of the acid and decreases at higher p_H. Uric acid does not combine with fats or lipins. W. McC.

Serinephosphoric acid obtained on hydrolysis of vitellinic acid. F. A. LIPMANN and P. A. LEVENE (J. Biol. Chem., 1932, 98, 109—114).—Vitellinic acid (I) (A., 1906, i, 913) with 0·25*N*-NaOH yields a dephosphorylated polypeptide (II). Acid hydrolysis of (I) and (II) yields 17·3 and 17·9% of NH_3, respectively, of which ≯25% originated in the amide N of the polypeptide. Hydrolysis of (I) with 2*N*-HCl, followed by suitable technique, gives rise to *Ba serinephosphate*, $BaO_2{:}PO\cdot OCH_2\cdot CH(NH_2)\cdot CO_2H$, and the *Ba* salt, $[BaO_2{:}PO\cdot OCH_2\cdot CH(NH_2)\cdot CO_2]_2Ba$, $[\alpha]_D^{25}$ +8·2°. F. O. H.

Clupein. V. K. FELIX, K. INOUYE, and K. DIRR (Z. physiol. Chem., 1932, 21, 187—202; cf. this vol., 954).—From the products of tryptic digestion of clupein there were isolated as flavianates or picrates five dipeptides: arginylarginine (*dipicrate*, decomp. 185° and then 275°), arginyloxyproline (*flavianate*, decomp. about 240°), and dipeptides of arginine with alanine (*picrate*, decomp. 250°), serine (*picrate*, decomp. 225°), and valine (*flavianate*, decomp. 250°). Free arginine was also found. J. H. B.

Micro-determination of carbon. Improvements in Nicloux' method. P. L. KIRK and P. A. WILLIAMS (Ind. Eng. Chem. [Anal.], 1932, 4, 403—404).—A modified technique is recommended (cf. A., 1927, 436). E. S. H.

Determination of fluorine and boron in organic compounds. D. J. PFLAUM and H. H. WENZKE (Ind. Eng. Chem. [Anal.], 1932, 4, 392—393).—The substance is oxidised with Na_2O_2, $KClO_3$, and sucrose in a Parr S bomb. The product is dissolved in H_2O and boiled with NH_4Cl to permit the determination of F′ by pptn. as CaF_2. Excess of Ca˙˙ is removed from the filtrate by means of 4*N*-NaOH, and H_3BO_3 is then determined by the mannitol method. E. S. H.

Determination of organic compounds by oxidation with chromate mixture. V. MICHL (Časopis Českoslov. Lék., 1932, 12, 57—68; Chem. Zentr., 1932, ii, 257).—AcOH is completely oxidisable only by long boiling with $K_2Cr_2O_7$ and H_2SO_4 after addition of $AgNO_3$; even in presence of $AgNO_3$ certain alkaloids cannot be determined by this method. Substances which afford EtCHO as intermediate product require more Cr_2O_7'' than is calc. A. A. E.

Determination of lactic acid. H. LIEB and M. K. ZACHERL (Z. physiol. Chem., 1932, 211, 211—216).—A simplified apparatus for determining $OH\cdot CHMe\cdot CO_2H$ is described. Absorption of MeCHO is facilitated by passing the gas stream through a sintered glass plate. J. H. B.

Iodometric determination of glucose. M. I. NAKHMANOVICH, S. L. BERMAN, and B. O. LYUBIN (Nauk. Zapsiki Tzuk. Prom., 1931, 14, 453—482).—The buffer solution (0·2*M*-$NaHCO_3$–Na_2CO_3) is replaced by 0·1*N*-NaOH (25 c.c.). CH. ABS.

Detection and determination of sucrose by means of invertase. V. ESTIENNE [with J. TRUSSART and G. JUBLOU] (Bull. Assoc. anc. Étud. Louvain, 1932, 32, 6—14; Chem. Zentr., 1932, i, 3236—3237).—Stable invertase solution is prepared by treating press yeast (25 g.) with H_2O (150 c.c.) for 7—14 days until acid to litmus, filtering through kieselguhr, and keeping in presence of toluene in a brown bottle. For the determination of sucrose 50 c.c. of a solution are treated with 2 c.c. of invertase solution, 5 drops of 20% AcOH, and 5 drops of toluene in a closely stoppered flask kept over-night at 53—55°; the invert sugar is determined by Bertrand's method. A. A. E.

Determination of glucose and maltose in aqueous solution and in broth and peptone solutions. M. L. Smith (Biochem. J., 1932, 26, 1459—1466).—Shaffer and Hartmann's method has been adapted. S. S. Z.

Colour reaction for lecithin, phytin, and phytosterol. H. Kühl (Pharm. Zentr., 1932, 73, 625—629).—Phytosterols, phytins, and lecithins give similar Salkowski–Hesse reactions. Tests are given to differentiate between Et_2O, light petroleum, C_6H_6, and $COMe_2$ extracts of soya-bean meal with regard to their reactions to H_2SO_4 and alcoholic NaOH. A. C.

Detection of inositol and of phytinates. A crystalline barium phytinate. F. Fischler and F. H. Kürten (Biochem. Z., 1932, 254, 138—147).—Inositol and the Ca, Ba, Mg, and Na salts of its phosphoric acids (also phytin and phytinates) yield characteristic colours when treated with H_2SO_4 after oxidation with BaO_2 and/or Na_2O_2. A cryst. Ba phytinate, $C_6H_{12}O_{24}P_6Ba_3,3H_2O$, has been prepared. W. McC.

Pine-shaving reaction of furan [derivatives]. T. Reichstein (Helv. Chim. Acta, 1932, 15, 1110—1112).—Only mono-substituted furan derivatives give a green colour in the pine-shaving test (modified technique); more highly methylated derivatives give red colours with pine shavings and with Ehrlich's reagent, indistinguishable from those given by pyrrole derivatives. Tetramethylfuran gives slowly a red colour with pure filter-paper. Shavings stained green and red (or reddish-violet) become nearly blue and violet, respectively, when washed with H_2O. Rules cannot be laid down for the colour to be expected. R. S. C.

Microchemical reactions of loretine. C. van Zijp (Pharm. Weekblad, 1932, 69, 1191—1197).—The reactions of loretine (2-iodo-1-hydroxyquinoline-4-sulphonic acid) with some 50 inorg. compounds are described. Zn yields a characteristic ppt., and with Ca, Sr, and Ba orange needles are formed, whilst the Mg derivative is colourless. The reagent may be employed to detect adulteration of ZnO and white lead with chalk, and the presence of $CaCO_3$ in $MgCO_3$; in the examination of dolomite; and for the detection of Zn in vegetable matter. H. F. G.

Colorimetric determination of histidine. E. Jorpes (Biochem. J., 1932, 26, 1507—1511).—Hanke and Koessler's application of the Pauli reaction for the colorimetric determination of histidine gives very unsatisfactory results. By modifying the technique it is, however, possible to obtain reproducible figures. S. S. Z.

Determination of arginine. E. Jorpes and S. Thorén (Biochem. J., 1932, 26, 1504—1506).—The Sakaguchi reaction (addition of α-naphthol and hypobromite) is used. S. S. Z.

Biochemistry.

Carbon dioxide in the blood; influence of carbon dioxide pressure, and determination of alkali reserve. M. Lora y Tamayo (Anal. Fís. Quím., 1932, 30, 664—672).—The Nicloux and Van Slyke methods for determining CO_2 in blood yield results which agree to within about 2%. The alkali reserve of five samples of blood saturated with CO_2 at pressures between 20 and 70 mm. has been determined. At pressures >40 mm. it may vary by up to 3% from the val. obtained at 40 mm., whilst at lower pressures the variation may be 5%. H. F. G.

Effects of salts and $[H^{\cdot}]$ on the oxygen dissociation constant of the hæmocyanin of *Busycon carnaliculatum*. A. C. Redfield and E. N. Ingalls (J. Cell. Comp. Physiol., 1932, 1, 253—275).—In solutions of KCl, NaCl, $MgCl_2$, and K phosphate the equilibrium between purified hæmocyanin and O_2 follows the law of mass action on the assumption that the various groups combining with O_2 react independently. Addition of $CaCl_2$ alters the shape of the O_2 dissociation curve. Changes in p_H cause salt formation with certain of the acid or basic groups of the protein and the affinity of the salts for O_2 differs from that of the original protein. No relationship is apparent between the O_2 dissociation const. and the degree of ionisation of the hæmocyanin mol. as a whole. A. G. P.

Spectrophotometric determination of certain blood-pigments. G. B. Ray, H. A. Blair, and C. I. Thomas (J. Biol. Chem., 1932, 98, 63—83).—A theoretical revision of the spectrophotometry of blood-pigments is followed by a description of its application to the determination of total pigment, O_2 content and capacity, and content of carboxy- or met-hæmoglobin, or reduced hæmoglobin in 0·05 c.c. of blood. F. O. H.

Cyanohæmatin standard for the Sahli hæmoglobinometer. R. D. Barnard (J. Lab. Clin. Med., 1932, 17, 824—825).—Cryst. hæmin is dissolved in 1% NaCN; the final dilution of the blood sample is made with 1% NaCN. Ch. Abs.

Oxyhæmoglobin reduction in living tissues, particularly in human skin. L. Nicolai (Pflüger's Archiv, 1932, 229, 372—384; Chem. Zentr., 1932, i, 3305—3306).—The reduction is shown by a photometric method to be unimol.; the half-val. period *in vitro* is 8 sec. A. A. E.

Oxidation potential of the hæmoglobin–methæmoglobin system. J. B. Conant and A. M. Pappenheimer, jun. (J. Biol. Chem., 1932, 98, 57—62).—The mid-point of the oxidation–reduction potential curve, determined by the direct electrochemical method (A., 1931, 40), gives a val. for E_0 of 152±5 mv. for p_H 7·0, in good agreement with the spectrophotometric method (A., 1928, 315). The val. for n in the electrochemical equation lies between 1 and 2·5, and hence the oxidation of hæmoglobin cannot be represented by the simple equation $Hb_4 - 4\epsilon \longrightarrow MHb_4$ unless some auxiliary assumptions are made. F. O. H.

Characterisation of blood spots and determination of their origin. R. Marcille (Ann. Chim. Analyt., 1932, [ii], **14**, 433—445).—An account of the methods employed for the detection of traces of blood. M. S. B.

Simultaneous enumeration of blood platelets and reticulocytes. W. Dameshek (Arch. Int. Med., 1932, **50**, 579—589).—Red cells, platelets, and reticulocytes are counted on the same slide after staining with an anticoagulating solution of brilliant-cresyl-blue. The abs. figure is then obtained after a red-cell count has been made. The normal platelet count by this method varies between 400,000 and 700,000 per cu. mm. The experimental error lies between 10,000 per cu. mm. for very low, and 70,000 per cu. mm. for normal, counts. H. G. R.

Protein component of the erythrocyte membrane or stroma. E. Jorpes (Biochem. J., 1932, **26**, 1488—1503).—This protein (stromatin) differs in its N, arginine, and histidine contents from hæmoglobin and globin. It also differs from fibrin or globulin in its content of tyrosine and tryptophan. The protein of the membrane or stroma amounts to about 4% of the total protein of the normal erythrocytes. S. S. Z.

Determination of blood-proteins by acid acetone. J. Race (Biochem. J., 1932, **26**, 1571—1584).—The serum-albumin and -globulin are pptd. with $CCl_3\cdot CO_2H$ and the albumin is extracted with acidified $COMe_2$, the globulin being insol. in this solvent. The process gives comparable results with those obtained by Howe's method (Na_2SO_4 pptn.) for normal sera and plasmata, but gives lower figures for globulin in pathological specimens. Howe's method gives in the case of $COMe_2$ extraction low globulin results; with pathological specimens more accurate figures are obtained by the acid $COMe_2$ method. Experiments with pure proteins and varying concns. of $COMe_2$ or EtOH suggest a change in the physical properties (surface tension) of the solvent at about 30 vol.-% concn. Blood-albumins from man, sheep, ox, and horse are entirely sol. in acid $COMe_2$ but ovalbumin is insol. The solubility of the various proteins is determined by the rate of denaturation and coagulation in acid. S. S. Z.

Action of phenylhydrazine on blood-protein. S. Láng (Z. ges. exp. Med., 1932, **80**, 637—639; Chem. Zentr., 1932, i, 3194).—In dogs injection of $NHPh\cdot NH_2$ increases the plasma-protein and the quantity of globulin, but not parallel with the fall in the no. of erythrocytes. A. A. E.

Comparison of the Wu and Kjeldahl methods of serum-protein determination. L. R. Tuchman and H. Sobotka (J. Biol. Chem., 1932, **98**, 35—41).—The method of Wu (A., 1922, ii, 406) is unsatisfactory when the serum-proteins are $< 6\%$. Thus in œdema the tyrosine contents of the albumin and globulin fractions appear to be increased and decreased respectively. F. O. H.

Precipitation and protection of vanadic acid by serum-proteins. E. Boyland (Biochem. J., 1932, **26**, 1383—1390).—Serum-albumin is pptd. by vanadic, molybdic, or tungstic acid, which form negative lyophilic semicolloidal solutions in low concns., but not in higher concns., since in the latter case protection occurs and a stable positive colloid is formed. Serum-globulin causes pptn. in all available concns. between p_H 3·0 and 5·3. If euglobulin is added to an amount of albumin great enough to cause protection when a poly-acid is added alone, pptn. will occur. The globulin will, however, remain in solution if excess of albumin is present. The amount of globulin which a definite amount of albumin can protect increases with the acidity of the solution. S. S. Z.

Albumin and globulin contents of serum under various conditions. V. Henriques and U. Klausen (Biochem. Z., 1932, **254**, 414—433).—Breathing a mixture of 50% CO_2 and 50% O_2 did not affect the albumin and globulin fractions of dog's serum. The changes in the serum-albumin and -globulin contents, respectively, are after poisoning with P decreases of 45% and 1—4%, after ligature of the bile duct decrease of 47% and increase of 17%, and after bleeding decreases of 30 and 47%. In comparable experiments, changes of albumin and globulin fractions are much greater in the lymph of the thoracic duct than in the blood itself. P. W. C.

Isoelectric point of serum-globulin as determined by cataphoresis. F. O. Howitt and E. B. R. Prideaux (Proc. Roy. Soc., 1932, B, **112**, 24—27).—The cataphoresis of ox serum-globulin in presence of colloidal Au was determined over a range of p_H 2·8—9·6. A zone of insolubility of p_H 4·5—6·5 and an isoelectric point of approx. p_H 5·4 were indicated. F. O. H.

Osmotic pressure, mol. wt., and stability of serum-albumin. N. F. Burk (J. Biol. Chem., 1932, **98**, 353—377).—The mol. wt. of cryst. horse serum-albumin, determined by osmotic pressure measurements, is 74,600 in aq. buffered solution at the isoelectric point, p_H 4·8, 76,000 in $(NH_4)_2SO_4$ solution, and 74,700 in 75% glycerol solution. In conc. urea solution, in which the albumin undergoes denaturation, the mol. wt. was 73,000, whilst the same val. was obtained for the heat-denatured protein dissolved in conc. urea solution. Denaturation therefore does not appreciably alter the mol. wt. Ovalbumin, denatured by urea and in $6\cdot66M$-urea solution, has a min. osmotic pressure at p_H 5·8, corresponding presumably with its isoelectric point, but the isoelectric point of the urea-denatured protein, estimated from the max. flocculation in aq. buffer solution, is at p_H 4·8—4·9, so that the more alkaline isoelectric point of the protein in urea solution is probably due to the effect of urea in the medium. W. O. K.

Determination of phenols in blood. J. García Blanco and F. Comesaña (Anal. Fís. Quím., 1932, **30**, 690).—The plasma (2 c.c.) is diluted to 10 c.c., and protein is removed by adding $0\cdot67N$-H_2SO_4 (1 c.c.) and Na tungstate solution. To 6 c.c. of the filtrate are added 1 c.c. of HCl (5—10%) and 1 c.c. of $NaNO_2$ solution (1%), and after heating to b.p. and cooling, 2 c.c. of aq. NH_3 (10%) are added. The yellow coloration is compared with that given by a 0·0005% PhOH solution. The PhOH content of samples of rabbits' blood varied between 1 and 2·5 mg. per 100 c.c. of plasma. H. F. G.

Determination of solids in blood and plasma. S. Balachovski and F. Ginsburg (Biochem. Z., 1932, **254**, 47—49).—The blood (0·5—2·0 c.c.), to which an anticoagulant may be added, is dried at 100° to const. wt. in a shallow dish made of Al or Sn foil. W. McC.

Concentration and distribution of potassium in the serum and cells in the blood of normal unanæsthetised dogs. A. R. McIntyre (J. Biol. Chem., 1932, **98**, 115—120).—For 10 dogs the content of the serum averaged 21·54 mg. per 100 c.c. and that of the cells 27·04 mg. per 100 g. The ratio K_s/K_c is 0·557±0·16 when the vals. are expressed in millimols. per kg. of H_2O. F. O. H.

Comparative determinations of the calcium contents of various blood-constituents. A. Heiduschka and H. Schmidt-Hebbel (Biochem. Z., 1932, **253**, 336—346).—Determinations of Ca by the $KMnO_4$ titration method in serum and plasma gave comparable results both when the non-deproteinised fluid and its ash were used. Uranyl acetate as protein precipitant gave the most accurate results. Determinations on the ultrafiltrates of serum and plasma show that 30 and 50%, respectively, of the total Ca is retained by the protein on the filter. Using whole blood, the results of determinations in the ash are comparable with those on the directly hæmolysed blood, but $CCl_3\cdot CO_2H$ must replace uranyl acetate as deproteinising agent and the excess of this acid must be removed from the filtrate by evaporation to dryness. Hirudin, liquoid, and germanin may be employed to prevent clotting without interference with Ca pptn. Oxalates and NaF cannot be used, but citrate gives fairly good results. Blood-corpuscles contain amounts of Ca only determinable spectroscopically. P. W. C.

Serum-calcium and the kidneys. J. Cheymol and A. Quinquaud (Compt. rend. 1932, **195**, 682—684).—In dogs, the serum-Ca of the renal vein is on an average 5% < that of the carotid. Ablation of the kidneys causes an average elevation of 10% in the serum-Ca. A. L.

Determination of small quantities of iodine in blood. E. N. Allott, J. A. Dauphinee, and W. H. Hurtley (Biochem. J., 1932, **26**, 1665—1671).—An improved colorimetric and a titrimetric method are described. In the former the blood is dried with KOH at 150° in a Ni basin, ashed at 500°, the ash first extracted with H_2O and then with EtOH. After removing the solvent, the contents are taken up in H_2O, the I is liberated with $NO_2\cdot SO_3H$, and determined by comparing with standards. It is possible to recover KI added to blood quantitatively. As little as 2×10^{-6} g. of I, added as *p*-iodobenzoic acid, is determined. In the titrimetric method details of the extraction, oxidation to HIO_3, and titration are given. S. S. Z.

Determination of iodine in blood. E. Widmann (Biochem. Z., 1932, **254**, 223—228).—The blood, dried at 80°, is ignited at 500—550° in an electric furnace (cf. Schwaibold and Harder, this vol., 102), any I which is not trapped by KOH being absorbed in CS_2. Normal human blood contains about 0·032 mg. of I per 100 c.c., but no inorg. I, thyroxine, or di-iodotyrosine. W. McC.

Comparative investigation of the iodine content of blood with dry and moist ashing. W. Möbius (Biochem. Z., 1932, **253**, 275—278).—Tables show the I contents of the whole blood and serum of a no. of patients, the determinations being carried out by both the Pfeiffer and the Fellenburg methods. The former method always gives results considerably higher than the latter. P. W. C.

Apparatus for micro-determination of blood-cholesterol. R. L. Dutton (Lancet, 1932, **223**, 787—788). L. S. T.

Determination of lipin-phosphorus in blood. A. Karssen and C. R. van Wering (Biochem. Z., 1932, **253**, 427—430).—Determinations of lipin-P by the Baumann (A., 1924, ii, 58, 498) and Whitehorn (A., 1925 i, 95) methods gave reproducible results with an error of <1%. P. W. C.

Determination of bilirubin in blood-serum. M. Pickens and L. Bauman (J. Lab. Clin. Med., 1932, **17**, 820—821).—For clinical determinations a solution of $Fe(CNS)_3$ in Et_2O is used as a standard. Ch. Abs.

Urobilin compounds. VII. Artificial urobilinæmia. I. M. Oshima (Japan. J. Gastroenterol., 1932, **4**, 41—51).—Urobilin injected intravenously into rabbits disappears from the blood within 0·5 hr.; it is converted into urobilinogen and excreted in the bile. Urinary urobilin is affected only by large injections. The liver does not convert bilirubin into urobilin. Ch. Abs.

