BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

NOVEMBER, 1931.

General, Physical, and Inorganic Chemistry.

Relationships between the continuous and the many-lined spectra of hydrogen. Y. Hukumoto (Sci. Rep. Tôhoku, 1931, 20, 433—449).—The variations in the intensity of the H spectra in the negative glow, Faraday dark space, and positive column have been followed. A. R. Powell.

Dependence on field strength of intensity and sharpness of lines in the Stark effect components of H_γ. R. Gebauer and H. R. von Traubenberg (Z. Physik, 1931, 71, 291—298).

Broadening of the resonance atomic line of helium. W. Weizel (Physical Rev., 1931, [ii], 38, 642—645).—Asymmetric broadening due to pressure is explained by the shape of the potential energy curves of the two-centre system of two He atoms. N. M. Bligh.

Perturbations in the helium band spectrum. G. H. Dieke (Physical Rev., 1931, [ii], 38, 646—657).

Continuous absorption in lithium and sodium vapours. B. Trumpy (Z. Physik, 1931, 71, 720—734).—The results of an investigation of the boundary continuum of the Li principal series are given. A. J. Mee.

Ultra-violet absorption spectrum of fluorine. H. von Wartenberg, G. Sprenger, and J. Taylor (Z. physikal. Chem., Bodenstein Festband, 1931, 61—68).—The ultra-violet absorption curve of F exhibits a max. at 2900 Å. Combination of this figure with the difference between the convergence and max. absorption wave-lengths obtained by extrapolation from the values for the other halogens yields for the convergence wave-length 4470 ± 50 Å., which corresponds with a heat of dissociation of $63\cdot3\pm0\cdot6$ kg.-cal. Although the conditions are comparatively favourable for the processes which would be involved, H_2 and F_2 do not unite as a result of exposure to radiation from a spark between Mg electrodes, except in as far as the reaction on the walls is favoured by the increased circulation of the gases. H. F. Gillbe.

Emission spectrum of sodium hydride. T. Hori (Z. Physik, 1931, 71, 478—531).—The emission spectrum, extending from 3540 to 5050 Å., is more complicated than the absorption spectrum. The analysis can be carried out only with the aid of the absorption spectrum. The moment of inertia of the normal state is $5\cdot65\times10^{-40}$ g.-cm.^{2}, that of the excited state $14\cdot66\times10^{-40}$ g.-cm.^{2} A. J. Mee.

Spectra of metals obtained by explosive reactions. T. Tucholski (Bull. Acad. Polonaise, 1931, A, 76—105).—Spectra from the detonation of the picrates of Na, K, Ca, Ba, Cu, and Fe with collodion and gelatin have been obtained and the temp. of explosion has been calc. W. R. Angus.

Low-voltage excitation of sodium. W. C. Michels (Physical Rev., 1931, [ii], 38, 712—717).—Using a new type of tube, the optical excitation function of the resonance lines in Na vapour excited by low-velocity electron impact was investigated for the range 1·8—4·2 volts. N. M. Bligh.

***f*-Values (oscillator strengths) of the *D*-lines from line-absorption measurements.** W. Zehden (Naturwiss., 1931, 19, 826—827; cf. A., 1928, 805; 1929, 1119).

Examination with large dispersion of a typical case of multiplet resonance in the vapour of diatomic sulphur. P. Swings and A. Legros (Bull. Acad. roy. Belg., 1931, [v], 17, 808—811).—Using the 2967·64 Hg line as exciting ray the resonance spectrum of S_2 vapour has been examined. W. R. Angus.

General formulation of the absorption bands of sulphur vapour. J. Genard (Bull. Acad. roy. Belg., 1931, [v], 17, 812—815).—The author's equation (*ibid.*, 387) and that of Christy and Naudé (this vol., 779) agree well with experimental data. Predissociation begins with $n'=10$. W. R. Angus.