Formation of ammonia in blood. J. Heller and A. J. Klisiecki (Biochem. Z., 1932, **253**, 300—312).—Two processes are concerned in the formation of NH_3 by sheep's and horse's blood, the first being associated with the serum and the second with the corpuscles, the latter occurring during hæmolysis. The first process yields 0·5 mg. per 100 c.c. of NH_3-N in 24 hr. at room temp. and in 7—8 hr. at 39° and is inhibited by borate, whilst the second process, which is also inhibited by borate, yields 1·0—1·2 mg. of NH_3-N per 100 c.c., corresponding closely with the content of adenine nucleotide (25—28 mg. per 100 c.c.). P. W. C.

Van Slyke's method of determination of ketonic substances applied to small volumes of blood and urine. S. H. Nanavutty (Biochem. J., 1932, **26**, 1391—1396). S. S. Z.

Changes in composition of cow's blood at the time of calving and a comparison of the blood of the calf with that of its dam. W. Godden and W. M. Allcroft (Biochem. J., 1932, **26**, 1640—1646).—There is a rise in the blood-sugar at the time of parturition, followed by a fall to a low level maintained for at least 1 week. Serum-Ca falls either just at or within 24 hr. of calving and returns to normal within 4 or 5 days. A sharp fall in inorg. P just prior to calving invariably indicates the onset of labour. The blood of the calf at birth has higher levels of blood-sugar, serum-Ca, inorg. P, non-protein-N, and a lower Cl level, than that of its dam. S. S. Z.

Blood-esterase. R. Tsuji (Pflüger's Archiv, 1932, **229**, 344—353; Chem. Zentr., 1932, i, 3307).—The decomp. of acetylcholine and the vagus substance is attributed to blood-esterase. Adrenaline *in vitro* arrests the ability of the serum to cause fission of tributyrin and acetylcholine. Adrenaline or choline *in vivo* causes a slight reduction in ester fission. A. A. E.

Loss of mitogenetic radiation by blood (*a*) on keeping *in vitro*, (*b*) after irradiation with ultra-violet light. A. M. Karpas and M. N. Lanschina (Biochem. Z., 1932, **253**, 313—317).—In hæmolysed blood after keeping *in vitro* glycolysis occurs and is accompanied by decrease or complete loss of mitogenetic radiation. Irradiation with ultra-violet light is able to replace the effect of the glycolytic enzyme. P. W. C.

Blood glycolysis. I. Sugar and phosphorus relationships during glycolysis in normal blood. II. Blood of infants and children with various diseases. G. M. Guest (J. Clin. Invest., 1932, **11**, 555—569, 571—587).—I. Glycolysis occurs in normal defibrinated blood at 37° at a const. rate (13—16 mg. per 100 c.c. per hr.) until the residual reducing substance is about 20 mg. per 100 c.c. Inorg. P remains const. or falls slightly. When the free sugar has been destroyed, P rises rapidly (at the expense of org. acid-sol. P) to 20—25 mg. per 100 c.c. in the 15th hr. The rise occurs quickly in hypoglycæmic blood following insulin. Addition of glucose or fructose delays the rise.

II. Changes in inorg. P in relation to blood-sugar are markedly altered, especially in gastro-intestinal intoxication and nephritis with acidosis, the P rising immediately. Ch. Abs.

Rôle of hexosephosphoric esters in blood. E. Widmann (Biochem. Z., 1932, **254**, 221—222).—The incorrectness of the view that hexosephosphoric esters are intermediate products in the glycolysis of hæmolysed red blood-corpuscles (cf. Roche and Roche, this vol., 956) is established by the author's work (A., 1930, 1312). W. McC.

Effect of arsenate on blood glycolysis. A. E. Braunstein (J. Biol. Chem., 1932, **98**, 379—384).—Polemical against Morgulis and Pinto (cf. this vol., 530). W. O. K.

Blood glycolysis. I. Effect of arsenate. S. Morgulis and S. Pinto (J. Biol. Chem., 1932, **98**, 385—387).—A reply (see preceding abstract). W. O. K.

Blood coagulation. II. Influence of antipyretics on blood coagulation and on coagulation components of blood. III. Influence of narcotics. Y. Babasaki (Folia Pharmacol. Japon., 1932, **14**, No. 2, 7—13, 14—19).—II. Antipyrine, pyramidone, and Na salicylate retard coagulation and decrease the Ca, thrombin, and fibrinogen. NHAcPh retards coagulation but decreases only Ca.

III. CH_4, chloral hydrate, veronal, luminal, and morphine retard coagulation. The coagulation components are variously affected. Ch. Abs.

Regular relation between blood-sugar and -coagulation time. VIII. A. Partos (Pflüger's Archiv, 1932, **229**, 336—343; Chem. Zentr., 1932, i, 3311).—Stuber and Lang's relation could not be found. The quantity of lactic acid present is not a measure of the glycolysis. A. A. E.

Effect of temperature on hæmolytic systems containing propyl alcohol. A. S. Gordon (J. Exp. Biol., 1932, **9**, 336—338).—Arrhenius' equation does not describe the effect of temp. Ch. Abs.

Blood effects in the living dog produced by the venom of *Lachesis atrox*. J. Vellard and M. Miguelote-Vianna (Ann. Inst. Pasteur, 1932, **49**, 445—472).—1 mg. of venom will render 1—2 c.c. of blood incoagulable *in vitro* and it is even more active *in vivo*. Considerable quantities of antithrombin are found in the blood soon after the spontaneous coagulation is abolished, and these often persist for 24 hr. after the injection of the venom. This property of the venom is attributed to the action of proteases on the fibrinogen rather than to the antithrombin. During the destruction of the fibrinogen the serum loses its normal hæmolytic power; subsequently it acquires a power $>$ normal by activation of the blood-phosphatides by the venom, and finally it loses all hæmolytic power and becomes strongly anti-complementary. P. G. M.

Heparin and complement formation. H. Kowarzyk (Z. Immunität., 1931, **72**, 301—308; Chem. Zentr., 1932, i, 3194).—Addition of heparin inhibits immunohæmolysis, but only at certain concns. of amboceptor; with excess of amboceptor hæmolysis is promoted by heparin. A. A. E.

Determination of proteins by the precipitation reaction. G. L. Taylor, G. S. Adair, and M. E. Adair (J. Hyg., 1932, **32**, 340—348).—Cryst. albumin in egg-white and globulin in horse serum were determined, and the results compared with those obtained by other methods. Only antisera prepared against pure proteins (prep. described) should be used. Ch. Abs.

Determination of nucleotides in blood and muscle. S. E. Kerr and M. E. Blish (J. Biol. Chem., 1932, **98**, 193—205).—The tissue is deproteinised with $CCl_3\cdot CO_2H$, the filtrate neutralised, and nucleotides are pptd. by $UO_2(NO_3)_2$ (A., 1923, i, 1255). The ppt. is hydrolysed by 10% H_2SO_4, U is removed by neutralising with 4% NaOH and acidifying with AcOH, and purines are pptd. by $Cu(OH)_2$, the pptd. material being purified by treatment with $NaHSO_3$ (cf. A., 1905, ii, 776). The final ppt. is dissolved in 25% HCl and N determined by the Kjeldahl method. Satisfactory results for adenine nucleotide are given for admixtures with adenosine. F. O. H.

Preparation of adenylic and inosic acids. P. Ostern (Biochem. Z., 1932, **254**, 65—70).—Methods by which the acids are obtained in good yield from horse flesh (3·5 g. of adenylic acid and 6 g. of Ba inosate from 10 kg.) are described. W. McC.

Muscle extracts. H. Steudel (Z. physiol. Chem., 1932, **211**, 253—260).—Neither fish nor ox-flesh of commerce is a suitable source for the prep. of adenylic acid. $H_2C_2O_4$ was isolated from fresh meat in a yield of 0·14 g. per kg. J. H. B.

Constitution of adenylpyrophosphoric acid. K. Lohmann (Biochem. Z., 1932, **254**, 381—397).—The preps. of adenylpyrophosphoric (I) and of adenylic (II) acids, and also of inosinepyrophosphoric acid (III) from (I) by treatment with HNO_2 are described, the velocity of deamination in the latter case being the same as for (II). Electrotitration of (I) before and after hydrolysis with acid shows that the basicity increases from 4 to 6. The velocities of separation of H_3PO_4 when heated in *N*-AcOH at 100° from (I), (III), $H_4P_2O_7$, and HPO_3 are investigated, the velocities with (I) and (III) being approx. the same. Hydrolysis of the nucleoside linking of (I) in 0·1*N*-HCl at 100° takes place as well as of the H_3PO_4 linking, but more slowly. P. W. C.

Osmotic relations between white and yolk in the hen's egg. J. B. Bateman (J. Exp. Biol., 1932, **9**, 322—331).—A real osmotic difference exists. The amount of bound H_2O is small in both. Urea dissolves in egg-white and depresses the v.p. Urea and Na lactate, but not glucose, are removed from solution when added to yolk. Ch. Abs.

I. Behaviour of proteins on incubation of the hen's egg. II. Production of the proteins of the egg in the hen's ovary and oviduct. III. Keratin of feathers. E. G. Schenck (Z. physiol. Chem., 1932, **211**, 111—153, 153—160, 160—163).—I. In the various portions of the eggshell, membrane, white, yolk, and embryo, the H_2O, proteins, and constituent NH_2-acids were determined at various stages of incubation. The changes in composition were followed and a balance was constructed for the total protein, and the amounts of the various components. The composition of the feather-proteins is not const., but follows the changes in the proteins of the embryo.

II. The proteins of the ovaries [globulin (I), albumin (II), nucleoprotein (III)], ripening follicles [(I), (II), (III), vitellin], yolk of the unincubated egg [(I), (II), (III)], oviduct [(I), (II)], and white were determined and compared. From the proteins of the ovaries and oviduct, rich in hexone bases, the yolk-proteins, low in hexone bases, are synthesised, but these again yield proteins rich in hexone bases on incubation.

III. The constituents of the keratin of various types of feathers were determined. The composition depends on that of the tissue from which they are formed. J. H. B.

Specificity of the protein of the pig's alimentary mucous membrane. T. Asao (J. Biochem. Japan, 1932, **16**, 17—47).—The isoelectric point of the protein varies with the position of the mucous membrane, viz., stomach, p_H 4·5—5·3; small intestine, 4·4—5·3; large intestine, 4·1—4·4. Differences also occur in the combination with HCl, NaOH, and Cl′, in the permeability to Cl′, in the resistance to proteolytic enzymes, and in the chemical constitution. F. O. H.

Cystine and wool production. A. H. H. Fraser and J. A. F. Roberts (Nature, 1932, **130**, 473).—A review of available evidence indicates that the cystine (I) content of pasture is too low to be a limiting factor in wool production, that (I) is synthesised in the sheep, and that the content of (I) in wool fibre is not const. (I) may be formed during keratinisation and synthesis of (I) may be a function of the wool follicle itself. L. S. T.

Union of biocolloids. IX. Starch and various proteins. S. Bartuszek (Biochem. Z., 1932, **253**, 279—287).—The extent of combination of starch with caseinogen is almost independent of p_H between 3·3 and 4·8, is not decreased by addition of salts, and is independent of dilution at p_H 3·3. The union with globulin in absence of salts is detected only on the acid side (up to p_H 5), salts decrease the extent of union at p_H 3·3 and 5 but make union possible at $p_H > 5$, and the union is independent of dilution and non-reversible. Union with albumin is dependent on p_H and is decreased by addition of salts at any p_H; it is independent of dilution at a $p_H <$ isoelectric point, but is proportional at a $p_H >$ isoelectric point. P. W. C.

Union of biocolloids. X. S. J. Przylecki and W. Bialek (Biochem. Z., 1932, **253**, 288—293).—The equilibrium between glycogen in liver pulp and in solution is investigated by shaking the pulp with solutions of various composition and vol. Samples of liver containing initially 2·68, 4·54, and 8·43%, respectively, of glycogen after treatment with 16 c.c. of solution contained 61·2, 85·6, and 73·8 mg., the concns. of glycogen in the solutions being 0·29, 0·55, and 1·65% and remaining in the pulp 1·53, 2·14, and 1·845%. P. W. C.

Source of amylase in the hen's gizzard. A. Bernardi and M. A. Schwarz (Biochem. Z., 1932, **253**, 383—386).—The mucous membrane of the hen's gizzard is concerned in the formation of amylase. P. W. C.

Variations in the dry weight and iodine content of the thyroid glands of sheep under uniform and varying conditions. M. C. Dawbarn and F. C. Farr (Austral. J. Exp. Biol., 1932, **10**, 119—142).—The I content, which varied from 0·096 to 1·26% of the dry wt., is increased under drought conditions, appears to have a seasonal variation, and is not influenced by sex or age (except during the period of growth). Access to I-containing salt-licks leads to only a slight increase in I content. F. O. H.

Chemical assay of thyroid gland. G. Middleton (Analyst, 1932, **57**, 603—609; cf. A., 1930, 505).—The previous method is improved by the addition of PhOH in AcOH before the liberation of I. Acid-insol. I is determined directly, after hydrolysis by the method of the B.P. 1932, in the ppt. insol. in acid, using the author's method. T. McL.

Bromine content of the pituitary and its relation to age. H. Zondek and A. Bier (Klin. Woch., 1932, **11**, 759—760; Chem. Zentr., 1932, i, 3192).—The Br content of the human pituitary is normally 15—30 and of other organs 1—2 mg. per 100 g.; the posterior lobe is practically free from Br. In men of 45—60 years the val. is min. (15), whilst in women of the same age it falls to 5. In old age the val. is low (5) in both sexes, and above 75 years Br is usually undetectable. A. A. E.

Ether-esters of glycerol, or ether-glycerides of shark-liver oil, *Scymnorhinus lichia*, Bonnaterre. E. ANDRÉ and A. BLOCH (Compt. rend., 1932, **195**, 627—629).—Chimyl, batyl, and selachyl alcohols do not exist as such in the liver-oil of *S. lichia*. The two remaining OH groups of the glyceryl residue in these alcohols are esterified with fatty acids giving an ether-glyceride. The liver-oil contains hydrocarbons (squalene) 57%, glycerides 21%, and ether-glycerides 21%. A. C.

Comparison of the body constituents of parasite and host. I. Reserve fat of *Balaninus dentipes*. T. SASAKI (Keijo J. Med., 1932, 3, 184—186).—The fat extracted from the cotyledons of *Castanea pubinervis* closely resembles that from the larvæ of *B. dentipes* parasitic on them. F. O. H.

Nutrition of dermestid beetles. I. Composition and nature of the ether extract of beetles. O. SINODA and M. KURATA (J. Biochem. Japan, 1932, **16**, 129—139).—The contents of N and chitin and the nature of the Et_2O extract were investigated in *Dermestes coarctatus* and *D. vulpinus*. The bearing of the data thus obtained on the metabolism of the beetles is discussed. F. O. H.

Arsenic content of large-mouth black bass (*Micropterus salmoides*, Lacepede) fingerlings. A. H. WIEBE, E. G. GROSS, and D. H. SLAUGHTER (Trans. Amer. Fish. Soc., 1931, **61**, 150—163).—Normal domesticated bass contain no As. Vals. for fish from Rock River and the Mississippi and for fish living in As-treated waters are recorded. CH. ABS.

Structure of dental enamel. IV. Cataphoretic determination of the effects of p_H and electrolytes on the electric charge resident on enamel particles. V. Effects of acidity and alkalinity on the nature of the electric charge resident on particles of tricalcium phosphate. VI. Electroendosmotic determination of the electric charge resident on the enamel pore wall; influence of acidity and alkalinity of the bathing salt solution. VII. Mechanism of production of membrane potentials in the enamel of dogs. VIII. Determination of the isoelectric point of enamel by means of membrane-potential measurements. H. KLEIN (J. Dental Res., 1932, **12**, 79—83). CH. ABS.

Solubility of dental enamel in various buffered solutions. H. C. BENEDICT and F. K. KANTHAK (J. Dental Res., 1932, **12**, 277—289).—Dental enamel is more complex than $Ca_3(PO_4)_2$ (I), but the solubility curves (p_H 2·38—7·80) are similar to those of (I). The enamel is sol. in an alkaline liquid. Saliva is usually saturated with respect to (I). CH. ABS.

Group-specific substance of horse saliva. K. LANDSTEINER (Science, 1932, **76**, 351—352).—An active prep. from horse saliva, obtained by treatment with acid and $COMe_2$, and fractionation with EtOH, gave a weak biuret reaction and yielded 48·5% of reducing sugar on hydrolysis. A second prep. (ash 3·37%) from saliva adsorbed with kaolin and C reacted strongly with anti-A immune sera and contained (ash-free) C 44·65, H 6·76, N 7·43%. L. S. T.

Gastric physiology. Rôle of duodenal regurgitation in the control of gastric acidity. H. SHAY, A. B. KATZ, and E. M. SCHLOSS (Arch. Int. Med., 1930, **50**, 605—620).—Duodenal regurgitation bears no relation to gastric acidity. H. G. R.

Relation of blood-chlorine to gastric secretion and gastric digestion. I. V. BUCHGALTER (Arkh. med. nauk., 1929, **2**, 301—309).—Variations are not a measure of gastric function. Atropine, or oral administration of NaCl (10 g.), does not affect blood-Cl. CH. ABS.

Alteration of stomach chemistry by bromide. T. EPSTEIN (Arch. exp. Path. Pharm., 1932, **168**, 57—63).—Br′ appeared in the gastric juice of man after oral administration of NaBr. The total and free acid was increased, the p_H was lowered, and the proteolytic action of the juice was greater. W. O. K.

Influence of the vegetative nervous system on the reaction and buffering power of the bile. T. ITOO (Biochem. Z., 1932, **254**, 50—58).—In dogs, section of the splanchnic nerves results in reduced secretion of bile (I) and of bile acids (II) and in reduction of the p_H (III) and alkali reserve (IV) of the bile. If only one of the nerves be cut (I), (II), (III), and (IV) first increase and then decrease to original vals., but are again increased by administration of bile acids. It follows that there is a close relationship between the function of the vegetative nervous system and secretion of (II) in the liver. W. McC.

Protein constituents and formation of bile acids. L. SCHINDEL (Arch. exp. Path. Pharm., 1932, **168**, 38—48).—The excretion of bile acids by dogs with a bile fistula and on a standard diet is increased when protein is administered. Of various NH_2-acids tested, the most active in producing increased secretion of bile acids was aspartic acid. Tryptophan and glucosamine were less active, whilst β-alanine was only slightly active. The effect is probably due to a stimulating action on the liver cells. W. O. K.

Behaviour of cholesterol and other bile constituents in solutions of bile salts. G. O. SPANNER and L. BAUMAN (J. Biol. Chem., 1932, **98**, 181—183).—The solubilities of cholesterol in aq. solutions of Na cholate, glycocholate, taurocholate, anthropodeoxycholate, deoxycholate, oleate, and bilirubinate and of lecithin were determined. Dialysis and ultrafiltration indicate that the combination between bile salt and sterol is readily dissociated. The bearing of the results on gallstone formation is discussed. F. O. H.

Human milk. X. Daily and monthly variations in milk components as observed in two successive lactation periods. B. NIMS, I. G. MACY, H. A. HUNSCHER, and M. BROWN (Amer. J. Dis. Children, 1932, **43**, 1062—1076).—The components fluctuate about a level characteristic of the individual and maintained without marked variation through successive lactation periods. The N decreases rapidly up to the sixth month and then remains const. The total ash and Ca decrease gradually, whilst the P, fat, and total solids decreased during the earlier months, regaining higher vals. during later months. CH. ABS.

Yield and composition of milk with special reference to the influence of climatic conditions and other factors. J. HOUSTON and R. W. HALE (J. Dairy Res., 1932, 3, 294—309).—Correlation data are recorded. The butter-fat yield shows greater variation than that of total milk or of solids-not-fat. The butter-fat and solids-not-fat do not show parallel variation. Solids-not-fat are depressed during the summer months, but seasonal changes in the butter-fat are small. Diurnal changes in the yields of whole milk and of solids-not-fat are independent of temp. A. G. P.

Lactation. I. Variations in properties of milk from individual quarters of a cow. E. C. V. MATTICK and H. S. HALLETT (J. Dairy Res., 1929, 1, 35—49).—In general, the yield, acidity, rennin coagulation time, and fat content varied, milks from the two front quarters being usually similar but differing markedly from milks from the two hind quarters. CH. ABS.

Phosphate fractions of cow's milk and changes in them during spontaneous acidification and during dairy treatment. K. LANG and M. MIETHKE (Biochem. Z., 1932, 254, 484—489).—The distribution of various P fractions of cow's milk (caseinogen-, lipin-inorg., readily and difficultly hydrolysable ester-P) and the behaviour of these fractions during spontaneous acidification, centrifuging, and pasteurising are investigated. None of the usual dairy manipulations seriously affects the P fractions. P. W. C.

Determination of iron in cow's milk and human milk. F. REIS and H. H. CHAKMAKJIAN (J. Biol. Chem., 1932, 98, 237—240; cf. A., 1931, 974).—The Fe content of cow's milk varied from 1·00 to 0·14 mg. per 100 c.c., whilst for human milk the corresponding limits were 0·29 and 0·45 mg. per 100 c.c. W. O. K.

Biochemical activators of milk. I. Relation between reducing power and vitamin-*C* content of milk. Chemical determination of this content. F. SCHLEMMER, B. BLEYER, and H. CAHNMANN (Biochem. Z., 1932, 254, 187—207; cf. Tillmans and others, this vol., 658).—The substance (I) in milk which reduces 2 : 6-dichlorophenolindophenol and can be determined by titration is probably identical with vitamin-*C*. Great variations (not depending on diet) are found in the amount of (I) in different samples of cow's milk, and the milks of sheep, goats, asses, and camels also differ greatly from each other in this respect. Human milk (especially colostrum) has a higher content of (I) than has cow's milk. Milk kept exposed to air rapidly loses much of its (I), but the loss can be reduced by cooling. Boiling the milk for short periods causes only slight loss. Cu and Ag destroy (I), but Ni, Cr, and Al do not. Chemical and biological examination of milks pasteurised in various ways indicates that their content of (I) runs parallel with their content of vitamin-*C*. W. McC.

Antirachitic value of milk from cows fed [with] irradiated yeast. E. T. WYMAN and A. M. BUTLER (Amer. J. Dis. Children, 1932, 43, 1509—1518).—The antirachitic property of the milk is not destroyed by boiling or pasteurisation. CH. ABS.

Influence of vitamins on the lactation of cows. H. POELT (Z. Vitaminforsch., 1932, 1, 289—294).—The feeding of irradiated yeast increases the amount of milk secreted. F. O. H.

Iron and thorium precipitation of biological fluids for sugar and other analyses. A. STEINER, F. URBAN, and E. S. WEST (J. Biol. Chem., 1932, 98, 289—293).—The proteins present in blood, laked blood, cerebrospinal fluid, milk, etc. may be removed by treatment with $Fe_2(SO_4)_3$ and $BaCO_3$, followed by filtration. The filtrates may be used for determination of sugar. Diluted blood or plasma may be deproteinised by treatment with $Th(SO_4)_2$ and $BaCO_3$. The filtrates may also be used for creatinine and urea determinations, but the non-protein-N vals. are about 25% < those found in tungstate filtrates. W. O. K.

Effect of urea on glucose determination by the formose reaction. H. W. LARSON (J. Biol. Chem., 1932, 98, 151—156).—The interference by urea in the Kingsbury method for urine-sugar (A., 1927, 1172) is due to the formation of NH_3. Attempts to inhibit the decomp. of urea by addition of NaCNO and EtOH to the reagent were only partly successful. Thus, whilst the reagent cannot be satisfactorily applied to urine, its use for NH_3- and urea-free glucose solutions and also for the determination of NH_3 is suggested. F. O. H.

Hippuric acid. I. Determination in urine. II. Determination in blood. III. Permeability to red blood-corpuscles. I. KANZAKI (J. Biochem. Japan, 1932, 16, 105—116, 117—123, 125—128).—I. The protein-free urine (20 c.c.) is acidified with H_2SO_4, extracted with Et_2O, and the residue after removal of Et_2O washed with petrol to remove BzOH. A hot aq. solution of the residue is then titrated with 0·1*N*-NaOH.

II. The blood (5—15 c.c.) is deproteinised with H_2WO_4, and an aliquot of the filtrate freed from lactic acid by $KMnO_4$ and extracted with Et_2O, the extract being treated as above. Ox blood is practically free from hippuric acid.

III. Hippuric acid is absent from the blood of man, ox, horse, cat, dog, guinea-pig, and rabbit. Oral administration of NaOBz to rabbits is not followed by the presence of hippuric acid in the blood. Rabbit erythrocytes are impermeable to hippurate *in vitro* or injected intravenously. F. O. H.

Direct determination of the titratable acidity of urine: correction for the hydrogen carbonate content. E. E. MARTINSON and N. G. BORODIN (Biochem. Z., 1932, 254, 292—300).—The urine is treated with a known amount of HCl, the CO_2 removed in vac., and the resulting fluid titrated, using a comparator to p_H 7·4 with *m*-$NO_2{\cdot}C_6H_4{\cdot}OH$

as indicator. On subtracting the amount of HCl a figure is obtained corresponding with the urinary acidity minus H carbonate. Comparison with a control determination without HCl enables the $NaHCO_3$ content to be calc. P. W. C.

Acid–base equilibrium with inhabitants of the tropics. I. Reaction of the urine, especially of the morning urine, obtained under basal conditions. W. Radsma, G. M. Streef, and J. V. Klerks (Arch. néerland. Physiol., 1932, **17**, 444—457).—With Europeans of Batavia, but rarely with the natives, there is a shift of the p_H to the alkaline side in the morning urine and, to a smaller extent, in the night or 24-hr. urine. The change in reaction is accompanied by polyuria. F. O. H.

Relationship between chemical structure and physiological response. III. Factors influencing the excretion of uric acid. A. J. Quick [with M. A. Cooper] (J. Biol. Chem., 1932, **98**, 157—169).—The possibility of a carbohydrate intermediary being essential for the normal excretion of uric acid is discussed. The stimulating action on uric acid elimination of glycerol, $AcCO_2H$, and various NH_2-acids is completely inhibited by BzOH and some of its substituted products, and $CH_2Ph{\cdot}CO_2H$, *i.e.*, by substances which decrease the excretion of uric acid. The excretion is increased by salicylic acid, cincophen, neocincophen, and, to a smaller extent, by p-$OH{\cdot}C_6H_4{\cdot}CO_2H$. Replacement of OH by OMe abolishes the stimulating action of o- and p-$OH{\cdot}C_6H_4{\cdot}CO_2H$. The mode of conjugation of these substances is discussed. F. O. H.

Excretion of lead by the kidneys, and the effect thereon of foods and drugs. II. So-called "normal" lead in urine. F. Weyrauch and S. Litzner (Arch. Gewerbepath. Gewerbehyg., 1932, **3**, 15—22; Chem. Zentr., 1932, i, 3460).—"Normal" Pb in urine (as found in persons not brought into contact with Pb during their work) is 0·01—0·055 (average 0·02) mg. per litre of 24-hr. urine. A. A. E.

Absorption and excretion of water and salts by the elasmobranch fishes. III. Use of xylose as a measure of the glomerular filtrate in *Squalus acanthias*. R. W. Clarke and H. W. Smith (J. Cell. Comp. Physiol., 1932, **1**, 131—143).—Xylose excreted by the dogfish is entirely filterable in the plasma and is neither secreted nor reabsorbed by the renal tubules. PO_4''', $Mg^{\cdot\cdot}$, and administered creatinine are freely secreted and excretion by filtration is small. The filtered urea is almost entirely reabsorbed from the glomerular filtrate. Thiourea is not so reabsorbed. Secretion of creatinine and possibly of PO_4''' and $Mg^{\cdot\cdot}$ is depressed by phloridzin. A. G. P.

Absorption of mineral constituents of the urine in the avian cloaca. E. Kryszczyński (Bull. Acad. Polonaise, 1931, B, 681—702).—The abs. concns. of Na and Cl and the ratio of these elements to N in the fæces of fasting hens are $<$ those in the urine. Hence any absorption of N compounds in the cloaca must be accompanied by a greater absorption of Na and Cl. Absorption of K, Ca, Mg, and P is less marked. During starvation absorption of H_2O leads to a urine hypertonic to the blood. F. O. H.

Iron content of normal and calcified aorta. I. H. Page and W. Menschick (Arch. path. Anat. Physiol., 1932, **283**, 626—630; Chem. Zentr., 1932, ii, 242).—The Fe content is not parallel with the degree of calcification, but the org. P increases with the latter. A. A. E.

Lubricating oils and cancer. J. B. Speakman and N. H. Chamberlain (Nature, 1932, **130**, 578).—The difficulty experienced in removing mineral oil from wool can be overcome by the addition of polar compounds which reduce the oil–H_2O interfacial tension without increasing adhesion sufficiently to make emulsification difficult. Fatty acids and glycerides are ineffective compared with oleyl alcohol, which brings about ready emulsification in 6% concn. Certain alcohols from lanolin are also effective. Dermatitis and tumours may be due to the difficulty of removing mineral oils from the skin by means of soap solution and the beneficial effect of the addition of lanolin may be due to its emulsifying action. L. S. T.

Lipin content of tumours. M. Yasuda and W. R. Bloor (J. Clin. Invest., 1932, **11**, 677—682).—Malignancy of tumours is associated with larger amounts of neutral fat, cholesterol, and (particularly) phospholipin. Ch. Abs.

Changes in the contents of cholesterol and phosphorus compounds of cancer tissue with growth. M. Uramoto (J. Biochem. Japan, 1932, **16**, 69—82).—During the growth of tumours in rats there is an increase in the contents of H_2O, free and combined cholesterol, and inorg. P, whilst those of lipin-, acid-sol. org., and protein-P decrease. The content of N remains practically const., whilst protein is degraded mainly during late growth and then only at the centre of the tumour. F. O. H.

Chemical composition of mouse carcinoma. Effect of varying diet on the composition. B. Kellner and B. Lustig (Biochem. Z., 1932, **254**, 214—220).—The content of free and combined carbohydrate of the tumours is affected by the type of diet given, free sugar being found when the diet is rich in carbohydrate. No increase in the lipin content results when the diet is very rich in fat. The type of diet, however, affects the chemical composition of the lipins. W. McC.

Factors affecting the calcium content of the tissues of the carcinoma-susceptible rat. H. C. Pitts and H. R. Johnson (Amer. J. Cancer, 1932, **16**, 854—862).—Subcutaneous injection of Ca gluconate or parathyroid extract, or administration of small doses of irradiated ergosterol, has no influence on the Ca content of the tissues. Parathyroid extract prevents hypervitaminosis arising from the administration of large doses of irradiated ergosterol. Ch. Abs.

Urinary excretion of melanogen by sarcomatous subjects. O. Fürth and H. Kaunitz (Biochem. Z., 1932, **253**, 231—238).—The urinary melanogen gives a black $FeCl_3$ colour, reduces $K_3Fe(CN)_6$ strongly and in presence also of $FeCl_3$

gives Prussian-blue even in great dilutions, does not reduce ammoniacal $AgNO_3$, gives a ppt. with $Pb(OAc)_2$ readily sol. in AcOH, is pptd. from MeOH solution by Et_2O, and is present in the H_2O-sol., EtOH-precipitable Ba salts of the urine. P. W. C.

Proteolysis in tumours. P. RONDONI (Biochem. J., 1932, 26, 1477—1487).—The optimum p_H (4·7) for the proteolytic action of mouse-tumour proteinase on the tumour-proteins varies a little with the age of the tumours. The activity of these enzymes is not $>$ those of some normal organs. Lecithin has a slight and cysteine a more or less pronounced accelerating action on proteolysis. The tumours have a varying content of dipeptidases. Aminopolypeptidases were absent in the one series examined, whilst the livers of the same mice contained them. Treatment of the tumour-bearing mice with lecithin delayed the tumour growth and produced some modification in the enzyme content. S. S. Z.

Metabolism of normal and tumour tissue. VII. Anaërobic conversion of fructose into lactic acid by tumour and adult normal tissues. F. DICKENS and G. D. GREVILLE (Biochem. J., 1932, 26, 1546—1556).—The anaërobic conversion by rat's retina, submaxillary gland, and spleen is negligible and that of kidney and testis is slight. There is a variability amongst tumour tissues in their ability to convert fructose anaërobically, similar to that possessed by embryonic tissues. The velocity of the anaërobic glycolysis and sugar concn. curves as measured in the second hr. during the action of Jensen sarcoma are similar for glucose and fructose. The spontaneous increase in anaërobic fructolysis could not be confirmed with the Jensen sarcoma. S. S. Z.

Phosphorylation in tumour glycolysis. R. WILLHEIM and J. SCHMERLER (Biochem. Z., 1932, 254, 355—363).—In aërobic glycolysis of mouse carcinoma suspended in physiological saline containing sugar and PO_4''', the inorg. PO_4''' decreases and the PO_4''' readily hydrolysed by acid increases, whilst the reverse is true when glycolysis is inhibited by addition of NaF. P. W. C.

Effect of carotene on glycolytic processes. Blood-glycolysis in cancer. C. WETZLER-LIGETI and R. WILLHEIM (Biochem. Z., 1932, 254, 364—373).—Carotene accelerates yeast fermentation of sugar solutions and glycolysis of defibrinated blood, the acceleration disappearing on addition of KCN. Blood-glycolysis in human cancer is not affected by addition of carotene. P. W. C.

Investigations in enzyme action directed towards the study of the biochemistry of cancer. Activation of pancreatic pro-lipase. D. L. WOODHOUSE (Biochem. J., 1932, 26, 1512—1527).—Gelatin, gum arabic, gum tragacanth, and agar augment the action of lipase in olive oil, but are unable to activate the pro-lipase. Starch, caseinogen, hæmoglobin, colloidal ZnS, and a suspension of powdered C have no activating power. On the other hand, a solution of egg-white or colloidal Fe activates the pro-lipase, as also do Pb salts. Na taurocholate has an effect in activating pro-lipase. Pro-lipase from the pancreas is inert towards cod-liver oil, olive oil, hog lard, and croton oil, but readily decomposes palm oil, chaulmoogra, and coconut oils even when these have been purified. EtOH-pptd. proteins from serum and the remaining residue, as well as that obtained by the pptn. of the serum-proteins by heat, have an activating effect. The activator in the latter case is dialysable. Urine, cerebrospinal and ovarian fluids are potent activators. The serum of cancer patients is just as efficient in activating lipase as is that from normal man and animals. S. S. Z.

[Alleged] inhibitory effect of magnesium salts on the growth of malignant tumours. A. A. ASHOUR (J. Egypt. Med. Assoc., 1932, 15, 740—744).—Egyptian soil contains no excess of Mg and cancer is not abnormally rare in Egypt. Hence the view that excess of Mg in the soil, H_2O, and foodstuffs reduces the incidence of cancer is not supported. W. O. K.

Analysis of teeth, roots, and crowns affected by pyorrhœa alveolaris and dental caries. II. Phosphorus and magnesium. L. I. KAUSHANSKY (Dental Cosmos, 1932, 74, 468—473).—Mg in the entire tooth and the crown is high in pyorrhœa and caries; in the roots it is normal in caries but high in pyorrhœa. In all cases the crowns contain less Mg than the roots. In the entire tooth, crown, and roots the P content falls in the order caries, pyorrhœa, normal. CH. ABS.

Phosphorus metabolism. IV. Phosphorus of saliva with special reference to dental caries. G. E. YOUNGBURG (J. Dental Res., 1932, 12, 267—275).—Normally, and in nephritis and dental caries, 96% of the saliva-P is present as inorg. PO_4''', the rest being combined with mucin. Vals. of inorg. P are: normal 17·50, nephritis 17·54, dental caries 18·13 mg. per 100 c.c.; apparently it plays no part in dental caries, increases slightly with age, and varies appreciably during the day and from day to day. CH. ABS.

Vitamin factor in dental caries. W. A. OSBORNE (Nature, 1932, 130, 630).—A discussion. The high incidence of caries in Australia indicates that the vitamin factor in the production of caries is unduly emphasised. L. S. T.

Significance of urinary "proteose" in idiopathic epilepsy. R. L. H. MINCHIN (Brit. Med. J., 1932, ii, 97—98).—The "proteose" isolated from the urine of epileptics (cf. Lancet, 1930, ii, 231) gives negative Millon, biuret, and xanthoproteic reactions and is of no marked significance in the production of fits. F. O. H.

Plasma-phosphatase in dairy cows suffering from fluorosis. P. H. PHILLIPS (Science, 1932, 76, 239—240).—The plasma-phosphatase increases practically in proportion to the level of F intake; it appears to be a good index of the degree of fluorosis in cattle. L. S. T.

Variations in the iodine content of the blood in hyperthyroidism and non-toxic goitre. E. C. DODDS, W. LAWSON, and J. D. ROBERTSON (Lancet, 1932, 223, 608—611).—Blood-I can be separated into two fractions by EtOH-extraction (cf. A., 1929, 595). The insol. fraction is increased in cases of toxic goitre and may be reduced by oral treatment with I. This fall is not necessarily associated with a reduction in the toxicity and the basal metabolic rate; the EtOH-insol. fraction is not a measure of the toxic secretion of the thyroid. L. S. T.

Mineral alkalinity and iodine content of goitrous tissue. M. Saegesser (Biochem. Z., 1932, **254**, 475—478).—Simultaneous determinations are made of the EtOH-sol. and -insol. I fractions of thyroid tissue in cases of goitre and unsuccessful attempts made to correlate them with the ash alkalinity and the Ca and P contents. P. W. C.

Calcium carbonate gallstones and calcification of the gall bladder following cystic-duct obstruction. D. B. Phemister, A. G. Rewbridge, and H. Rudisill (Ann. Surg., 1931, **94**, 493—576).—Obstruction by gallstones leads to deposition of $CaCO_3$ in the gall bladder and on the stones. Ch. Abs.

Blood-lactic acid in hepatic disease. A. M. Snell and G. M. Roth (Proc. Staff Mtgs. Mayo Clinic, 1932, **7**, 288—289).—Abnormally large increases are reported. Ch. Abs.

Bilirubin. VII. So-called direct and indirect diazo-reactions and their application to the determination of bilirubin. W. Kerppola and E. Leikola (Acta med. Scand., 1931, **76**, 479—490; Chem. Zentr., 1932, i, 2980).—The "direct reaction," as given in sera of static icterus, indicates the presence of alkali-bilirubin. Bilirubin in $0{\cdot}1N$-Na_2CO_3 is immediately coloured pink by the reagent, and brown on further addition. A. A. E.

Inflammation. VIII. Inhibition of fixation by urea. Mechanism of fixation by the inflammatory reaction. V. Menkin (J. Exp. Med., 1932, **56**, 157—172).—A conc. solution of urea dissolves fibrin. Injection into the peritoneal cavity of urea solution with or after an inflammatory irritant partly or wholly prevents local fixation of foreign substances introduced subsequently, this fixation being primarily due to mechanical obstruction caused by a fibrin network and thrombosed lymphatics. Ch. Abs.

Ketosis. II. Comparative ketolytic action of glucose, galactose, fructose, and sucrose. H. J. Deuel, jun., M. Gulick, and J. S. Butts (J. Biol. Chem., 1932, **98**, 333—351).—In man with ketosis induced either by fasting or by an exclusive protein–fat diet, the acetonuria is more efficiently reduced by administration of galactose (I) than by an equal quantity of glucose (II). The protein-sparing action is also greater in the case of (I) than of (II). Sucrose and fructose appear to be intermediate in antiketogenic activity between (I) and (II). W. O. K.

Excretion of carbohydrate in urine in diseases other than diabetes. Relation of the excretion to the carbohydrate of blood. B. Lustig and M. Löbl (Biochem. Z., 1932, **254**, 208—213).—The amount of carbohydrate excreted in human urine does not vary greatly with varying pathological conditions (apart from those of diabetes). It is affected by the type of food consumed and by individual factors, but not by body temp. (fever). No relationship can be traced between the carbohydrate content of the blood of diseased persons and that of their urine. W. McC.

Electrolyte distribution and the acid–base equilibrium in the serum in cases of nephritis and nephritic acidosis. C. H. Greene, E. G. Wakefield, M. H. Power, and N. M. Keith (Biochem. J., 1932, **26**, 1377—1382).—In some cases there was a reduction in total base. Ca was reduced in several cases, usually associated in part with reduction in the serum-proteins and perhaps in part with the retention of PO_4''' and SO_4''. There was no accumulation of undetermined org. acids. Cl′ was normal in the majority of cases. There was an accumulation of PO_4''' and SO_4'', which play an appreciable part in the production of acidosis. The changes in HCO_3' depend on the balance between the opposing effects of loss of Cl′ on the one hand and the loss of base and retention of PO_4''' and SO_4'' on the other. Usually the HCO_3' is decreased. S. S. Z.

Mechanism of nephrotic œdema. R. F. Loeb, D. W. Atchley, D. W. Richards, jun., E. M. Benedict, and M. E. Driscoll (J. Clin. Invest., 1932, **11**, 621—639).—Quant. differences between normal and nephrotic patients regarding excretion etc. following ingestion of KCl, NH_4Cl, and NaCl are recorded. Ch. Abs.

Kidney weight, body size, and renal function. E. M. MacKay (Arch. Int. Med., 1932, **50**, 590—594).—In man renal function, as measured by the ratio urinary urea rate : blood-urea concn., and kidney wt. are both directly proportional to the body surface. H. G. R.

Urea clearance test as an index of renal function. III. Bright's disease. IV. Urea clearance test in relation to other tests of renal function. M. Bruger and H. O. Mosenthal (Arch. Int. Med., 1932, **50**, 544—555, 556—568).—III. A clearance val. $> 75\%$ of normal usually indicates no impairment of renal function, whilst vals. $< 50\%$ always imply decreased renal efficiency. In Bright's disease with definite impairment of renal function, moderate exercise is without influence on the urea clearance.