Rotation quantum numbers of the resonance doublets of sulphur. P. Swings (Bull. Acad. roy. Belg., 1931, [v], 17, 972—974).—The rotation quantum numbers corresponding with the doublets in the spectrum of S excited by various Hg lines have been calc. as 9, 20, 46, and 47. The optimum rotation quantum no. is 25. J. W. Smith.

Intensities of the components of the rotation doublets in the resonance spectrum of sulphur. P. Swings (Bull. Acad. roy. Belg., 1931, [v], 17, 956—971).—Some regrouping of the rotation doublets observed in the S_2 spectrum excited by Hg arc is suggested. J. W. Smith.

Zeeman effect of quadrupole radiation. E. Segrè and C. J. Bakker (Naturwiss., 1931, 19, 738).—The Zeeman effect in K has been studied longitudinally and obliquely ($\alpha=45°$). W. R. Angus.

Nuclear spin of potassium. F. W. Loomis and R. W. Wood (Physical Rev., 1931, [ii], 38, 854—856).—Photographs of certain bands in the absorption spectrum of the K mol. show branches with alternating intensities. The phenomenon of alternating missing lines does not occur, showing that the nuclear spin of K^{39} is not zero. N. M. Bligh.

Fluorescence radiation of manganese vapour. J. Fridrichson (Bull. Acad. Polonaise, 1931, **A**, 69—75).—The fluorescence of Mn vapour which has been heated to 700—800° and excited by a Mn spark consists of two sets of triplets. Only the longer wave-length triplet is produced by excitation with various light sources. W. R. Angus.

Fine structure of the spectrum lines of the zinc arc in vacuum and the energy levels of zinc. W. Mohammad and P. N. Sharma (Phil. Mag., 1931, [vii], **12**, 726—728).—A revision of an earlier investigation (cf. this vol., 7). F. J. Wilkins.

Comparison of sources for zinc resonance radiation. A. C. G. Mitchell (J. Franklin Inst., 1931, **212**, 305—316).—Three sources are described and compared. H. J. Emeléus.

Structure of the spectrum Se III. J. S. Badami and K. R. Rao (Nature, 1931, **128**, 496).—A system of energy levels characteristic of the spectrum of Se III has been identified. L. S. Theobald.

First spark spectrum of rubidium (Rb II). O. Laporte, G. R. Miller, and R. A. Sawyer (Physical Rev., 1931, [ii], **38**, 843—853).—Ultraviolet and visible spectra were photographed; wavelengths, separations, classifications, and intensities are tabulated for 121 lines. The ionisation potential of Rb II is 27·3 volts. N. M. Bligh.

First spark spectrum of indium, In II. R. J. Lang and R. A. Sawyer (Z. Physik, 1931, **71**, 453—459).—The term analysis of In II singlet and triplet terms resembles that of Al II and Ga II. The ionisation potential derived from the lowest term is 18·79 volts. A. J. Mee.

Nuclear moment of the indium atom. J. C. McLennan, (Miss) E. J. Allin, and K. E. Hall (Proc. Roy. Soc., 1931, **A**, **133**, 333—335).—Lines in the ultra-violet region of the arc spectrum of In have been studied, using a quartz Lummer plate. I is probably $\frac{1}{2}h/2\pi$. L. L. Bircumshaw.

Fine structure in the arc spectra of indium and thallium. A. L. Narayan (Nature, 1931, **128**, 675).—Measurements of fine structure of the lines 4511, 4101, 3259, and 3256 Å. support Jackson's complex structure for In (A., 1930, 1075); the probable val. of the nuclear moment is 5/2 or 7/2. The nuclear moment of ½ for Tl is confirmed (cf. A., 1929, 1354). L. S. Theobald.

Spark spectrum of tellurium. Te IV and Te VI. K. R. Rao (Proc. Roy. Soc., 1931, **A**, **133**, 220—228).—The spectrum has been examined in the region 1500—500 Å., and photographs of discharges through Te vapour in capillary tubes have been taken in the region 4000—2200 Å. The ionisation potentials are Te IV 37·7 and Te VI 72·0 volts approx. L. L. Bircumshaw.