IV. The test usually demonstrates impairment of renal function before the urea, uric acid, or creatinine is increased in the blood, although occasionally cases of early renal insufficiency may show an elevation of blood-uric acid first. H. G. R.

Phosphatide–fatty degeneration of brain, liver, and spleen in Niemann–Pick disease. II. E. Epstein and K. Lorenz (Z. physiol. Chem., 1932, **211**, 217—230; cf. A., 1931, 115).—Various constituents of the brain, liver, and spleen in a case of Niemann–Pick disease were determined. The liver showed a heavy accumulation of Et_2O-sol. as compared with EtOH-sol. lipins. Extracted N and P were particularly augmented. The liver showed the highest % of lecithin. The free cholesterol : cholesteryl ester ratios for brain and liver were 19 : 1 and 64 : 1, respectively, the normal vals. being 1·56 : 1 and 3·6 : 1. This total phosphatide content of liver and spleen was about 10 times the normal. J. H. B.

Cerebrospinal fluid in paralysis. K. Takeno (Arb. Med. Univ. Okayama, 1932, 3, 31—36).—Albumin and globulin increase and, as indicated by N content, their constitutions differ from those of the serum constituents. In paralytic cerebrospinal fluid N is high; purine-N is 13·15%. Ch. Abs.

Mineral metabolism during pregnancy and lactation. II. K. U. Toverud and G. Toverud (Biochem. J., 1932, 26, 1424—1434).—The clinical appearance of two puppies each with Ca and P deficiencies during fœtal life and during the lactation period, but one receiving cod-liver oil and the other deprived of it after weaning, was the same. There was a lowering of Ca, P, and Mg in both cases. The histological examination showed, however, that the animal not receiving cod-liver oil was rachitic. S. S. Z.

Acid-base equilibrium in abnormal pregnancy. D. M. Kydd, H. C. Oard, and J. P. Peters (J. Biol. Chem., 1932, 98, 241—251).—In six cases of eclampsia, there occurs, as compared with normal pregnancy, a considerable lowering of CO_2 of the blood, accompanied by an elevation of the total base, Cl′, and undetermined acids of the serum, whilst the proteins are reduced during convulsions. The acidosis is probably the effect, rather than the cause, of convulsions. In six cases of vomiting of pregnancy, blood-cell vol. and serum-protein content were high, the CO_2 content was low, and the undetermined acids were increased. Cl′ was either normal or low, and the p_H was unchanged. The amount of HCl in the vomitus was < the total base and never contained free HCl. In œdematous patients with impaired kidney function, the serum-protein content was reduced as compared with normal pregnancy, whilst the other results showed no significant change. W. O. K.

Acid-base balance disturbance of pregnancy. V. C. Myers, E. Muntwyler, and A. H. Bill (J. Biol. Chem., 1932, 98, 253—260).—Polemical against Kydd *et al.* (preceding abstract). The decrease in blood-CO_2 content during normal pregnancy is probably caused primarily by hyperventilation. W. O. K.

Alleged alkalosis in pregnancy. D. M. Kydd and J. P. Peters (J. Biol. Chem., 1932, 98, 261—266).—Polemical against Myers *et al.* (preceding abstract). W. O. K.

Alleged alkalosis in pregnancy. V. C. Myers, E. Muntwyler, and A. H. Bill (J. Biol. Chem., 1932, 98, 267—268).—A reply. W. O. K.

Early acidosis in acute eclamptic nephritis and the concentration and dissociation constants of the acids produced. K. Hoesch (Zentr. inn. Med., 1932, 53, 484—490; Chem. Zentr., 1932, i, 3312).—Up to about 25% of the acid is lactic; only small amounts of fatty acids are concerned, whilst P_2O_5, AcOH, and hydroxybutyric acid do not take part. Possibly the increase in acidity is due to aromatic OH-acids. A. A. E.

[H˙] of blood of psychotics. R. H. Hurst (Biochem. J., 1932, 26, 1536—1541).—There is no significant difference between the p_H of arterial and venous blood of schizophrenics and of normal subjects, whether in the resting condition or in the early stages after alkali ingestion. As a result of exercise the schizophrenic has a blood-p_H < that of the normal for a given lactic acid content. S. S. Z.

Rickets in rats. XIII. Effect of various levels and ratios of calcium to phosphorus in the diet on the production of rickets. XIV. A diet which demonstrates the effect of the acid-base content on the production of rickets and also causes idiopathic tetany. H. B. Brown, A. T. Shohl, E. E. Chapman, C. S. Rose, and E. M. Shurwein (J. Biol. Chem., 1932, 98, 207—214, 215—224).—XIII. With a const. ratio of Ca : P, a diet deficient in vitamin-*D* becomes decreasingly rachitogenic as the salt content is raised. At a given level of Ca (or P) rickets becomes increasingly severe as the ratio Ca : P increases, until the ratio exceeds 12 : 1, when the opposite occurs and the animals fail to gain wt. and die early. In all cases the blood-Ca is 10—11 mg. per 100 c.c., whilst the inorg. serum-P decreases as Ca : P increases for every level of Ca in the diet, and with const. Ca : P the serum-P increases with increase in the total salt. The rachitogenic properties of most of the standard diets may be correlated with the above findings.

XIV. In a series of diets deficient in vitamin-B_1 the rachitogenic effect is more marked with an acid than with a neutral or basic diet when the Ca : P ratio is kept const. When this ratio was 2·5, only rats on the acid diet developed mild rickets, whilst when it was 4·0 all diets produced severe rickets. The acid-base content of a diet is therefore a distinct although secondary factor in its power of producing rickets, the Ca : P ratio being more important. Evidence of latent idiopathic tetany was found in rats with mild healing rickets. W. O. K.

Phosphatase content of the cartilage of normal and rachitic rats. W. Fabisch (Biochem. Z., 1932, 254, 158—169).—Examination of the rates of hydrolysis of Na glycerophosphate and Na hexosediphosphate by preps. of the cartilage from normal and rachitic rats and from rats recovering from rickets after administration of irradiated ergosterol shows that the phosphatase content of the cartilage is the same in all cases. W. McC.

Iodine in cod-liver oil. F. E. Chidester, A. L. Ashworth, G. A. Ashworth, and I. A. Wiles (Nature, 1932, 130, 544—545).—The I in cod-liver oil appears to play an important rôle in the prevention of rickets. L. S. T.

Blood-lipase, -diastase, and -esterase in multiple sclerosis. L. A. Crandall, jun., and I. S. Cherry (Arch. Neurol. Psych., 1932, 27, 367—374).—A lipase capable of splitting olive oil appeared in 78% of cases of multiple sclerosis, 80% of cases of liver disease, and 7·6% cases of other disease. High diastase vals. were found in 47·6, 75, and 8·3% (controls), respectively. Blood-esterase showed no significant changes. Ch. Abs.

Basal metabolism of Australian aborigines. H. S. H. Wardlaw and W. J. Lawrence (Austral. J. Exp. Biol., 1932, 10, 157—165).

Bioluminescence. I, II. K. Hayasi and M. Okuyama (Okayama Igakkai-Zasshi, 1929, **41**, 185—187, 270—272).—The effects of various treatments on the luminescence of the luminescing organ of the firefly were studied. Luminescence disappears at a partial O_2 pressure $< 0{\cdot}025$ atm., increasing proportionally to the partial pressure up to 1 atm., and being max. at 15 atm. CO and HCN have no effect. O_2 is also necessary for, and HCN has no effect on, the luminescing gland of *Cypridina hilgendorfi*, Müller; this active substance is not a fat or a lipin, but is partly conc. by fractional pptn. with EtOH. The luminescence reaction does not belong to the peroxidase or glutathione systems. Acids and alkalis prevent luminescence of the luminescent bacteria of the sword fish; again HCN has no effect.

Ch. Abs.

Effect on tissue respiration of salts of organic acids. B. Kisch (Biochem. Z., 1932, **253**, 347—372).—The respiration of various tissues of ox, pig, dog, cat, and rat shows a small increase (20—30%) on addition of salts of the lower fatty acids, the increase being greater with the straight- than with the corresponding branched-chain acids. HCO_2Na is inactive. $OH{\cdot}CHMe{\cdot}CO_2H$ and $AcCO_2H$ with most tissues have little effect, but with heart muscle and retina cause a large increase (+100% to 500%), the latter acid being more effective. The respiration of normal kidney tissue is inhibited by $0{\cdot}02$—$0{\cdot}01M$-pyruvate. Glucose exerts its greatest action on the respiration of heart and striated muscle and on the retina. P. W. C.

Effect of methylglyoxal on tissue respiration. B. Kisch (Biochem. Z., 1932, **253**, 373—376).—The respiration of kidney, retina, diaphragm, liver, and Jensen sarcoma is considerably inhibited by high concns. of AcCHO and is either little affected or slightly increased by low concns. The inhibition is greatest with kidney tissue. The respiration only of heart tissue is increased by $0{\cdot}01M$-AcCHO (30—160%). P. W. C.

Optimum p_H for the respiration of various tissues. B. Kisch (Biochem. Z., 1932, **253**, 377—378).—A table summarises the Q_{O_2} vals. in Ringer's solution for diaphragm, heart, liver, kidney, retina, and tumour tissue of rat, ox, dog, and cat. The optimal p_H of respiration was the same for different tissues of the same animal, with rats at p_H 7·2—7·5, ox 7·2, and cat 7·5—7·8. P. W. C.

Influence of the salts of organic acids on the respiration of tumours. II. B. Kisch (Biochem. Z., 1932, **253**, 379—382).—The respiration of Jensen sarcoma, in contrast with normal, tissue is not increased by salts of fatty acids. With lactate the respiration of fresh tissue is unaffected, but of older tissue is increased. It is also increased by pyruvate. The respiration of the tissue in Ringer's solution falls away more quickly than in this solution containing lactate or pyruvate. P. W. C.

Energy changes and exchange of phosphoric acid esters in muscle extract. O. Meyerhof and K. Lohmann (Biochem. Z., 1932, **253**, 431—461).—The heat of hydrolysis of creatinephosphoric acid is 12,000 g.-cal. per mol. and of adenylpyrophosphoric acid 33,000 g.-cal. per mol. (8000 g.-cal. for separation of NH_3 and 25,000 g.-cal. for hydrolysis of $H_4P_2O_7$). Addition of adenyl- and inosine-pyrophosphoric acid to inactive extracts results in phosphagen synthesis; addition of adenylic acid causes synthesis of adenylpyrophosphate. Examples of the energy exchanges involved in these processes are given and discussed.

P. W. C.

(*a*) Energy exchange of the kidney. (*b*) Pharmacological effects on the rate of perfusion and of the energy exchange of the kidney. H. Glaser, D. Laslo, and A. Schürmeyer (Arch. exp. Path. Pharm., 1932, **168**, 139—161, 175—189).—(*a*) In the dog the energy exchange of the kidneys is usually between 5% and 10% of that of the whole animal, but may exceptionally amount to >20%. Only about 1% of the energy exchange of the kidney is required to carry out the osmotic work performed in the formation of urine from the blood, and the O_2 consumption does not, in fact, bear any relation to this osmotic work. The same kidney shows marked and unaccountable variations. Intravenous administration of hypertonic NaCl, Na_2SO_4, NH_4Cl, $(NH_4)_2CO_3$, and acid phosphate produces an increase in O_2 consumption not apparently directly related to the effect on secretory activity. The R.Q. tends to rise with a fall in the total metabolism.

(*b*) When hypertonic NaCl or glucose is administered to a dog the blood-flow through the kidney increases, but the O_2 consumption of the organ does not increase proportionately. The smaller increase in blood-flow which is produced by NH_4Cl and Na_2SO_4 is accompanied by a more than proportionate rise in O_2 consumption. Cantharides or $HgCl_2$ reduces the blood-flow, the reduction in O_2 consumption being less in proportion. Glucose raises the perfusion rate of the poisoned kidney practically to the normal and the O_2 consumption simultaneously increases. With adrenaline the blood-flow is reduced, but the effect on the O_2 consumption is inconst., as it sometimes remains unaltered and sometimes falls.

W. O. K.

Influence of halogen salts on tissue metabolism. I. Influence of sodium halides on the respiration and glycolysis of kidney tissue. R. Iwatsuru, N. Hosoda, and Y. Nakai (Biochem. Z., 1932, **254**, 301—321).—The effect of gradual replacement of the NaCl of Ringer's solution by NaBr, NaI, and NaF on tissue metabolism is investigated. Br′ accelerates respiration and inhibits glycolysis. Mean replacement by NaI leads to an increase, min. and complete replacement to a decrease, of respiration. Min. replacement by NaBr accelerates, and mean or complete replacement inhibits, glycolysis. NaF in min. concn. accelerates respiration and increases glycolysis and in greater concn. decreases respiration and completely inhibits glycolysis. P. W. C.

Differences of oxidation and reduction properties of tissues with sex. II. S. Kagiyama (J. Biochem. Japan, 1932, **16**, 99—104).—The oxidative power of rabbit skeletal muscle, as indicated by the O_2 consumption and the distribution of oxidase granules in the fibres, is greater in the male than in the female. F. O. H.

Effect of dietary deficiencies on phospholipin metabolism. B. R. Monaghan (J. Biol. Chem., 1932, 98, 21—33).—A decrease in the rate of growth of rats due to any type of dietary deficiency is accompanied by a decrease in the phospholipin content of the tissues, the degree of unsaturation remaining unchanged. Whilst the results uphold the conception of phospholipins acting as intermediaries in fat metabolism, no support is given to the theory representing them as indispensable constituents of the protoplasm. F. O. H.

Ergosterol resorption in the laying hen. R. Schönheimer and H. Dam (Z. physiol. Chem., 1932, 211, 241—245).—The eggs of hens receiving 50 mg. of ergosterol daily showed an increase of 0·15 mg. (50%) in the ergosterol content of the yolk. J. H. B.

Resorption of unirradiated ergosterol. Determination of ergosterol. W. Menschick and I. H. Page (Z. physiol. Chem., 1932, 211, 246—252).—An improvement in the method of ergosterol determination, whereby amounts $>$ 0·1% can be determined with an error $\not>$ 20%, is described. The feeding of ergosterol to hens increases the ergosterol content of the eggs by 40—50%, beginning on the 4th day after commencement of the dose. J. H. B.

Effect of bile acids on carbohydrate metabolism. XIX. Synthesis of glycogen by the liver after administration of phosphates of different p_H values. S. Fuzita (Arb. Med. Univ. Okayama, 1932, 3, 154—162).—Parenteral or oral administration of phosphates of p_H 7·504 increases the synthesis of glycogen from glucose by the liver. It is further increased by cholic acid so long as the p_H of the phosphates is below 8·054; above this val. the synthesis by cholic acid decreases. The corresponding increase and decrease vary with the mode of administration of the phosphates. Ch. Abs.

Pentose metabolism. I. Rate of absorption of *d*-xylose and formation of glycogen in the organism of the white rat after oral administration of *d*-xylose. II. Pentose content of tissues after oral administration of *d*-xylose. M. M. Miller and H. B. Lewis (J. Biol. Chem., 1932, 98, 133—140, 141—150).—I. Xylose was absorbed from the gastrointestinal tract more slowly than glucose (cf. A., 1926, 429). Over a 3-hr. period the rate of absorption of xylose increased. Absence of liver-glycogenesis indicated that xylose, unlike glucose, is not utilised.

II. The tissues were deproteinised with $CCl_3{\cdot}CO_2H$ and pentoses determined in the filtrates (A., 1926, 1283). The contents of the liver, kidney, and blood, but not that of the muscle, were increased, whilst no change occurred in the content of reducing substances other than pentoses in any tissue. Oral administration of glucose had no effect on the pentose content of the tissues investigated. F. O. H.

Liver-glycogen and excretion of nitrogen in the fasting dog after administration of xylose. H. Magendantz (Biochem. Z., 1932, 254, 170—175).—Xylose (20—25 g. per day), administered to fasting dogs, is not converted into glycogen in the liver, but leads to decrease in the amount of N excreted, and hence to reduction in the amount of protein degraded in the organism. W. McC.

Lactose in nutrition. O. L. Kline, J. A. Keenan, C. A. Elvehjem, and E. B. Hart (J. Biol. Chem., 1932, 98, 121—131).—Addition of lactose, but not of maltose or of citric acid, to a basal rachitic diet increases the absorption of Ca, bone formation, and acidity of the intestinal tract in young chicks; growth, however, is subnormal. These beneficial effects of lactose are enhanced by addition of vitamin-*D* to the diet, whilst the rate of growth is improved. F. O. H.

Effect of disappearance of sexual activity on creatine metabolism. F. Lasch (Z. ges. exp. Med., 1932, 81, 314—320; Chem. Zentr., 1932, i, 3455).—In the child excretion of injected creatine is quant., whilst in the senile it is partial. In aged persons the blood-creatinine is normal, but the total creatinine (creatine+creatinine) is lower than in middle age. A. A. E.

Tryptophan metabolism. III. Rate of absorption of *l*- and *dl*-tryptophan and tryptophan derivatives from the gastrointestinal tract of the rat. C. P. Berg and L. C. Bauguess (J. Biol. Chem., 1932, 98, 171—180).—The rates of absorption observed gave the following descending order: acetyl-*dl*-tryptophan, acetyl-*l*-tryptophan, *l*-tryptophan, *dl*-tryptophan, *dl*-tryptophan Et ester, and *l*-tryptophan Et ester. No enzymic destruction of the Ac derivatives occurs prior to absorption. F. O. H.

Influence of relative vitamin value of milk on growth, digestion, and nitrogen and mineral metabolism in calves. E. G. Sveshnikova (Zap. Leningrad Selsk. Choz. Inst., 1929, 7, 120—142).—Addition of cod-liver oil to the ration increases the vitamin-*D* content of the milk, but reduces the fat content; it depresses the utilisation of the fat in the feed. The vitamin content of the milk did not affect the rate of digestion or the N or mineral metabolism of calves. Ch. Abs.

Nutritional requirements of trout and composition of the entire trout body. C. M. McCay, A. Tunison, M. Crowell, D. K. Tressler, S. P. MacDonald, J. W. Titcomb, and E. W. Cobb (Trans. Amer. Fish. Soc., 1931, 61, 58—82).—The min. protein requirement is $>$ 14% of the total cal. Administration of $CaCO_3$, bone meal, and NaCl is advantageous; trout fed low protein levels supplemented with inorg. mixtures grow more rapidly, but die sooner, than controls. Factor *H* is destroyed when dry diets are stored in air. Analyses of variously fed trout were performed. Trout secure sufficient Ca for bone formation from meat diets rich in P and poor in Ca. Ch. Abs.

Acid–base metabolism of a normal child on diets that increase in fat content. C. A. Weymuller and S. Ratner (Amer. J. Dis. Children, 1932, 43, 1092—1100).—The blood of a normal boy maintained on a ketogenic diet shows a fall in p_H and HCO_3', a rise in Cl, and the appearance of ketone substances$=$5·7 c.c. of 0·1N-β-hydroxybutyric acid.

The excretion of PO_4, Cl, SO_4, and total fixed acid and base was increased. Approx. 82% of the org. acids in the urine was present as ketonic substances.
Ch. Abs.

Relative values of meals from oily and white fish for growth and calcification. J. C. Kernot and N. E. Speer (Biochem. J., 1932, **26**, 1435—1440).—Fat-free meal prepared from oily fish induces better growth in rats than white fish meal. It also promotes better calcification of the bones. S. S. Z.

Influence of bile acids on calcium metabolism. V. Fæcal calcium and phosphoric acid during administration of bile acids and adrenaline to normal and splanchnicotomised dogs. I. Okii (J. Biochem. Japan, 1932, **16**, 217—235).—Administration of cholic acid decreases whilst that of adrenaline increases the fæcal Ca and PO_4 of normal dogs. Splanchnicotomy also produces a decrease but weakens the action both of adrenaline and of cholic acid, which, in this connexion, are therefore related to the autonomic nervous system.
F. O. H.

Urinary excretion of inorganic phosphate in fasting with particular reference to the effect of exercise. A. G. Mulder, I. E. Phillips, and M. B. Visscher (J. Biol. Chem., 1932, **98**, 269—279).—During fasting, the urinary excretion of P usually increases during the first few days, the total P excretion exceeding that attributable to the protein metabolised. Exercise during fasting results in an initial rise in P excretion, followed by a fall so low as to reduce the total P excretion during a 4-hr. period of exercise to < the resting level.
W. O. K.

Œstrous cycle in rats on a manganese-free diet. E. R. Orent and E. V. McCollum (J. Biol. Chem., 1932, **98**, 101—102).—Rats fed on a Mn-free diet or on cow's milk supplemented with Cu and Fe exhibit normal œstrous cycles. Growth on the milk diet is below normal, a deficiency corrected by the addition of 0·5 mg. of Mn per 100 c.c.
F. O. H.