Remarkable resonance series in the vapour of diatomic tellurium. A. Legros (Bull. Acad. roy. Belg., 1931, [v], **17**, 816—822).—The resonance spectrum excited in Te vapour by the 4481 Å. line of a Mg spark consists of five anti-Stokes lines and some 30 positive terms. W. R. Angus.

New resonance series in diatomic tellurium vapour. J. Pierard (Bull. Acad. roy. Belg., 1931, [v], **17**, 974—979).—On illumination with a condensed spark between Pb electrodes, Te_2 vapour at about 750° shows intense fluorescence. Two series have been measured, excited by the spark lines 4058 and 4248 Å. respectively. J. W. Smith.

Nuclear moment of cæsium. H. Barth and W. Schütz (Naturwiss., 1931, **19**, 774).—The nuclear moment of Cs, calc. from the intensity ratio of the hyperfine structure components of the Cs blue doublet, is 3/2. W. R. Angus.

Fluorescent excitation of mercury by the resonance frequency and by lower frequencies. Further studies. (Lord) Rayleigh (Proc. Roy. Soc., 1931, **A**, **132**, 650—666; cf. A., 1929, 1207).—The fluorescence of Hg vapour is excited by light of the frequency of the core of the resonance line 2537 (core excitation), and light of less frequency absorbed in the band which begins at the resonance line (wing frequency). L. L. Bircumshaw.

Triple-spectrum discharge tube. R. W. Shaw and G. B. Sabine (Science, 1931, **74**, 179).—The construction of an inexpensive substitute for a Hg-vapour lamp is described. Three distinct types of discharge can be obtained. L. S. Theobald.

Band absorption of mercury vapour in the extreme ultra-violet. N. Kremenevski (Z. Physik, 1931, **71**, 792—797).—Continuous bands were observed at 1850, 1807, 1694, 1403 Å. In the region of the Steubing fluorescence bands a series of diffuse absorption bands converging to 1900 Å. was found. A. J. Mee.

Ultra-ionisation potentials in mercury vapour. A. G. Shenstone (Physical Rev., 1931, [ii], **38**, 873—875). N. M. Bligh.

Effect of temperature on the continuous band spectrum of mercury vapour. W. M. Nielsen (Physical Rev., 1931, [ii], **38**, 888—898).—The structure and intensities of the 4850 and 3300 Å. bands are described. N. M. Bligh.

Hyperfine structure of thallium II. J. B. Green and J. Wulff (Nature, 1931, **128**, 409).—Details of a magnetic analysis are recorded. L. S. Theobald.

Isotopic displacement in hyperfine structure. J. H. Bartlett, jun. (Nature, 1931, **128**, 408—409).—A discussion relating to Tl. L. S. Theobald.

Hyperfine structure of thallium II. H. Schuler and J. E. Keyston (Nature, 1931, **128**, 409—410).—McLennan and Crawford's failure to discover an isotope effect (this vol., 993) is due to the limited resolving power employed. L. S. Theobald.

Resonance series of bismuth vapour. J. Parys (Z. Physik, 1931, **71**, 807—813).—The fluorescence spectrum of saturated Bi vapour at 800° consists of three doublet series. A. J. Mee.

Sparking potential of air for high-frequency discharges. E. W. B. Gill and R. H. Donaldson (Phil. Mag., 1931, [vii], **12**, 719—726).—The sparking potential of air for high-frequency discharges has been studied at different pressures with the electric field

parallel to the axis of the discharge tube, or at right angles to it. The results are discussed.
F. J. Wilkins.

Stark effect in band spectra. B. Svensson (Z. Physik, 1931, **71**, 450—452).—The four CO bands at 4835, 4511, 4393, and 4123 Å. have been studied; they show no appreciable splitting or displacement.
A. J. Mee.

Theory of hyperfine structure. G. Racah (Z. Physik, 1931, **71**, 431—441).—The causes of the deviations noted between experiment and theory in the case of hyperfine structure are investigated. The experimental deviations cannot be completely explained.
A. J. Mee.

Intensity changes of hyperfine structure. H. Schüler and J. E. Keyston (Z. Physik, 1931, **71**, 413—415).—Using identical light sources, but different excitation conditions, considerable intensity changes in the hyperfine structure of Cd, Tl, and Hg have been found.
A. J. Mee.

Intensity summation rules and perturbation effects in complex spectra. G. R. Harrison and M. H. Johnson, jun. (Physical Rev., 1931, [ii], **38**, 757—778).—Intensity rules and formulæ are summarised, and a new *J*-group sum rule is derived and discussed.
N. M. Bligh.

High-power source of continuous ultra-violet spectrum. G. B. Kistiakowsky (Rev. Sci. Instr., 1931, [ii], **2**, 549—550).—A modified form of the hydrogen discharge tube of Bay and Steiner (A., 1927, 1117) is described.

Evidence for the spin of the photon from light scattering. G. Placzek (Nature, 1931, **128**, 410).
L. S. Theobald.

Relation of line absorption and brightness of spectral lines. W. Schütz (Z. Physik, 1931, **71**, 301—305).—The curves show a min. which is explained by the Doppler effect.
A. B. D. Cassie.

Energy relations in complex spectra. D. R. Inglis (Physical Rev., 1931, [ii], **38**, 862—872).
N. M. Bligh.

Electrodeless discharge: method of measuring induced current; variation of current with pressure for various gases. C. T. Knipp and J. K. Knipp (Physical Rev., 1931, [ii], **38**, 948—954).
N. M. Bligh.

Output of fluorescence in the *L*-region. G. von Hevesy and E. Alexander (Naturwiss., 1931, **19**, 825—826).
C. A. Silberrad.

Simple theory of *X*-ray spectra according to wave mechanics. V. S. Vrkljan (Z. Physik, 1931, **71**, 403—411).—An attempt to form a theory of *X*-ray spectra analogous to that of the optical spectra of He and ionised Li.
A. B. D. Cassie.

Interference bands of large path differences. E. Lau (Ann. Physik, 1931, [v], **10**, 71—80).—These are produced with the aid of the multiplex-interference spectroscope.
W. Good.

Diffraction of cathode rays by thin films. E. T. Jones (Phil. Mag., 1931, [vii], **12**, 641—657).—Films of Au and celluloid were used.
F. J. Wilkins.

Diffuse scattering of *X*-rays from sylvine. G. G. Harvey (Physical Rev., 1931, [ii], **38**, 593—603; cf. this vol., 896).—Regarding the sylvine crystal as consisting of one kind of A-like atoms, values of the scattered intensity at room temp. are obtained, and when plotted as a function of the scattering angle and wave-length give a curve similar to that for rock-salt. The curve is compared with that of Wollan for A (cf. this vol., 781).
N. M. Bligh.

Effect of temperature on the intensity of *X*-rays diffusely scattered from rock-salt. W. D. Claus (Physical Rev., 1931, [ii], **38**, 604—617).—Scattered intensity ratios for the temp. range 120—750° abs. preclude the Debye formula for the decrease in intensity with fall of temp., agree with Waller's modified formula at low temp., and satisfy the formula of Jauncey and Harvey (this vol., 896) at the higher temp.
N. M. Bligh.

Shape of the Ag-*L*, Mo-*K*, and Cu-*K* lines. R. C. Spencer (Physical Rev., 1931, [ii], **38**, 630—641).—Using the double *X*-ray spectrometer, components, widths, separations, and intensities were investigated.
N. M. Bligh.

Reflexion of *X*-rays in thin sheets. E. Nähring (Physikal. Z., 1931, **32**, 730—733).—With small angles of reflexion the reflective power of thin sheets of Ag and Pt is greater than that of thick sheets.
W. R. Angus.