Significance of iron in the diet. III. F. Reimann and F. Fritsch (Z. klin. Med., 1932, **120**, 16—39; Chem. Zentr., 1932, ii, 83).—Treatment with Fe-rich food (liver) alleviates Fe-sensitive anæmia. There is no important difference between food-Fe and $FeCl_2$. The food-Fe is converted into Fe^{II} in the gastro-intestinal canal, chiefly in the stomach with the aid of HCl and enzymes. Only 25—33% of the total food-Fe is so converted, and only Fe^{II} can be resorbed. A. A. E.

Action of Ferrum reductum. II. F. Reimann and F. Fritsch (Z. klin. Med., 1931, **117**, 304—320; Chem. Zentr., 1932, i, 3197—3198).—Fe^{II} compounds are formed (chiefly by the HCl) in the gastro-intestinal canal and resorbed. The amount of $FeCl_2$ formed cannot be calc. from the HCl secreted and Fe administered, since large quantities of Fe accelerate dissolution. Therapeutically active quantities of Fe^{II} are also formed in the intestine. Peroral administration of Fe can be replaced by that of Fe^{II} compounds. The quantity of Fe^{II} compounds formed from Fe depends on the velocity of passage through the stomach and intestine, as well as on the gastric acidity. A. A. E.

Iron deficiency. H. Nakamura (Keijo J. Med., 1932, **3**, 230—249).—Methods for the prep. of Fe-free food materials are described. Mice on a diet with cod-liver oil or butter-fat as the sole source of vitamins and containing Fe survive 1—2 weeks longer than those on a similar but Fe-free diet.
F. O. H.

Action of copper in iron metabolism. C. A. Elvehjem and W. C. Sherman (J. Biol. Chem., 1932, **98**, 309—319).—The addition of pure Fe to the milk diet of anæmic rats has no effect on hæmoglobin, but increases the total Fe content of the liver from vals. as low as 0·1 mg. up to 1·0 mg. per 1 g. of dry tissue, whilst the Fe content of the spleen is also increased. Inorg. Fe is stored in the liver more efficiently than is org. Fe in the form of hæmatin. When the Fe is replaced by Cu, blood regeneration takes place, and the Fe content of the liver, but not of the spleen, decreases. When Cu as well as Fe is added to the diet, increase in hæmoglobin takes place, and no increase in the Fe content of the liver is observed, until the Fe intake exceeds 0·3 mg. per day. W. O. K.

Body desiccation. T. Takai (J. Biochem. Japan, 1932, **16**, 49—68).—Rats fed on a diet containing excess protein and deficient in salts suffer a greater loss in body-wt. on withdrawal of H_2O than rats on a normal diet. A diet rich in fats tends to prolong life on a H_2O-free diet. With desiccation the oxidase activity and the cysteine, pyrophosphate, and hexosephosphate contents of the tissue decrease, whilst the phosphagen and inorg. PO_4 levels are unchanged. F. O. H.

Rôle of fat in development of the chicken. B. Konopacka (Bull. Acad. Polonaise, 1931, **B**, 643—648).—Development of the hen's egg in the ovary and through successive stages of the embryo up to hatching has been studied by the application of microchemical staining methods. H. G. R.

Development of silkworm eggs. A. Akao (Keijo J. Med., 1932, **3**, 250—261).—Variations in the total wt. and in the content of protein, sugar, total P, cholesterol, phosphatide, and total, non-protein-, purine-, and chitin-N of the eggs, incubated at 25°, were determined and correlated with morphological changes in the embryo. F. O. H.

Phosphorus metabolism in embryonic life. II. Phosphagen in cephalopod development. J. Needham, D. M. Needham, J. Vudkin, and E. Baldwin (J. Exp. Biol., 1932, **9**, 212—221).—The embryo, but not the yolk, of *Sepia* contains arginine phosphate (max. after 86 days). The inorg. P rises continuously throughout development. Ch. Abs.

Effect of soap solutions and of varying hydrogen-ion concentration on cell growth in tissue cultures. J. Manger and A. Hock (Biochem. Z., 1932, **254**, 176—180).—At p_H 5·7, 7·21, and 7·58 the growth of the cells in cultures of embryonic chicken hearts is accelerated by addition of Na oleate, but at p_H 7·94 the salt inhibits the growth. Smallest growth occurs in a neutral medium and greatest (on the third day) in alkaline medium (p_H 7·94). Growth is also increased, although to a smaller extent, by acid medium (p_H 5·7), especially on the second and third days. W. McC.

Utilisation of proteoses by chicken heart fibroblasts growing *in vitro*. E. N. Willmer and L. P. Kendal (J. Exp. Biol., 1932, 9, 149—178).—The presence of plasma, possibly to supply enzymes producing NH_2-acids, is necessary. A thermolabile substance isolated from Witte's peptone and fibrin digests stimulates the activity and division of cells. Ch. Abs.

[Pharmacological] action of derivatives of choline. A. Simonart (J. Pharm. Exp. Ther., 1932, 46, 157—193).—The muscarine-like action, the contracting action on denervated muscle, and the nicotine action on the blood-pressure of the following derivatives of choline are studied : Ac, Pr, and Bu esters, Me, Et, vinyl, and Bu ethers, α- and β-methylcholine, acetyl- and propyl-α- and -β-methylcholine, and β-methylcholine Et ether. Of these, acetyl-β-methylcholine has the greatest clinical usefulness, being more stable than, and as potent as, acetylcholine in lowering the blood-pressure, and having no nicotine-like action on the circulation. A. L.

Action of urine in lowering the blood-pressure. A. Bauer (Arch. exp. Path. Pharm., 1932, 168, 111—120).—Urine contains a depressor substance which is stable to heat and is dialysable and is therefore not identical with "callicrein" (I) (cf. A., 1930, 1069). Its possible relationship to various depressor substances is discussed. (I) could not be detected in plasma. W. O. K.

Complex compound of aminopyrin with strontium sulphosalicylate. H. Berning (Arch. exp. Path. Pharm., 1932, 168, 206—216).—The compound, $C_7H_4O_6SSr,2C_{13}H_{17}ON_3$, has stronger antipyretic and respiration-stimulating actions than correspond with its pyramidone content, but possesses a relatively slight convulsive action. W. O. K.

Harmine. E. Švagr and V. Štolc (Chem. Listy, 1932, 26, 476—479).—Phosphotungstic acid gives a bluish-white ppt. with harmine (I). Reinecke's salt gives a ppt. with (I) in dilutions of $\not<$ 1 : 200,000. (I) is best determined in organs by Florence's procedure, titrating the extract with 0·01N-H_2SO_4, with iodoeosin as indicator. Using Florence's method of extraction, 98·9% of (I) present in organs is recovered, as compared with 97·7—101% using the Stas–Otto method. A no. of new colour and pptn. tests for (I) are given. R. T.

Influence of quinine hydrochloride on purine metabolism in hyperthyroidism. T. Ogawa (Folia endocrinol. Japon., 1931, 6, 112—113).—Quinine is antagonistic to thyroid gland in regard to purine metabolism. Ch. Abs.

Photobiological sensitisation to ultra-violet rays. F. M. Kuen and P. Rosenfeld (Biochem. Z., 1932, 254, 181—186).—Quinine sulphate and æsculin have no appreciable sensitising effect (measured by degree of hæmolysis produced in blood) to ultra-violet light, but acridine hydrochloride and trypaflavine sensitise to rays of $\lambda > 302$ mμ (especially 365 mμ), although these two substances do not sensitise to visible light. Et chlorophyllide and MeOH extracts of spinach sensitise to rays of $\lambda > 297$ mμ (especially 313 and 365 mμ) as well as to visible light, whilst MeOH extracts of *Selaginella* sensitise especially to rays of λ 254 mμ. W. McC.

Chronic morphine poisoning in dogs. IV. Excretion of morphine in tolerant and non-tolerant animals. I. H. Pearce and O. H. Plant (J. Pharm. Exp. Ther., 1932, 46, 201—228).—A method for the determination of morphine in urine and fæces is described. Whilst the amount of morphine excreted in the urine varies from day to day and depends on the fluid intake of the animal, it is approx. proportional to the dose and > that in the fæces, in which the amounts are nearly const. Of the daily dose approx. 12·5% was excreted, this being greater with small doses than with large. The amounts excreted by tolerant and non-tolerant animals are almost equal ; part of a single dose is retained in the body longer than 24 hr. in both cases. A. L.

Nicotine in tobacco smoke. V. L. Nagy (Biochem. Z., 1932, 254, 94—96).—In smouldering cigarettes all the nicotine passes unchanged into the smoke. W. McC.

Mechanism of internal secretory equilibrium. Influence of tobacco smoke on blood-sugar. E. Lundberg and S. Thyselius-Lundberg (Acta med. Scand., 1931, Suppl. 38, 5—65 ; Chem. Zentr., 1932, i, 3080—3081).—Immediately after the commencement of smoking the blood-sugar rapidly rises to 1·5 times the normal val., to which it falls more slowly during 0·5 hr. The phenomenon is not observed with nicotine-free material. The rise is particularly marked in diabetes. A. A. E.

Drugs employed as antidiabetics in Chinese medicine. VII. Mechanism of the hypoglycæmic action of phellodendronelactone. N. Sugihara and S. Hirano (Keijo J. Med., 1932, 3, 333—339).—Injection of the drug significantly lowers the blood-sugar of normal but not of depancreatised guinea-pigs, pigeons, and rabbits (cf. this vol., 877). Hence this drug increases the secretion of insulin. F. O. H.

Effect of intravenous phosphatide on the sugar excretion of the phloridzinised dog. I. H. Page and F. G. Young (Biochem. J., 1932, 26, 1528—1531).—Injection of aq. brain phosphatide emulsion does not appreciably alter the glucose/N ratio of the urine. There is no apparent conversion of fatty acid into sugar. S. S. Z.

Biological assay of digitalis and strophanthus. C. W. Chapman and C. A. Morrell (J. Pharm. Exp. Ther., 1932, 46, 229—250).—Frogs are used, and the method eliminates seasonal and individual variation. The results of assays are reported, and variations in the animals are discussed. A. L.

Narcosis and oxidations of the brain. J. H. Quastel and A. H. M. Wheatley (Proc. Roy. Soc., 1932, B, 112, 60—79).—Narcotics inhibit the oxidation by brain tissue of glucose, Na lactate and pyruvate, and, to a smaller extent, of glutamic acid, but not that of Na succinate or *p*-phenylenediamine.

Concns. of narcotics effectively inhibiting oxidation by brain tissue do not influence the respiration of yeast. With narcotics of the same type (*e.g.*, dialkylbarbituric acids) the inhibitive action on brain oxidation is proportional to the hypnotic activity. Brain tissue of mice narcotised by $CHCl_3$ exhibits a diminished ability to oxidise glucose. A theory of narcosis is advanced. F. O. H.

Percutaneous resorption of narcotics. M. Lazarev (Arch. exp. Path. Pharm., 1932, 168, 162—170).—When applied to the skin of rabbits in $CHCl_3$, EtOH, Et_2O, fat, oil, or H_2O, narcotics are (1) strongly active [*e.g.*, $OH\cdot CMe_2\cdot CCl_3$, $CCl_3\cdot CH(OH)_2$, $CCl_3\cdot CHMe\cdot OH$, $NH_2\cdot CO_2Et$, $CEt_2Br\cdot CO\cdot NH_2$], (2) moderately active (*e.g.*, $CMe_2Et\cdot OH$, paraldehyde), or (3) inactive or only slightly active (*e.g.*, barbituric acid derivatives). W. O. K.

Fate of chloral hydrate in the organism. N. E. Renescu and B. B. Olszewski (Compt. rend., 1932, 195, 624—626).—The narcotic action of chloral is not due to $CHCl_3$ formed from it, since the organs of dogs poisoned with chloral hydrate intravenously contain large quantities of the latter, but only traces of $CHCl_3$. Chloral is fixed by the brain, liver, kidney, and intestines; its concn. in the blood falls rapidly after injection. The chloral content of the brain is not related to the dose, whilst that of the liver and fat increases with duration of narcosis. Chloral does not survive more than 2—3 months' putrefaction. A. C.

Oxygen consumption of muscles treated with bromoacetate. C. I. Wright (J. Cell. Comp. Physiol., 1932, 1, 225—235).—Sartorius muscles treated with bromoacetic acid or salts sufficient to inhibit lactic acid formation retained 60—70% of their normal resting O_2 consumption. Chemical or electrical stimulation is followed by excessive O_2 consumption proportional to the tension developed. A. G. P.

Effects of monobromoacetic acid on metabolism. K. Hikiji (Arch. exp. Path. Pharm., 1932, 168, 1—18).—Rabbits to which 15—30 mg. $CH_2Br\cdot CO_2Na$ (I) are administered subcutaneously develop marked œdema and weakness and die after a few days. The gas metabolism is not much affected, but the glycogen content of the muscles is reduced whilst the lactic acid content is unaltered or slightly reduced. Muscle-creatine falls, whilst a marked creatinuria takes place with no increase in the creatinine output. Phosphagen and muscle-pyrophosphate decrease. The blood-sugar increases a few hr. after administration of the poison. The surviving muscle taken from a rabbit poisoned by (I) has a markedly reduced capacity for work, whilst the production of lactic acid during work is reduced, but does not disappear. W. O. K.

Mechanism of thiocyanate poisoning. K. Yamada (Arch. exp. Path. Pharm., 1932, 168, 19—31).—In rabbits poisoned for some hr. by KCNS, the glycogen content of the muscles after some hr. has decreased, phosphagen content usually has fallen, and the lactic acid concn. has only slightly changed. Surviving muscles from chronically poisoned animals have a decreased capacity for work. W. O. K.

Effect of age and sex on resistance of Daphnids to mercuric chloride. J. Breukelman (Science, 1932, 76, 302).—In *Daphnia magna* susceptibility to $HgCl_2$ decreases with age of the animal. Males are more susceptible than females, with the parthenogenetic forms intermediate between the two. L. S. T.

Biology of aluminium. II. H. Steudel (Biochem. Z., 1932, 253, 387—394).—Al salts added to the diet of white rats over four generations did not injure reproduction, nor did the animals appear to store Al in the liver, kidney, spleen, or heart. P. W. C.

Influence of -thiol and -sulphoxide on differential growth within the regenerating chela of the Hermit crab (*Pagurus longicarpus*). F. S. Hammett and D. W. Hammett (Protoplasma, 1932, 16, 253—286).—Regeneration was accelerated by $\cdot SH$ (in thiocresol) and retarded by $:SO$ (in Ph_2SO). The rôle of S equilibrium in cellular differentiation is indirectly the result of the action on cell proliferation. A. G. P.

Inhibition of the concentration of dye in the liver by organic non-electrolytes and organic salts. R. Höber (Pflüger's Archiv, 1932, 229, 402—421; Chem. Zentr., 1932, i, 3316).—The inhibitory effect of various org. substances on the retention of dyes by the isolated frog's liver perfused with isotonic dil. dye solution is considered. A. A. E.

Permeability and cytolysis of the sea-urchin egg with regard to some fertilisation problems. W. A. Dorfman (Protoplasma, 1932, 16, 56—78).—The presence of univalent cations increases and of bivalent cations decreases the permeability of the egg, the relative effects of univalent ions being in the order of the lyotropic series. In still greater concn. cations (especially $Al^{\cdot\cdot\cdot}$ and $Th^{\cdot\cdot}$) bring about coagulation of the cell colloids. A. G. P.

Iodine compounds and fertilisation. IV. Capacity for fertilisation in washed and unripe eggs of *Echinus esculentus* and *E. miliaris*. V. Agglutination and chemotaxis of the sperm. VI. Physiological properties of extracts of the ovaries and testes of *E. esculentus*. VII. Nature of the egg secretions and theory of fertilisation. G. S. Carter (J. Exp. Biol., 1932, 9, 238—248, 249—252, 253—263, 264—270). Ch. Abs.

Influence of small doses of iodine and sulphur and of pituitrin on the liver- and muscle-glycogen. K. Muras (Folia endocrinol. Japon., 1931, 6, 118).—S causes an increase; I and pituitrin are without effect. Ch. Abs.

Iodine content of the blood: its relation to potassium iodide feeding. E. M. Mason (New Zealand J. Sci. Tech., 1932, 14, 32—37).—Changes in the I content of the blood of cows following the feeding of KI are recorded. Max. vals. were attained within 5 hr. of feeding and were proportional to the amount administered. In no case did the calc. total amount of I in the blood approach the quantity ingested. A. G. P.

A new oxidation enzyme and its absorption spectrum. O. Warburg and W. Christian (Biochem. Z., 1932, 254, 438—458).—The enzyme (from bottom yeast) does not dialyse through cellophane and is inactivated at 60°. Aq. solutions are yellowish-red, but on reduction give a colourless leuco-form which reoxidises in air or more quickly on adding methylene-blue. The enzyme can therefore be titrated by methylene-blue and the abs. concn. of the active groups be determined. That part of the respiration of yeast juice insensitive to either CO or HCN is due to the enzyme. The absorption spectra of the oxidised and reduced enzyme solutions are given. P. W. C.

Dehydrogenations by brain tissue. Effects of narcotics. D. R. Davies and J. H. Quastel (Biochem. J., 1932, 26, 1672—1684).—The dehydrogenating powers of brain tissue (I) of various animals have been studied and the Michaelis consts. determined for a no. of substrates. Velocity–concn. curves exhibit max. above which increase of concn. leads to decreased reduction velocities. Grey matter is three to four times as active as white matter. Glucose, fructose, galactose, and mannitol are activated as H donators by fresh (I). The activations of glucose and fructose are less than those of Na succinate, lactate, and pyruvate. The activations of the sugars disappear more quickly on storage of (I) at 0° or on incubation at 37° than those of Na succinate and glycerophosphate. Exposure of (I) to narcotics results in an elimination of the activation of the sugars, those of Na succinate and glycerophosphate being relatively unaffected. The activations of Na lactate and pyruvate at low concn. are inhibited by the narcotics. The narcotic and Na lactate compete for the same activating enzyme or centre. The former does not inactivate irreversibly the lactic dehydrogenase, but its inhibiting action depends on the concn. of lactic acid present. S. S. Z.

Kinetics of fumarase. K. P. Jacobsohn, F. B. Pereira, and J. Tapadinhas (Biochem. Z., 1932, 254, 112—137; cf. this vol., 880).—Fumarase acts as a true catalyst in so far as the enzyme concn., the p_H, and the presence of salts have no effect on the ratio of the components in equilibrium. The equilibrium fumarase $\rightleftharpoons$ *l*-malic acid is true and notably dependent on temp. Fumarase of animal origin sets up a different equilibrium from that of fumarase of vegetable origin. While the equilibrium is being attained the mass action coeff. remains that for a reversible unimol. reaction. When the concn. of substrate is increased the velocity coeff. falls and the reaction velocity is directly proportional to the concn. of enzyme, but there is not complete conformity with the law of mass action. The affinity of liver-fumarase for fumaric acid is twice that for *l*-malic acid. W. McC.

Catalase groups. O. T. Rotini (Giorn. Chim. Ind. Appl., 1932, 14, 456—461).—Determination of the chemico-kinetic consts. (relative crit. energy, entropy const., etc.) of catalases of org. (animal, bacteria, mould) origin and of inorg. nature renders it possible to classify the catalases. Catalases from blood, liver, fat, *Streptococcus*, *Penicillium glaucum*, and germinated pumpkin seeds appear to be identical, but they differ from those of milk, colostrum, and lactic acid bacteria. The characteristic relative crit. energy, and hence the nature, of pumpkin-seed catalase is changed on germination of the seeds. Inactivation of blood-catalase by $NaNO_3$ is regarded as due, not only to diminution of the velocity coeff., but also to variation in the relative crit. energy with a consequent change in the quantic order of the reaction; the same holds for the toxic action of NaCl on the catalase of cow's milk. The toxic action of CN′ on blood-catalase shows the revivification observed with colloidal metals and tissue-catalases. The catalase actions of $Fe(OH)_3$ and MnO_2 are highly activated by small proportions of KCN and $NaNO_2$. T. H. P.

Gas burette for catalase apparatus. D. A. Pack (Ind. Eng. Chem. [Anal.], 1932, 4, 393).—The design of the apparatus permits all the chambers containing gas to be immersed in a const.-temp. bath. E. S. H.

Tyrosinase of potato tubers. I. M. Robertson (Proc. Roy. Soc. Edin., 1931—1932, 52, 309—314).—The tyrosinase reaction is unimol. and can be used to distinguish different varieties of potato. Tuber wt., environment, season, or storage does not influence the enzyme activity; this depends on tuber maturity and is affected by the presence of certain diseases. W. R. A.

Quinones as enzyme models. VII. Catalytic deamination of amino-acids in absence of oxygen and with the use of hydrogen acceptors. K. Schuwirth (Biochem. Z., 1932, 254, 148—157; cf. this vol., 1165).—The catalytic deamination of glycine, glycylglycine, and glycyltyrosine (hydroxyquinol, adrenaline, gallic acid, resorcinol as catalysts) is an aërobic process, but *m*-$C_6H_4(NO_2)_2$ or nitroanthraquinone can act as substitutes for O_2 (air). Methylene-blue, alloxan, or isatin, however, cannot act thus. The mechanism of the reaction is the same with the H acceptor as with O_2, but the latter gives much greater yields of NH_3. W. McC.