Intensity of total scattering of *X*-rays by gases. I, II. Y. H. Woo (Proc. Nat. Acad. Sci., 1931, **17**, 467—475).—The general theory of the intensity of total scattering of *X*-rays by a polyat. mol. is considered on the assumption that only the coherent scattered radiations from the different atoms will interfere with each other, whilst the incoherent radiation will be simply added up.

II. The theory is applied to Barrett's experiments on the scattering of *X*-rays by O_2 and N_2 for various wave-lengths.
A. J. Mee.

Scattering by diatomic gases. E. O. Wollan (Proc. Nat. Acad. Sci., 1931, **17**, 475—479).—The theoretical work of Woo (cf. preceding abstract) is applied to the scattering data of the author for A, Ne, O_2, H_2, and N_2.
A. J. Mee.

Reflexion of long *X*-rays. C. B. O. Mohr (Proc. Roy. Soc., 1931, **A**, **133**, 292—303).—The refractive indices of long wave-length *X*-rays have been investigated by the total reflexion method, using a vacuum spectrograph.
L. L. Bircumshaw.

Reflexion and diffraction of *X*-rays. T. H. Laby and R. T. W. Bingham (Proc. Roy. Soc., 1931, **A**, **133**, 274—291).—Experiments are described which verify the existence of reflexion at angles greater than the calc. crit. angle. The intensity of reflexion of C radiation from a glass mirror has been determined.
L. L. Bircumshaw.

Vacuum spectrometer for long wave-length *X*-rays. R. T. W. Bingham (Proc. Roy. Soc., 1931, **A**, **133**, 266—274).—The Seeman form of spectrometer is used, together with a method of measuring angles on a single circle. The instrument is used to measure the wave-length of the Al-$K\alpha_{12}$ line relative to the 5th and 6th orders of the Cu-$K\alpha_{12}$ doublet, using a sugar crystal. L. L. Bircumshaw.

Fine structure of the K-absorption edge of potassium. G. A. Lindsay (Z. Physik, 1931, 71, 735—738).—Determinations of the K-absorption of potassium have been carried out by reflexion from crystals of KCl, KBr, and KI. A. J. Mee.

Satellites of the M-series X-ray lines. F. R. Hirsh, jun. (Physical Rev., 1931, [ii], 38, 914—924).—Four satellites of the diagram line $M\alpha_1$ in the at. no. range U (92)—Yb (70), and 3 of the line $M\beta$ in the range U (92)—Gd (64) were measured and revealed, respectively, two satellites each, not previously reported. N. M. Bligh.

New effect produced by action of X-rays on matter. G. I. Pokrowski (Physical Rev., 1931, [ii], 38, 925—930).—The weak radioactivity acquired by Sn, W, Hg, Pb, and Bi after irradiation by X-rays was investigated by measurement of ionisation produced by the sample, and by counting scintillations produced by emitted particles. The mean energy of each emitted particle is of the order 10^{-6} erg, indicating a nuclear origin. N. M. Bligh.

New form of Geiger point counter. M. Steenbeck (Z. Physik, 1931, 71, 422—430).—A counter is described which will indicate single quants, and for a single charge deals with about 100 times the charge of the former instrument. A. J. Mee.

Counting device for use with the Geiger counter. J. C. Jacobsen (Nature, 1931, 128, 674). L. S. Theobald.

Application of the point counter for determination of external photo-electric effect. H. Bauer (Z. Physik, 1931, 71, 532—550).—The use of the counter for determining the no. of electrons discharged from a surface (metal or insulator) by the action of light is described. The position of the long-wave limits for the vaporised metals Au, Ag, Cu, Zn, Pb, Cd, and Al in vac. and for a variety of insulators was determined. A. J. Mee.