Plant amylases. I. Effect of starch concentration on the velocity of hydrolysis by the amylase of germinated barley. C. S. Hanes (Biochem. J., 1932, 26, 1406—1421).—The relationship is in close agreement with that predicted by the Michaelis theory. In the case of the initial reaction velocity it is linear over a wide range of enzyme concn. S. S. Z.

Optimal ratio of α- and β-diastase in saccharification of potato starch. W. Syniewski and S. Zeminski (Biochem. Z., 1932, 253, 266—274).—The ratio is 70 α : 30 β. P. W. C.

Secretion of enzymes. P. Albertoni (Rend. R. Accad. Sci. Bologna, 1929—1930, 34, 67—68).—Dog's saliva remains without diastatic action after intravenous injection of takadiastase. Circulation of digestive enzymes does not occur. R. K. C.

Dilatometric investigation of enzymic processes. III. Hydrolysis of α- and β-methylglucoside. P. Rona and N. Neuenschwander-Lemmer (Biochem. Z., 1932, 254, 322—328).—Tables show the changes in vol. of solutions of α- and β-methylglucosides during hydrolysis with maltase and emulsin, respectively (cf. this vol., 649). P. W. C.

Enzymic conversion of synthetic methylglyoxal into lactic acid. K. Lohmann (Biochem. Z., 1932, 254, 332—354).—Aq. muscle and liver extracts lose their power of converting synthetic AcCHO into OH·CHMe·CO$_2$H on dialysis against dil. salt solutions and on oxygenation in alkaline (NaHCO$_3$) solution, whilst dry preps. of yeast and of *B. pasteurianum* lose their power on washing with distilled H$_2$O. The power is, however, regained on adding glutathione. The relationship of the reaction velocity and the glutathione concn., the temp. sensitivity of the enzyme, and the temp. coeff. of methylglyoxalase are investigated. Glutathione is similarly necessary for the conversion of BzCHO. Of the heavy metals (0·001*M*) with glutathione (0·002*M*) Cu, Ag, and Hg inhibit almost completely, whilst Fe, Mn, Ni, Co, Zn, and Pb do not inhibit. The effect of Cu is abolished by larger amounts of glutathione. Aldehydemutase does not require glutathione as does glyoxalase. The breakdown of glycogen into OH·CHMe·CO$_2$H also occurs in the absence of glutathione. P. W. C.

Action of co-enzyme. III. Activation of lactic acid formation in muscle extracts by various forms of adenosinetriphosphoric acid. H. K. Barrenscheen and K. Müller. **IV. Activation of the dismutation of aldehyde.** H. K. Barrenscheen and K. Braun. **V. Chemistry of adenosinetriphosphoric acids.** H. K. Barrenscheen and W. Filz (Biochem. Z., 1932, 253, 408—413, 414—421, 422—426).—III. The adenosinetriphosphoric acid obtained by the AcOH–NaNO$_2$ method activates OH·CHMe·CO$_2$H formation in extracts free from or poor in co-enzyme more strongly than does the triphosphoric acid directly extracted from muscle

IV. Dismutation of MeCHO in liver extracts is activated by co-enzyme, but not by muscle-adenosinetriphosphoric acid, whereas in muscle extracts poor in or devoid of co-enzyme, cozymase is not and the triphosphoric acid is considerably active. Hexosediphosphate in muscle extracts increases the rate of disappearance of MeCHO enormously, and glucose, glycogen, dihydroxyacetone, glyceraldehyde, and lactate but not AcCHO cause a fleeting activation which is increased by the triphosphoric acid.

V. See this vol., 1064. P. W. C.

Alleged decarboxylation of pyruvic acid by liver. G. Gorr and J. Wagner (Biochem. Z., 1932, 254, 5—7).—In sterile mixtures liver preps. produce COMe$_2$ but no MeCHO from AcCO$_2$Na. W. McC.

Production of acetoacetic acid by liver. G. Gorr (Biochem. Z., 1932, 254, 8—11; cf. preceding abstract, and Embden and Oppenheimer, A., 1912, ii, 1075).—The enzymic production of COMe$_2$ from AcCO$_2$H by liver preps. does not depend on the presence of CaSO$_3$ and these preps. produce no COMe$_2$ from Na formate, acetate, propionate, *n*-butyrate, *n*-valerate, fumarate, succinate, *dl*-lactate, or *d*-alanine. The activity of the preps. varies greatly with the species of animal from which they are obtained and with its state of nourishment. The COMe$_2$ produced is entirely derived from CH$_2$Ac·CO$_2$H; MeCHO is not an intermediate product. From EtOH or MeCHO under the same conditions no CH$_2$Ac·CO$_2$H is produced. W. McC.

Animal carboligase. G. Gorr (Biochem. Z., 1932, 254, 12—14).—Preps. of heart-muscle produce acetoin from AcCO$_2$Na. If sulphite is present MeCHO is produced, but practically no acetoin. W. McC.

[Formation of] diacetyl and acetoin by the action of pepsin on milk. I. W. Ciusa (Annali Chim. Appl., 1932, 22, 594—597).—The formation of these substances is not peculiar to rennin, but has been found in small amounts by steam-distilling a mash of peas and artichokes. By the action of pepsin on milk they are obtained in quantities up to 0·0087%. In this case they are formed by the sp. action of pepsin on some milk protein, not caseinogen. O. F. L.

Pepsin. A. Heiduschka and J. Förster (Arch. Pharm., 1932, 270, 419—423).—The activity of pepsin is decreased by various antipyretics, narcotics, xanthine derivatives, and antiseptics, but not by a no. of alkaloids and tinctures, sucrose, or gum arabic. The depression of activity is not proportional to the concn. of the drug added, but is relatively great with small additions. R. S. C.

Formation of enterokinase from a precursor in the pancreas. J. Pace (Biochem. J., 1932, 26, 1566—1570).—The crit. increment of the process precursor ⟶ enterokinase (I) is 9500 g.-cal. per mol. The precursor-like dipeptidase is adsorbable by Fe(OH)$_3$, from which both can be eluted, (I) being ultimately formed in the elution. The presence of glycine does not affect the rate of formation of (I). S. S. Z.

Influence of bile acids on the digestion of nucleins. I. Digestion of nucleic acid by intestinal juice. T. Kuramoto (J. Biochem. Japan, 1932, 16, 141—152).—Bile acids (cholic, taurocholic, and glycodeoxycholic) in low concns. accelerate and in high concns. inhibit the hydrolysis of nucleic acid by dog's intestinal juice to an extent characteristic of each acid. F. O. H.

Urease. III. Action of fluoride on urease. IV. Action of sodium tungstate on urease. A. Ruchelmann (Biochem. Z., 1932, 253, 294—299, 254, 479—483).—III. In the reaction of urease on urea, added NaF unites with both substrate and enzyme; it affects the velocity of hydrolysis of carbamate, the action being more energetic in strongly buffered solutions (cf. this vol., 777).

IV. A table and curves show the inhibiting effect of Na$_2$WO$_4$ on the action of urease. P. W. C.

Action of dyes on enzymes. III. Urease. J. H. Quastel (Biochem. J., 1932, 26, 1685—1696).—Most basic dyes, especially of the CHPh$_3$ series (I), are toxic, whilst acidic dyes are inert, towards urease. The toxicity of compounds such as Janus-green or neutral-red increases, and that of (I) diminishes, with increased purification of the enzyme. A substance is present in soya bean which enhances greatly the toxicity of the basic CHPh$_3$ dyes towards purified urease. This is present in soya-bean oil and is confined to the unsaturated glycerides, linseed oil being particularly effective. Urea, α-NH_2-acids, sarcosine, $C_2H_4(NH_2)_2$, NH_2Me, $NHMe_2$, N_2H_4, and NH_2OH protect urease from the toxic action of dyes. NMe_3, betaine, urethane, methyl- and diethyl-carbamide, oxamic acid, etc. are without effect. Glycine combines reversibly with urease. The dissociation const. of the urease–glycine complex has been determined. The combining group of the protective substances is either a basic NH_2- or NH-group. Combination of α-NH_2-acids, basic amines, etc. takes place reversibly at acidic or negatively-charged groups which constitute either wholly or partly the active centre of urease. Basic dyes appear to combine with these groups irreversibly. Urea is combined at these groups, activation of the mol. then occurring.

S. S. Z.

Inactivation of lipase in dairy products by traces of heavy metal salts. W. L. Davies (J. Dairy Res., 1932, **3**, 254—263).—The presence of heavy metal salts (up to 25 p.p.m.) inhibited the action of lipase in butter prepared from unpasteurised sweet cream. Of the metals examined Cu was the most active, Fe, Ni, Co, Mn, and Cr being less effective, and Sn and Al without action. The acidity produced during lipase activity was accompanied by fat peroxides in directly proportional amounts. The latter are associated with the free oleic acid formed.

A. G. P.

Hydrolysis by phosphatase of stereoisomeric diarylphosphoric acids. F. von Brücke (Biochem. Z., 1932, **253**, 470—481).—The extents of hydrolysis respectively of K *o*-, *m*-, and *p*-ditolylphosphate using takaphosphatase (I) at p_H 6·5 for 5 days are 100, 100, and 28%, using (I) at p_H 4·3 for 5 days are 82, 97, and 83%, using pig's liver-phosphatase at p_H 6·5 for 5 days are 5·9, 84·8, and 81·5%, using pig's kidney-phosphatase for 8 days are 52·7, 84·9, and 66%, and using rabbit's kidney-phosphatase for 20 days are 11·1, 32·5, and 28·3%. P. W. C.

Action of bone-phosphatase on the esters of phosphoric acid of the blood. E. J. King (Biochem. J., 1932, **26**, 1697—1703).—At p_H 9, the optimum [H$^{\cdot}$] for the enzyme, bone-phosphatase liberates about ¼ of the total acid-sol. P of the neutralised acid extract of the pancreas. At or near p_H 7 a somewhat larger proportion was hydrolysed during 24 hr. With acid extracts of liver, kidney, and muscle the p_H effect is not so marked, max. hydrolysis taking place at p_H 7—9. In the case of blood the esters of H_3PO_4 contained in $CCl_3\cdot CO_2H$ extracts consist of at least two fractions. One is hydrolysed by bone-phosphatase at p_H 9, whilst the other is hydrolysed preferentially at a p_H near neutrality. Both fractions are almost completely hydrolysed at or near neutrality during 2 days at 37·5°. S. S. Z.

Adenosinetriphosphatase of liver. H. K. Barrenscheen and S. Láng (Biochem. Z., 1932, **253**, 395—407).—The enzyme reacting with adenosinetriphosphoric acid (I) shows a p_H optimum at 8·2—9 and a temp. optimum of 37°. The enzyme is very sp. and does not react with pyrophosphate or glycerophosphate and the hydrolysis curve up to 50% hydrolysis is approx. linear. Embden's adenylic acid is dephosphorylated by the triphosphatase (II) and (I) is hydrolysed by bone-phosphatase at p_H 9·4 to a slight extent. (II) is inhibited by F′, CN′, and inorg. PO_4''' but accelerated by cysteine and SO_4''. In contrast with bone- and kidney-phosphatase, (II) is inhibited by $Mg^{\cdot\cdot}$. P. W. C.

Influence of bile acids on glycerophosphatase. III. H. Takata (J. Biochem. Japan, 1932, **16**, 83—97).—Cholic acid inhibits the hydrolysis of β-glycero- or hexosemono-phosphoric acid by rabbit bone-phosphatase and, to a smaller extent, that by liver- or kidney-phosphatase. The inhibition of bone-phosphatase may also be achieved by subcutaneous injection of cholic acid into guinea-pigs. Obstruction of the bile duct in rabbits also results in a decreased phosphatase content of the liver and kidney, whilst *in vitro* addition of cholic acid to these tissues still further diminishes the phosphatase activity. The influence of this inhibition on the urinary excretion of PO_4 is discussed. F. O. H.

Growth and enzymic activity of *Saccharomyces cerevisiæ* in presence of sodium and potassium cations. I. Novi (Rend. R. Accad. Sci. Bologna, 1929—1930, **34**, 74—75).—Growth of brewer's yeast is retarded by $>0·5\%$ of NaCl, but is accelerated by up to 2% of KCl. Glycolysis by cultures heated to 100° is increased by NaCl up to 5% or by KCl up to 1%, but is retarded by greater concn. of KCl.

R. K. C.

Action of organic compounds on alcoholic fermentation. II. Olefinic compounds. E. Mameli and A. Mossini (Giorn. Chim. Ind. Appl., 1932, **14**, 450—455).—In small proportions, saturated org. compounds may have an accelerating, a retarding, or zero effect on the rate of fermentation (measured by the CO_2 evolved in 3 hr.). Unsaturated compounds (naphthenes, terpenes, halogen derivatives, alcohols, aldehydes, ketones, phenol derivatives, acids, salts), however, always accelerate the fermentation, the effects being > those of the corresponding saturated compounds. Taking the rate for the control fermentation as 100, the max. rates obtained were, with PrOH 104·1, EtCHO 113, $CH_2{:}CH\cdot CH_2\cdot OH$ 106·7, $CH_2{:}CH\cdot CHO$ 117·5, $CH_2Ph\cdot CH_2\cdot OH$ 103·1, and $CH_2Ph\cdot CHO$ 108·1. The accelerating influence of a $C{:}C$ compound is > that of the corresponding $C{:}O$ compound. T. H. P.

Formation of malic acid in alcoholic fermentation in presence of asparagine and aspartic acid. E. Glimm and M. Nitzsche (Biochem. Z., 1932, **253**, 318—335).—Fermentation by yeast of sugar in pure solution did, but in presence of NH_4 salts did not, give malic acid (I), whilst fermentation with addition of 0·3—0·5% of asparagine always gave an amount of (I) equal to 1/10 of the asparagine. With addition of 0·3—0·5% of aspartic acid, only traces of (I) were formed, although almost all the aspartic acid disappeared. Addition of the monoamide of (I) did, but of succinic acid did not, give rise to (I). Asparagine either added or formed from yeast-protein appears to be the source of (I).

P. W. C.

An enzyme, in yeast, which oxidises alcohol. F. Windisch (Naturwiss., 1932, **20**, 673).—When the solution is sufficiently aërated, yeast converts EtOH into AcOH. Since AcOH-bacteria contain also desmolytic enzymes (cf. A., 1930, 447), the physiological criteria of yeast and AcOH-bacteria are no longer sp. R. S. C.

Amidases of yeast. G. Gorr and J. Wagner (Biochem. Z., 1932, **254**, 1—4).—Brewers' and bakers' yeasts and also *Torula utilis* contain asparaginase, but do not liberate NH_3 from urea, HCO·NH_2, oxamide, succinamide, or NH_2Bz. *Torula*, however, liberates NH_3 from NH_2Ac, Et·$CONH_2$, and lactamide. The amount of NH_3 produced from asparagine by dried *Torula* is 300% greater than that produced by the fresh material. With the other amides on which *Torula* acts the increase produced by drying is much smaller. W. McC.

Physiological behaviour and enzymic hydrolysis of ureidolactose and ureidomaltose. E. Hofmann (Biochem. Z., 1932, **253**, 462—469).—Emulsin and the enzymes of certain lactose-fermenting yeasts (*S. fragilis*, Jörgensen, *S. Kefir*) hydrolyse lactoseureide with the same velocity and to the same extent as they hydrolyse lactose, the products being *d*-galactose and *d*-glucoseureide. Maltoseureide is similarly decomposed without severing the ureide linking. *Aspergillus oryzæ* will not grow on solutions containing lactoseureide and inorg. salts, but *Mucor javanicus*, *A. niger*, and *S. fragilis* readily grow and utilise the galactose part of the mol. without attacking the remaining glucoseureide. P. W. C.

Influence of organic substances on the growth of *Aspergillus niger*. L. E. Kiessling and A. Schmidt (Arch. Pflanzenbau, 1932, **9**, 293—305).—Under conditions adopted in determinations of assimilable K in soils by means of *A. niger*, the growth of the organism is markedly affected by the presence of org. plant constituents. In soil-free cultures, additions of filter-paper shreds, washed peat, powdered barley roots, etc. considerably increased the wt. of mycelium produced. A. G. P.

Citric acid production by *Aspergillus niger*. N. Porges (Amer. J. Bot., 1932, **19**, 559—567).—With a strain of *A. niger* isolated from soil, a high sugar content (15—20%) in the medium was necessary for max. production of citric acid (I). With 5% of sugar (I) was utilised by the organism as an energy source and accumulation was small. $NaNO_3$, as the N source, was more favourable than NH_4NO_3 or NH_4Cl to formation of (I). Fe and Zn were essential for the rapid growth of the organism and for the production of (I). The latter did not accumulate in aërated media. A. G. P.

Biological conversion of glucose into glucosone. T. K. Walker (Nature, 1932, **130**, 582).—Glucosone is produced when the fully-developed mycelium of a mould belonging to the *flavus* section of the *flavus–oryzæ* group of *Aspergilli* acts on 5% aq. glucose in presence of a small amount of PhMe at 27—28°. L. S. T.

Biochemistry of micro-organisms. XXIV. Metabolic products of the *Penicillium brevicompactum* series. P. W. Clutterbuck, A. E. Oxford, H. Raistrick, and G. Smith (Biochem. J., 1932, **26**, 1441—1458).—From twelve species or strains of this series mycophenolic acid ($C_{17}H_{20}O_6$) (I) and the following cryst. *products* were isolated from the medium in which they were grown: $C_{10}H_{10}O_5$, m.p. 145—153°; $C_{10}H_{10}O_6$, m.p. 193—203°; $C_{10}H_{10}O_7$, m.p. 125—135°; $C_8H_6O_6$, m.p. 188—190°. *P. stoloniferum*, Thom, and *P. Biourgeianum*, Zaleski, gave no (I), but in the first case considerable amounts and in the second case small amounts of the other metabolic products, whilst the third species, *P. aurantio-griseum*, Dierckx, var. *Poznaniensis*, Zaleski, gave none of these products. After keeping cultures over long periods in artificial cultivation (20 years) the power of forming (I) but not the products of smaller mol. wt. is lost. S. S. Z.

Agar-digesting bacteria. H. E. Goresline (Science, 1932, **76**, 255).—Three new species which can digest agar are described. *Achromobacter pastinator* liquefies agar media and uses carbohydrates as sources of C; *Pseudomonas lacunogenes* softens agar and often utilises carbohydrates, cysteine, asparagine, aspartic acid, tyrosine, alanine, glutamic acid, NH_4 succinate, and peptone as sources of C or N, and $(NH_4)_2SO_4$, NH_4Cl, and NH_4 phosphate as sources of N when glucose is present; *P. segne* also softens agar, has the same action on carbohydrates as *P. lacunogenes*, but is unable to utilise any of the above compounds, except peptone, as sources of N. L. S. T.

Degradation of methyl alcohol, formaldehyde, and formic acid by living and killed acetic acid bacteria. D. Müller (Biochem. Z., 1932, **254**, 97—101; cf. A., 1931, 1192).—MeOH and CH_2O in low concn. are almost completely converted into CO_2 and H_2O by living *B. Pasteurianum*. Higher concns. (0·25—0·50%) of CH_2O and HCO_2H are only incompletely oxidised by the bacteria. The killed bacteria oxidise MeOH (with production of CH_2O, but not of HCO_2H) and CH_2O incompletely, but not HCO_2H. It is concluded that alcoholdehydrase, aldehydrase, and an enzyme which is very sensitive towards $COMe_2$ and decomposes HCO_2H, partake in the degradation of MeOH. W. McC.

Oxidases of killed acetic acid bacteria. III. Behaviour of the bacteria towards oxygen and quinone as hydrogen acceptors. D. Müller (Biochem. Z., 1932, **254**, 102—111; cf. A., 1931, 1192).—$Pr^{\beta}OH$ is dehydrogenated by killed AcOH bacteria when either O_2 or benzoquinone is present as H acceptor, O_2 having 25—30% of the activity of quinone. Even if the activity of the preps., which is almost as great as that of the living bacteria, varies greatly the ratio $COMe_2$–O_2 : $COMe_2$–quinone is const. This ratio cannot be altered by washing the bacteria with H_2O nor by pptg. with EtOH–Et_2O, and these treatments affect their activity towards the acceptors in the same degree. The temp. of destruction of alcoholdehydrase is 54·5° with both acceptors. It follows that the alcoholdehydrase of the bacteria can utilise O_2 as acceptor without the intervention of an O_2 carrier (cf. Tamiya and Tanaka, A., 1931, 656). Benzoquinone as acceptor is much less sensitive to the inhibiting action of HCN than is O_2. Killed bacteria are less sensitive to HCN than are living. In the absence of HCN the amount of $COMe_2$ produced corresponds with that of O_2 absorbed, but when $0{\cdot}1M$-HCN is present only 67—74% of the calc. amount of $COMe_2$ is produced. W. McC.

Products of decomposition of sugar by beri-beri bacteria. Isolation of methylglyoxal, and its physiological action. T. Ariyama (J. Agric. Chem. Soc. Japan, 1931, 7, 763—768).—Mg hexosediphosphate afforded AcCHO (I) in 73·5% of the theoretical yield from 8·73% of hexosediphosphate decomposed. (I) was not obtained from sucrose or fructose. Oral administration of (I) to pigeons did not accelerate avitaminosis-*B*. Ch. Abs.

Lipins of tubercle bacilli. XXIX. Polysaccharides in tubercle bacilli. H. Dumont and R. J. Anderson. **XXX.** S. Ludewig and R. J. Anderson (Z. physiol. Chem., 1932, **211**, 97—102, 103—110; cf. this vol., 307).—XXIX. Polysaccharides from human and avian tubercle bacilli were isolated by pptn. with basic Pb acetate. Mannose, *d*-arabinose, and inositol were isolated from the former and mannose and inositol from the latter polysaccharide. By acetylation of the polysaccharide of avian tubercle bacilli and hydrolysis of the *Ac* derivative, m.p. 118—120°, it was obtained almost free from N and P. The analysis of the purified material corresponds with a trisaccharide (2 mols. of mannose, 1 mol. of inositol).

XXX. From the crude polysaccharide of human tubercle bacilli after addition of basic Pb acetate, a purer product was obtained by addition of aq. NH_3. By acetylation and hydrolysis of the *Ac* derivative, m.p. 85—86°, $[\alpha]_D^{27}$ +64° in MeOH, a product free from P and containing only traces of N was obtained. On hydrolysis the purified product gave small amounts of inositol and reducing sugars consisting of 27% of *d*-mannose and 33% of *d*-arabinose + *d*-glucose. Probably other substances (acids) are present in the non-reducing portion. J. H. B.

Lipins of tubercle bacilli. XXXI. Composition of the acetone-soluble fat of the timothy bacillus. M. C. Pangborn, E. Chargaff, and R. J. Anderson (J. Biol. Chem., 1932, 98, 43—55).—The fat (cf. A., 1931, 526; this vol., 197) contains no glycerides and only traces of volatile fatty acids, whilst the unsaponifiable matter (27%) is an unsaturated oil free from sterols. The saturated acids consist mainly of palmitic acid and the unsaturated acids are principally C_{16} members. A saturated acid, $C_{18}H_{36}O_2$, isomeric with stearic acid and similar to tuberculostearic acid, is the main constituent of the liquid fatty acids. F. O. H.

Bacterial synergism. Formation by *B. typhosus* or *B. coli anaërogenes* from mannitol of an intermediate substance from which Morgan's bacillus produces gas. J. G. Thomas (J. Hyg., 1932, 32, 385—395).—The mixture of gases formed by synergic action differs in $H_2 : CO_2$ ratio from that obtained with the glucose-fermenting organism alone on glucose or by *B. coli* on mannitol. The intermediate production of formate is suggested. Ch. Abs.

Effects of ammonia, of the fatty acids, and of their salts on the luminescence of *B. fischeri*. S. E. Hill (J. Cell. Comp. Physiol., 1932, 1, 145—159).—NH_3 rapidly penetrates and kills the bacteria. NH_4Cl penetrates the cells slowly and eventually causes cytolysis. HCl and NaOH enter only after the destruction of the cell surface. Below p_H 3·5 fatty acids are more toxic than HCl of the same p_H. With a given p_H the destruction of luminescence by the fatty acids increased in the series valeric to formic. The rates of penetration of the free acids and their NH_4 and Na salts increased with the mol. wt. Cytolysis occurring in certain ranges of p_H in $0{\cdot}5M$ solutions of the NH_4 salts of the fatty acids increased with the mol. wt. and results from the penetration of mol. NH_3 and fatty acid. A. G. P.

Electric charge of bacterial antigens. L. Olitzki (J. Immunol., 1932, 22, 251—256).—The H-antigen (I) of *B. proteus* X.19 carries a negative charge at p_H 12·0—4·4 and the O-antigen (II) at p_H 12·0—3·4. By cataphoresis of whole bacteria at p_H 4·0 large amounts of pure (II) are obtained at the positive pole. By cataphoresis of bacterial extracts at p_H 4·0 (II) is completely removed, leaving pure (I) in the middle vessel. Ch. Abs.

Welch–Fraenkel bacillus; toxins and antitoxins. S. Shiraishi (Japan. J. Exp. Med., 1931, 9, 613—618).—A true toxin, thermolabile, non-dialysable, and strongly antigenic, and an "acute" toxin, thermostable, dialysable, and non-antigenic (histamine or -like), are present, together with a hæmolysin. The true toxin appears to be species-sp., but considerable differences between strains exist. Ch. Abs.

Purification and concentration of diphtheria toxoid by means of electrodialysis. L. Reiner (J. Immunol., 1932, 22, 439—443).—$[H^{\cdot}]$ at the end of dialysis is approx. p_H 3·9, apparently optimal for pptn. of the toxoid. The yield of toxoid was 30—40%; by pptn. with acid it is <10%. Ch. Abs.

Purification of Shiga dysentery toxin. S. Hosoya, S. Terao, and S. Takata (Japan. J. Exp. Med., 1932, 10, 97—99).—Removal of toxin from culture filtrates by adsorption, followed by extraction and purification by dialysis, leads to a very potent material giving only a weak ninhydrin reaction. Ch. Abs.

Dissociation of the specific protein precipitate of antipneumococcus horse serum and comparison with a protein isolated by chemical means from immune serum. L. D. Felton (J. Immunol., 1932, 22, 453—467).—After heating in 0·85% NaCl, with or without Na_2CO_3, the relation protection : N was approx. the same in ppt. and supernatant fluid of the pneumococcus carbohydrate–protein complex. The sol. sp. substance was dissociated from the protein by Ca or Sr phosphate. Protein obtained by dissociation from type I contained 14·9% N, and from type II 15·2% N. In three preps. by the Zn method the N content was 15·3—15·7%. Ch. Abs.

Purification of concentrated antitoxins. T. D. Gerlough and W. White (J. Immunol., 1932, 22, 331—350).—The potency and amount of protein in the isoelectric ppts. of diphtheria and tetanus antitoxins varied with the age, previous treatment of the antitoxin, and conductivity of the dialysed solution. Heating the plasma renders the subsequent isoelectric purification of the concentrates more effective for the removal of P-bearing materials. After removal of isoelectric protein from tetanus and diphtheria antitoxins, and especially after electrodialysis, the potencies of the fractions pptd. at lower concns. of $(NH_4)_2SO_4$ were increased.

Ch. Abs.

Bacterial endotoxin. Search for a specific intracellular toxin in *S. pullorum*. J. H. Hanks and L. F. Rettger (J. Immunol., 1932, 22, 283—314).—The cell bodies contain a relatively thermostable poison; the toxic principle is stable at p_H 3·0—12·0, is unaffected by direct sunlight during 24 hr., and is destroyed by prolonged action of pepsin and trypsin. It is not dialysable through parchment, and can be pptd. by $(NH_4)_2SO_4$ or AcOH–EtOH. Sp. agglutinin antibodies result from its injection.

Ch. Abs.

Effect of some chemical factors on survival of purified vaccine virus. H. Yaoi and H. Kasai (Japan. J. Exp. Med., 1931, 9, 619—625).—Most of the substances tested, including H_2O, were toxic. Glycerol (50%) and phenol (0·5%) are preservatives.

Ch. Abs.

Biological properties of cerebrospinal fluid. A. C. Marie (Ann. Inst. Pasteur, 1932, 49, 429—434).—The fixed virus of rabies loses much of its virulence when incubated at 38° with physiological saline for 4 hr. If the saline is replaced by cerebrospinal fluid or dialysed serum the virulence is maintained and infected animals show symptoms on the 6th—8th day. Similar results are recorded with tetanus toxin. P. G. M.

Protein-free suspensions of viruses. IV. Antigenic properties and serological reaction of protein-free suspensions of phage. I. J. Kligler and L. Olitzki (Brit. J. Exp. Path., 1932, 13, 237—248).—The pure phage is a definite antigenic entity. Union of phage and antibody is accelerated by raising the temp. and by addition of complement. Reaction between phage and sp. antibody appears irreversible. The phage antibody is associated with the globulin fraction of the serum. Ch. Abs.

Purification of bacteriophage. S. Hosoya, K. Nagase, and T. Yoshizumi (Japan. J. Exp. Med., 1932, 10, 101—111).—Pptn. with Zn salts is followed by removal of Zn and dialysis; the non-dialysable residue is conc. by evaporation at low temp. Active phages, giving no protein reactions, were obtained for *Eb. typhi* and *S. dysenteriæ*. Lytic activity is destroyed by org. solvents and by some metallic salts. The bacteriophage is probably a non-living agent.

Ch. Abs.

Bacteriophages of the root nodule organisms. S. V. Desai (Indian J. Agric. Sci., 1932, 2, 138—156).—The medium used for the isolation of the bacteriophage should contain little or no sugar; the virulence of the isolated bacteriophage is enhanced in a medium containing 0·5% of sugar. Small amounts of KNO_3 or $(NH_4)_2SO_4$ which assist isolation are adverse to the enhancement of virulence. The optimal p_H for bacteriophage action was p_H 7·6—8·2. Ch. Abs.

Structures produced in blood-agar by electric currents between gold and platinum electrodes. I. W. A. G. van Everdingen and J. Idzerda. **II.** J. Idzerda and W. A. G. van Everdingen (Biochem. Z., 1932, 254, 59—64, 88—93; cf. this vol., 969).—I. Zones similar to those produced by Hg, H_2O_2, and streptococci are produced in the medium when electric currents are passed between Au or Pt electrodes embedded in it. At the anode the mechanism by which the zones are produced is identical with that caused by the agents named.

II. The changes in the resistance of the erythrocytes to which are due the formation of the zones produced at the anode when an electric current is passed between Au or Pt electrodes are caused by a process of oxidation taking place in an acid medium. The changes can be imitated *in vitro* with the help of H_2O_2. W. McC.

Changes of resistance of blood-corpuscles in blood-agar under the influence of streptococci, mercury, and hydrogen peroxide. G. Woker (Biochem. Z., 1932, 254, 410—413).—The formation of ring structures in blood-agar cultures by streptococci, H_2O_2, and Hg as described by Brown and by Idzerda and Everdingen (this vol., 969) is discussed.

P. W. C.

Effect of heat on sugar solutions used for culture media. M. L. Smith (Biochem. J., 1932, 26, 1467—1472).—Autoclaving at 15 lb. pressure causes hydrolysis of maltose to glucose and slow destruction of the latter with production of acid. This change is accelerated by the presence and increasing concn. of PO_4'''. Heating for 1 hr. at 100° causes a similar change in the sugar equiv. to 20 min. autoclaving under 15 lb. excess pressure. S. S. Z.

Nitrogen content of certain proteins. M. L. Smith, A. M. Brown, and C. Gross (Biochem. J., 1932, 26, 1473—1476).—The N content of certain proteins derived from diphtheria toxin and from diphtheria and other sera when determined by the micro-Kjeldahl method varies from 13·57 to 14·64% (average 14·18%). S. S. Z.

Germicidal activity of alkyl sulphur ethers. E. Miller and R. R. Read (J. Amer. Chem. Soc., 1932, 54, 4113).—The germicidal activity of $SAlk{\cdot}C_6H_4{\cdot}OH$ increases with increase in the size of the alkyl group and reaches a max. at Bu. A rise in the temp. (of the bacterial examination) raises the max. to higher members of the series. The *iso*alkyl ethers have lower PhOH-coeffs. than the *n*-alkyl derivatives. The *O*-ethers, $OR{\cdot}C_6H_4{\cdot}SH$(?), of PhSH are probably much less active than the corresponding *S*-ethers of PhOH. C. J. W. (*b*)

Evolution of hormones. D. L. Thomson (Nature, 1932, 130, 543).—A discussion. L. S. T.

Adrenal cortical extracts and sex changes. F. G. Young and H. W. Benham (Nature, 1932, 130, 700—701).—Swingle and Pfiffner's extract of "Eucortone" had no effect on the sexual functions of male or female mice. (Eucortone keeps completely adrenalectomised cats alive for long periods.) In view of the contrary findings of other authors, it is suggested that the adrenal cortex may secrete two distinct hormones. L. S. T.

Influence of the cortex of the suprarenal capsule on purine metabolism. T. Ogawa (Folia endocrinol. Japon., 1931, 7, 5—6).—Feeding adrenal cortex (0·25 g. per kg. per day) to dogs led to a marked decrease in the purine-N excreted. Ch. Abs.

Effect of adrenaline on lipin excretion. E. Hill and A. E. Koehler (J. Biol. Chem., 1932, 98, 185—192).—Administration of adrenaline (0·02 mg. per 100 g. body-wt.) to rats fed on a diet poor in fats results in a definite increase in the fæcal lipins. F. O. H.

Carbohydrate balance sheet for the adrenalinised fasting rat killed in the recovery period. M. L. Long and F. Bischoff (J. Biol. Chem., 1932, 98, 85—91).—The muscle- and urine-lactic acid, the urine-sugar, and the total and fermentable carbohydrate of the muscles, liver, and organs other than the liver were determined in fasting rats which had received either 0·02 or 0·10 mg. of adrenaline per 100 g. body-wt. and also in non-adrenalinised control animals. The balance sheet thus obtained shows that only 30—40% of the carbohydrate lost from the peripheral tissues is accounted for by a gain in liver-carbohydrate or urinary sugar. Of the total fermentable carbohydrate of the whole body of the control rats, 82 and 76% are accounted for in the rats receiving respectively 0·02 and 0·10 mg. of adrenaline. F. O. H.

Hexosemonophosphate content of mammalian muscle. I. Experiments on rats injected with adrenaline. D. J. Bell (Biochem. J., 1932, 26, 1601—1605).—It is confirmed that the injection of adrenaline and insulin raises the percentage of hexosemonophosphate in rat muscle (this vol., 199). Amputation and freezing of the whole limb of the animal prior to the removal of the muscle for analysis yields equally satisfactory results with the method of dissection from the living animal. S. S. Z.

Influence of protein amino-acids on adrenaline hyperglycæmia. S. Minami and H. Nishiyama (Folia Pharmacol. Japon., 1932, 14, No. 2, 200—234).—Glycine, tryptophan, cystine, and glutamic acid (I), when injected (with adrenaline) into rabbits, cause hyperglycæmia, whilst histidine (II), leucine (III), and phenylalanine (IV) produce hypoglycæmia. Alanine (V) has little effect. (III) and (IV) decrease adrenaline hyperglycæmia, whilst (I), (II), and (V) do not affect it. The action of combinations of NH_2-acids is < that of the individual acids. Ch. Abs.

Influence of insulin and adrenaline on hippuric acid synthesis. T. Koyasako (Folia endocrinol. Japon., 1931, 6, 110—111).—Insulin alone has no effect on urinary hippuric acid; it diminishes the increase caused by glucose. After injection of BzOH, insulin promotes and adrenaline retards hippuric acid synthesis. Ch. Abs.

Crystalline insulin. XVI. Action of ammonium hydroxide and of iodine on insulin. H. Jensen, E. Schock, and E. Sollers (J. Biol. Chem., 1932, 98, 93—99).—Insulin is partly inactivated by 0·5*N*- and *N*-NH_3 on treatment for 6 days at room temp. Subsequent treatment with acid does not reactivate the hormone; this is contrary to Witzemann and Livshis (A., 1924, i, 448), whose results are explained by the apparent decrease in activity of aq. NH_3 solutions injected subcutaneously, a loss due to tissue adsorption. 1 mg. of insulin is inactivated by 0·3 c.c. of 0·1*N*-I, a quantity much smaller than that absorbed in the course of 17 hr. The inactivation by I is probably due to oxidation of the cystine S·S linking. F. O. H.

Crystalline insulin. XVII. Hydrolysis products of insulin. H. Jensen and O. Wintersteiner (J. Biol. Chem., 1932, 98, 281—287).—Re-examination of the hydrolysis products of insulin (cf. this vol., 972) gives no evidence for the presence of aspartic or hydroxyglutamic acids, or glycine, the presence of proline and valine being doubtful. A tentative distribution of the NH_2-acids in cryst. insulin is: tyrosine 12%, cystine 12%, glutamic acid 21%, leucine 30%, arginine 3%, histidine 8%, lysine 2%. J. W. B.

Insulin. I. Cataphoresis of insulin alone and in presence of glucose; the question of an insulin–glucose reaction *in vitro*. F. O. Howitt and E. B. R. Prideaux (Proc. Roy. Soc., 1932, B, 112, 13—24).—Using colloidal Au (0·01%) as an indicator of the migration (cf. A., 1930, 159), the cataphoresis of insulin was determined in buffer solutions of p_H 2·7—9·6. Under these conditions the protein exhibits a zone of insolubility of p_H 4·5—6·5 and an isoelectric point of p_H 5·4. Insulin behaves cataphoretically as a chemical entity. Simple addition of glucose (0·1%) or incubation with glucose at 37° for 24 hr. does not influence the velocities for reactions $< p_H$ 8: this confirms the non-existence of an insulin–glucose reaction *in vitro* at the reaction of the blood. With greater alkalinity and at room temp. such a reaction occurs and is emphasised by incubation at 37°. Incubation of insulin (0·02%) at 37° and p_H 8—9 for 24 hr. is followed by a change in the ζ-potential of the insulin micelle without any concomitant appreciable change of physiological activity. F. O. H.

Insulin dosage and blood-sugar changes. E. L. Scott and L. B. Dotti (Arch. Int. Med., 1932, 50, 511—537).—The relative drop in blood-sugar for doses between 1/16 and 1/2 unit per kg. body-wt. of rabbits is proportional to the logarithm of the dose, blood samples being drawn 30 min. after the injection. There is no evidence that extremely small doses do not have the full expected effect, nor is the response affected if the dose is not administered > once a week or for a longer period than 20 months. Diet may influence the concn. of blood-sugar, but does not affect the relative changes after insulin. H. G. R.

Does insulin contain a specific antigen? P. Barral and J. Roux (Compt. rend. Soc. Biol., 1931, 106, 292—293; Chem. Zentr., 1932, ii, 82).—Experiments on the sensitisation of guinea-pigs to anaphylactic shock suggest that insulin contains a sp. antigen. A. A. E.

Attenuating effect of blood on action of thyroid juice in fowls. E. Giacomini (Rend. R. Accad. Sci. Bologna, 1929—1930, 34, 99—109).—The deplumation and depigmentation caused in fowls by large doses of ox-thyroid press-juice dried at 55—60° are less intense when the juice has been mixed before drying with dried ox, sheep, horse, pig, or fowl blood, or has been mixed in a paste with dried blood and H_2O and again dried. R. K. C.

Respiratory metabolism in infancy and childhood. XIV. Effect of thyroid therapy on metabolism of protein in normal infants. L. E. Wey-Muller, T. C. Wyatt, and S. Z. Levine (Amer. J. Dis. Children, 1932, 43, 1544—1551).—The calorigenic action appears to be due to accelerated combustion of fat and carbohydrate as well as of protein, and not to excessive combustion of protein. Ch. Abs.

Comparison of anti-diuretic and oxytocic potencies of commercial pituitary extracts. F. Wokes (Pharm. J., 1932, **129**, 241).—The two activities of these extracts are not consistently related. W. S.

Distribution of fat and glycogen after the subcutaneous injection of extracts of the posterior pituitary gland. A. Hynd and D. L. Rotter (Biochem. J., 1932, 26, 1633—1639).—Subcutaneous injection of pituitrin (I) into carbohydrate-fed rats produces effects on the liver- and muscle-glycogen similar to those obtained with pitressin (II) (this vol., 885). On the other hand, (I) is much less efficient than (II) in producing an infiltration of fat into the liver. An artificial mixture of equal parts by vol. of (II) and pitocin inhibits fatty infiltration, and the increase in liver-glycogen is greatly depressed. The effects produced by the several extracts vary with the interval elapsing after the injection. S. S. Z.

Pituitary and sleep. H. Zondek and A. Bier (Klin. Woch., 1932, **11**, 760—762; Chem. Zentr., 1932, i, 3192—3193).—Distribution of Br in the brain is changed during sleep. In dogs (somnifen sleep) the medulla contained 0·61—0·64 mg. Br per 100 g. (normally 0·38—0·41). In animals killed during sleep the pituitary contained 5—7 (normally 15—30) mg. Br per 100 g. Intravenous injection of tetrabromodeiodothyroxine (man, 1 mg.; dog, much larger doses) produces languor and sleep. The Br-containing pituitary extract is more active, the amount of Br thus injected being 0·25 mg. NaBr (20 mg.) was inactive. A. A. E.

Standardisation of male sexual hormone by means of the comb-growth reaction. J. Freud, P. de Fremery, and E. Laquer (Pflüger's Archiv, 1932, **229**, 763—786; Chem. Zentr., 1932, i, 3192).—The cock unit is the smallest dose which, when given during 4 days subcutaneously or intramuscularly in oil (2×0·5 c.c. daily), produces by the fifth day a 15% increase in comb growth. Larger doses are not proportionally more effective than small ones. Standardisation by means of the concn.–activity curve is rejected. No fixed relation was observed between the reactions of cocks and rats; rats require the simultaneous administration of menoformone. A. A. E.

Vitamins. E. Abderhalden (Med. Klinik, 1932, 28, 466; Chem. Zentr., 1932, i, 2969).—It is suggested that foodstuffs contain only precursors of vitamins, these being converted into the active vitamins after resorption. The relation between vitamins and hormones is discussed. A. A. E.

Quantity of vitamin-*A* present in the human liver. L. K. Wolff (Lancet, 1932, **223**, 617—620).—Data for 957 specimens of human liver are recorded and indicate that 16% of the population of the Netherlands have sub-normal vitamin-*A* reserves. In chronic diseases this proportion increased to 24·2%, indicating a connexion between vitamin-*A* and certain chronic diseases. In embolism, pregnancy, whooping-cough, syphilis III and IV, chronic nephritis, and enteric fever vals. below the average were found. The vitamin-*A* reserves of the newly-born fall much below the mean. L. S. T.

Vitamin-*A* reserves of the human liver in health and disease. T. Moore (Lancet, 1932, **223**, 669—674).—The vitamin-*A* reserve varies widely even among healthy subjects dying from accidental causes, but can be used to give a " normal " val. In cases of diabetes which had received dietetic treatment, vitamin-*A* reserves were much above this val., but tended to be below the normal in org. heart diseases, non-tuberculosis respiratory diseases, org. kidney diseases, and in septicæmias and certain septic conditions. Vitamin-*A* should not be regarded as a positive anti-infective agent, indiscriminate in action. L. S. T.

Vitamin-*A* content of the liver in puerperal sepsis. H. N. Green (Lancet, 1932, **223**, 723—726).—Low vitamin-*A* reserves were found in puerperal sepsis even after administration of large doses of the vitamin. L. S. T.

Determination of vitamin-*A* in cod-liver oils: biologically, chemically, physically, with a statistical examination of the results. II. Intensity of absorption at 328 mμ and biological activity of vitamin-*A*. K. H. Coward, T. J. Dyer, and R. A. Morton (Biochem. J., 1932, 26, 1593—1600; cf. A., 1931, 1196).—In re-testing of old oils, the blue val. of the unsaponifiable fraction again gave better agreement with the biological val. of the oil than did the blue val. of the oil itself. This difference was not found with freshly-prepared oils. S. S. Z.

Vitamin-*A* deficiency in castrated male rats. M. M. Sampson and V. Korenchevsky (Biochem. J., 1932, 26, 1542—1545).—There is no essential difference between normal and castrated rats in respect to the effects of vitamin-*A*-deficient diets on them. H. W. D.

Administration of ferrous iodide and linoleic acid to rats deprived of vitamin-*A*. L. L. Reed, L. B. Mendel, and H. B. Vickery (Science, 1932, 76, 300—301).—Contrary to Chidester and co-workers (Anat. Rec., 1930, 47, 304) the administration of FeI_2 and linoleic acid, alone or in combination, is ineffective as a cure for xerophthalmia, as a growth stimulant, or as a preventive of infection or renal disturbance in rats deprived of vitamin-*A* (cf. this vol., 972). L. S. T.

Effects of *A*- and *B*-avitaminosis on the bones and teeth. P. E. Simola (Biochem. Z., 1932, **254**, 245—250).—Anatomical, histological, and X-ray examination of the bones and teeth of rats suffering from B-avitaminosis (I) and receiving diets said to cause scurvy, gives no support to the view of Kollath that scurvy is thus caused. The changes produced in the bones of rats by A-avitaminosis are very similar to those produced by (I), but in their teeth (I) only causes notable pathological changes.

W. McC.

Fat metabolism with special reference to nutrition on diets devoid of fat. E. Gregory and J. C. Drummond (Z. Vitaminforsch., 1932, **1**, 257—287).—Whilst the view that "scaly tail" in rats is due to an ill-balanced diet is confirmed, no support is forthcoming for the theory that the condition is due to an inadequate supply of linoleic acid (I) or other related unsaturated acids (A., 1929, 853; 1930, 810). The condition is relieved by increasing the intake of vitamin-B complex. That the liver-fat of animals fed on a fat-free diet contains considerable amounts of (I) or some very similar fatty acid indicates the ability of the animal to synthesise (I). Omission of vitamin-B_1 or -B_2 from fat-containing diets gives results indicating the non-existence of a "sparing" action of fats on vitamin-B (A., 1929, 852, 1203). Analytical data for the fatty material of the fæces of rats on a fat-free diet are given.

F. O. H.

Photochemical synthesis of vitamin-B_1. B. C. Guha and P. N. Chakravorty (Nature, 1932, **130**, 741).—Adenine sulphate, but not guanine chloride, has been activated into vitamin-B_1 by ultra-violet radiation.

L. S. T.

Assay of vitamins-B_1 and -B_2 as influenced by coprophagy. N. B. Guerrant and R. A. Dutcher (J. Biol. Chem., 1932, **98**, 225—235).—The fæces of rats on a diet deficient in vitamin-B_1 or in -B_2 were as potent sources of these vitamins as were the fæces of rats on a complete diet, even after a prolonged period on the deficient diet. Vitamins-B_1 and-B_2 are apparently synthesised in the animal organism.

W. O. K.

Co-zymase and co-carboxylase content of rats suffering from B-avitaminosis. P. E. Simola (Biochem. Z., 1932, **254**, 229—244).—No appreciable change occurs in the co-zymase content of the livers and brains of rats when their food is deprived of vitamin-B, but since the co-carboxylase content of these organs decreases as a result of this deprivation and since the administration of co-carboxylase has a favourable effect in B-avitaminosis, there may be a relation between this enzyme and the vitamin-B complex.

W. McC.

Antiscorbutic vitamin. III. O. Rygh and A. Rygh (Z. physiol. Chem., 1932, **211**, 275—284; cf. this vol., 310).—On a vitamin-C-free diet guinea-pigs cease to excrete glycuronic acid (I) in the urine. Although (I) alone added to the diet does not prevent scurvy, in conjunction with methylnornarcotine (II) it maintains the animals in full health. A cryst. prep. of the hydrochloride of (II) was obtained from the products of hydrolysis of narcotine with conc. HCl for 40 hr. at 60°. The activation of narcotine by irradiation is now regarded as due to inefficient cooling.

J. H. B.

Narcotine as the alleged precursor of vitamin-C. R. L. Grant, S. Smith, and S. S. Zilva (Biochem. J., 1932, **26**, 1628—1632).—Narcotine could not be detected in unripe or partly ripe oranges. Attempts to prepare an antiscorbutic fraction by extraction of neutralised lemon-juice with H_2O-free Et_2O failed. The administration of methylnornarcotine obtained by demethylation of narcotine under various conditions to guinea-pigs on a scorbutic diet failed to modify the development or character of the ensuing scorbutic symptoms and the experimental animals died in the usual time of typical scurvy.

S. S. Z.

Non-specificity of the phenol-indophenol reducing capacity of lemon-juice and its fractions as a measure of their antiscorbutic activity. S. S. Zilva (Biochem. J., 1932, **26**, 1624—1627).—These is no parallelism between the reducing capacity and the antiscorbutic activity.

S. S. Z.

Experimental scurvy. XIV. Blood-fatty acids and -lipins of guinea-pigs fed on a vitamin-C-free diet. XV. Changes in the blood of guinea-pigs fed on a vitamin-C-free diet. S. Ohata (J. Biochem. Japan, 1932, **16**, 191—206, 207—215).—XIV. Scurvy is accompanied by an increase of blood-fatty acids (I) and -phospholipins. The cholesterol level (II) remains fairly const. except in severe scurvy, when it decreases. The ratio (II) : (I) is proposed as a criterion of the degree of scurvy for vitamin-C investigations in guinea-pigs.

XV. The H_2O content and the time of coagulation are increased, the serum-proteins are unchanged, while the following factors are decreased to varying degrees: viscosity, red cell and platelet counts, and the contents of hæmoglobin, fibrinogen, thrombin, and cephalin.

F. O. H.

Determination of vitamin-D by means of its growth-promoting property. K. H. Coward, K. M. Key, and B. G. E. Morgan (Biochem. J., 1932, **26**, 1585—1592).—The growth response is graded to the dose of vitamin-D administered, that of the bucks being greater than that of does. Logarithmic equations express the responses of the bucks and does, respectively. Tests of the same substances by the line test and by the growth method give identical results. There is an indication that the rat's need for vitamin-A is greater than its need for vitamin-D.

S. S. Z.

Vitamin-D potency of egg-yolk from irradiated hens. G. H. Maughan and E. Maughan (Brit. J. Phys. Med., 1932, **7**, 137—138).—Ultraviolet irradiation of hens increases the vitamin-D content of the egg-yolk.

W. O. K.

Free fatty acids in cod-liver oil and vitamin-D. O. Schultz (Z. Vitaminforsch., 1932, **1**, 287—289).—Six samples of oil containing from <1 to 20% of free fatty acids were tested for vitamin-D (I) on rats over a period of 2 years. The loss in potency was the same (approx. 30%) for all the oils, indicating that the free fatty acid content does not influence the stability of its (I). With the exception of bleaching, no method of commercial prep. influences the (I) content. F. O. H.

Fertility of bees and vitamin-*E*. L. Hill and E. F. Burdett (Nature, 1932, **130**, 540).—Experiments on the fertility of rats indicate that the secretion (" royal jelly ") from the pharyngeal glands of the bee contains an amount of vitamin-*E* which is absent from honey and pollen. L. S. T.

Action of weak electric currents on chlorophyll assimilation in *Elodea canadensis*. F. Górski (Bull. Acad. Polonaise, 1931, **B**, 85—101).—In all normal cases the assimilation of chlorophyll decreases gradually during the 2 hr. required for an experiment. This gradual decrease is unaffected by the passage of weak electric currents in solutions of various salts, with the exception of $(NH_4)_2SO_4$, which delays it. P. G. M.

Starch synthesis in the variegated leaves of *Pelargonium*. A. G. Chapman and W. H. Camp (Ohio J. Sci., 1932, **32**, 197—217).—Starch synthesis normally does not occur in the non-green portion of the leaf of *P. hortorum*, but occurs if the leaf is placed in (preferably 0·5*M*) glucose solution. Under normal greenhouse conditions green tissue contains approx. twice as much sugar as non-green tissue. The p_H val. or temp. is not the limiting factor of starch synthesis. Ch. Abs.

Mannose and the first sugar of photosynthesis. H. F. Clements (Plant Physiol., 1932, **7**, 547—550).—Mannose was not detectable in leaves of numerous plants. Glucose and fructose are probably produced simultaneously as the initial sugars of the photosynthetic process. A. G. P.

Mechanism of the action of light and other factors on stomatal movement. G. W. Scarth (Plant Physiol., 1932, **7**, 481—504).—All movements of stomata are associated with reversible transformations of carbohydrates and changes of p_H in the guard cells, the latter being largely dependent on the pressure of CO_2 in the immediate environment of the guard cells. Closure of stomata is associated with CO_2 pressure. A. G. P.

Carbohydrate and nitrogen metabolism in the celery plant as related to premature seeding. H. Platenius (New York [Cornell] Agric. Exp. Sta. Mem., 1932, No. 140, 66 pp.).—The accumulation of carbohydrate in growing celery plants was considerably influenced by temp., the starch and sugar contents increasing on transferring plants to a higher temp. During the growing season the total N and carbohydrate contents declined at similar rates. Exposure of young plants to low temp. increased the proportion of protein and decreased that of sol. N. Temp. did not appreciably affect the synthesis of NH_2-acids. There was an inverse relationship between the variations of NO_3' and NH_2-N and, less consistently, between NH_2- and protein-N. The NH_3 content was low throughout growth. Premature seeding can be induced in young plants of low carbohydrate content if exposed to low temp., but does not necessarily occur in plants of high carbohydrate content exposed to medium to high temp. The C : N ratio of the plants was higher in the later stages of growth and was the result of morphological changes. The tendency to seed production is probably unconnected with nutritional factors. A. G. P.

Composition of current and previous season's branch growth in relation to vegetative and reproductive responses in *Pyrus malus*, L. W. Thomas (Plant Physiol., 1932, **7**, 391—445).—The proportions of glucose and sucrose in the current season's growth decreased rapidly during the active season and increased again later. Trees receiving $NaNO_3$ had higher contents of the simple sugars than did unmanured trees in which the inhibition of invertase activity was marked. The starch cycle in the wood lagged behind that in the bark. Swelling of buds was associated with a lowered N content of the bark, especially in trees receiving N. In unmanured trees starch accumulation was high until the autumn, but where $NaNO_3$ was applied the starch content diminished rapidly as growth proceeded. The effect of varied fertiliser treatments on starch and total available carbohydrate contents was in the order N–P–K<N–P<N–K<N<P–K<P<control. Starch utilisation was controlled mainly by the N concn. in the tissues, but was also accelerated by increased K and P concns. resulting in fruit bud formation. The ratio carbohydrate : N is a sensitive index of the physiological balance and was affected by fertiliser treatments in the order N–P–K<N–P<N–K<P–K<P<control. Applications of N and K increased the absorption of P by the trees. Variations in the ratios starch : P_2O_5 and available carbohydrate : P_2O_5 indicated that P favoured an accelerated respiration only if a sufficiency of P and K was present. Fertilisers affected the moisture content of the tissues in the order N–P–K>N–P=N>N–K>P–K>P>control and the ash constituents in the order N–P–K>N–P>N–K>P–K>N>P>control. A. G. P.

Relation of age and seasonal conditions to composition of root, petiole, and leaf blade in rhubarb. C. W. Culpepper and J. S. Caldwell (Plant Physiol., 1932, **7**, 447—479).—The total-solid content of leaf blades decreased rapidly from the emergence of the leaf and reached a stationary val. when growth ceased. In the petioles the decline in total solids during rapid elongation was followed by an increase later in the season. The EtOH-sol. and -insol. solids of leaves and petioles declined steadily through the growing period, but increased later in the petioles. The leaf mesophyll and petioles were practically free from starch throughout growth and their sugar contents were small. Acid-hydrolysable polysaccharides in leaves and petioles varied only to small extents, the % contents being low throughout growth. The titratable acidity of leaves and petioles increased during vigorous growth and subsequently declined. In all stages the petioles were the more acid. Nitrates occurred in small amounts in young leaves and increased considerably after growth was completed. A. G. P.

Influence of nutritive conditions of seeds and cuttings on the development of the roots. M. E. Reid (IX Int. Hort. Cong., 1930, Rep. Proc., 165—169).—The amount of synthesised carbohydrate is important. In addition to furnishing material for respiration and cell growth, carbohydrates may assist in the formation of other types of nutritive compounds. CH. ABS.

Changes in the enzyme content of seeds and fruits. N. N. IVANOV (Biochem. Z., 1932, **254**, 71—87).—The enzyme (catalase, lipase, peroxidase, urease, invertase, amylase) content of seeds and fruits (peas, barley, wheat, soya bean, pumpkin) frequently indicates the degree of physiological ripeness, often decreasing as that degree increases, but geographical and climatic factors as well as the strain of plant used and its chemical composition also affect the content. During artificially accelerated ripening with the aid of low concn. of C_2H_4 the decrease in enzyme content with ripeness is followed by an increase. W. McC.

Wheat as food and seed. G. TALLARICO (Mem. Accad. Italia, 1931, **3**, [Biol. 1], 5—325).—The results of 6 years' (1925 1931) study on qual. graniculture are considered from the static and genetic viewpoints. The caryopsides in their physical, chemical, and biological aspects, and as regards the relation of their vol. to their nutritive val., are discussed. Emphasis is laid on the val. of physiological predetermination, according to which the grain is influenced in its activities by external factors acting during the crit. periods of its existence. T. H. P.

Relationship between soil and associated plants in the Czerwone Wierchy and Bielskie Tatry districts (Tatra mountains). J. WŁODEK, K. STRZEMIENSKI, and E. RALSKI (Bull. Acad. Polonaise, 1931, **B**, 103—122).—*Versicoloretum Tatricum* and *Trifidi-distichetum* grow in a soil richer in humus than that required by *Disticho-versicoloretum*; the first-named requires a soil richer in Ca than the two last. All the plants examined grow in soils which have a reaction varying from strongly acid to mildly alkaline (p_H 3·7—7·1). *Festuca versicolor* and *Sesleria Bielzii* require a soil with relatively high Ca content, in contrast to *Juncus trifidus* and *Sesleria disticha*. P. G. M.

Effects of physical environment on the physicochemical properties of plant saps and the relation of these properties to leaf temperature. G. A. GREATHOUSE (Plant Physiol., 1932, **7**, 349—390).—Changes in the osmotic pressure of leaf juices with age and exposure to various temp. are recorded and discussed. A. G. P.

Determination of the isoelectric point of protoplasts. VI. Precipitation by buffer and salt solutions of varying acidity. VII. Retardation of the pulsation frequency of contractile vacuoles. H. PFEIFFER (Protoplasma, 1932, **16**, 237—243; 244—252).—VI. Microscopical observations of the pptn. of cell colloids by NaOAc solutions buffered to varying extents or containing NaCNS were in accord with vals. for the isoelectric point determined cataphoretically.

VII. The inhibitory effect of alkaloids increased with falling $[H^{\cdot}]$ and that of Na salts of org. acids with rising $[H^{\cdot}]$. Relationships between these observations and the isoelectric point are examined. A. G. P.

Tobacco. VI. Colloid responsible for the water capacity of tobacco. N. I. GAVRILOV and E. I. GINSBERG (Biochem. Z., 1932, **254**, 286—291).—The H_2O capacity of tobacco depends chiefly on substances removed by H_2O at 75°, and to a smaller extent on the H_2O capacity of cellulose. Treatment with C_6H_6 and $CHCl_3$ increases the capacity by removing resinous substances which prevent the diffusion of H_2O into the deeper leaf tissue. P. W. C.

Wood of Spanish *Pinus sylvestris*. L. LEMMEL (Anal. Fís. Quím., 1932, **30**, 601—610).—The work of Wedekind (A., 1931, 941) and others on the phenol- and acetylphenol-lignins has been confirmed. *Pyrogallol-lignin*, m.p. 195—215° after sintering at 183°, is dark violet; the *Ac* derivative has m.p. 150—154° after darkening at 140°. H. F. G.

Red colouring matter of *Hiviscus babdariffa*, L. (new glucoside, hiviscin). R. YAMAMOTO and Y. OSIMA (Sci. Papers Inst. Phys. Chem. Res., Tokyo, 1932, **19**, 134—141).—The dried calyx of the fruits of *H. babdariffa* yield to 1·5% HCl–MeOH an anthocyanin, *hiviscin chloride* (I), +4·5 H_2O, m.p. 192° (2 g. of pure salt from 1·2 kg.) [corresponding *picrate*, m.p. 185° (decomp.)], hydrolysed by HCl (1 : 1) to cyanidin and a dextrorotatory carbohydrate (*phenylosazone*, m.p. 192°; p-*bromophenylosazone*, m.p. 162°), shown by colour reactions to be a pentose. Colour reactions, the distribution no., and the $FeCl_3$ test show (I) to be a 3-pentoside. R. S. C.

Survey of anthocyanins. II. G. M. ROBINSON and R. ROBINSON (Biochem. J., 1932, **26**, 1647—1664).

Determination of starch in plant tissues. R. L. SHRINER (Plant Physiol., 1932, **7**, 541—546).—The method is based on the conversion of starch by taka-diastase followed by a Cu–iodometric determination of the reducing sugars. A. G. P.

Nitrogen fixation in the dead leaves from forest beds. C. OLSEN (Compt. rend. Lab. Carlsberg, 1932, **19**, No. 9, 36 pp.).—N fixation occurs during the decomp. of oak and beech leaves. Addition of $CaCO_3$ increases the amount of N fixed, which is greatest in the range p_H 6·0—7·7, slight at p_H 5·0—6·0, and ceases at p_H 5·0. The fixed N is retained by the organisms until the total N content of the mass reaches approx. 2·2% (about 1 year), when nitrification begins and further fixation ceases. With hornbeam leaves (1·75% total N) decomp. and NH_3 formation begin early and no fixation occurs. A. G. P.

Discoloration of oak leaves resulting from magnesium deficiency. C. BLATTNÝ (Z. Pflanz. Düng., 1932, **26A**, 216—218).—Typical forms of leaf discoloration are described. A. G. P.

Detection of inositol and phytinates. F. FISCHLER and F. H. KÜRTEN.—See this vol., 1270.

Determination of glucose and maltose. M. L. SMITH.—See this vol., 1270.

Determination of histidine. E. JORPES. **Determination of arginine.** E. JORPES and S. THORÉN.—See this vol., 1270.