Physico-chemical nature of metal surfaces in the selective photo-electric emission of alkali metals. R. Suhrmann (Z. Elektrochem., 1931, 37, 678—682).—When K is exposed to the vapour of a substance which reacts feebly with it and a layer of K is subsequently condensed on the surface there is a selective max. in the photo-electric emission for certain wave-lengths. The position of the max. depends on the thickness of the intermediate layer of K compound and its intensity on the degree of subdivision of the surface layer of K. The ready reactivity and volatility of the alkali metals suggest that the observed selective max. in photo-electric emission can be traced to this cause. E. S. Hedges.

Photo-electric properties of potassium surfaces under the influence of hydrogen atoms. S. Rijanov (Z. Physik, 1931, 71, 325—338).—The photo-electric sensitivity of K increases to 20—40 times its original val. in an atm. of H_2, and then diminishes. The H atoms adsorbed increase to 3×10^{16} per sq. cm. and then remain const. A. B. D. Cassie.

Selective photo-effect and light absorption. R. Fleischmann (Naturwiss., 1931, 19, 826). C. A. Silberrad.

Ionisation of Kr and Xe by positive alkali ions and the ionisation potentials of Ne, A, Kr, and Xe. O. Beeck and J. C. Mouzon (Physical Rev., 1931, [ii], 38, 967—968; cf. this vol., 542).—The most efficient ionisers are Cs^+ for Xe, K^+ and Rb^+ for Kr; K^+ is more efficient than Rb^+ for Xe, and Rb^+ is slightly less efficient than K^+ for A. N. M. Bligh.

Cathode sputtering in mercury vapour at very low pressures. K. Meyer and A. Günther-Schulze (Z. Physik, 1931, 71, 279—290).—The quantity of metal sputtered from a cathode surface in Hg vapour is independent of pressure near 0·005 mm. It is proportional to lower voltages across the tube, and at 1000 volts each Hg ion liberated one atom from Al, Si, Mn, Fe, Ni, Zr, Mo, Ta, and W cathodes, but Be, Co, Cr, Cu, Pd, Pt, and Ag showed no such relation. A. B. D. Cassie.

Electron terms of the hydrogen molecule. E. A. Hylleraas (Z. Physik, 1931, 71, 739—763).—Theoretical. A comparatively simple method is given for calculating the characteristic function of H ions and the electron terms of the excited H_2 mol. A. J. Mee.

Excitation probabilities for electrons in helium, neon, and argon. L. C. Van Atta (Physical Rev., 1931, [ii], 38, 876—887).—Energy losses for electrons scattered inelastically in He, Ne, and A were determined as 21·13±0·04, 16·64±0·05, and 11·53±0·05 volts, respectively. N. M. Bligh.

Numerical calculations of atomic scattering factors. R. W. James and G. W. Brindley (Phil. Mag., 1931, [vii], 12, 729).—Correction of errors of an earlier paper (cf. this vol., 889). F. J. Wilkins.

Structure of absorption constants of light elements measured by means of the electron counting tube. H. Neufeldt (Z. Physik, 1931, 71, 412).—Errors in a previous paper (this vol., 781) are corrected. A. B. D. Cassie.

Diffraction experiments with very fast electrons. E. Rupp (Ann. Physik, 1931, [v], 10, 927—946).—The "atom form" factor for Au with electrons of 220 kv., the appearance of a new type of diffraction rings which can be characterised by fractional nos., and the proof of the de Broglie relation from voltage measurements in the region 100—250 kv. are dealt with. W. R. Angus.

Augular distribution of electrons scattered by gas molecules. C. Ramsauer and R. Kollath (Ann. Physik, 1931, [v], 10, 143—154).—An extension of previous investigations (cf. this vol., 782) to Ne, Kr, Xe, N_2, CO, CO_2, and CH_4. W. Good.

Energy loss and scattering of electrons by passage through gases. II. Neon and argon. M. Renninger (Ann. Physik, 1931, [v], 10, 111—128).—In essentials the results for Ne and A are similar to those for N_2 (cf. this vol., 782) and are not more favourable than the latter for comparison with Bethe's calculations. W. Good.

Polarisation of a beam of electrons by scattering. N. F. Mott (Nature, 1931, **128**, 454).
L. S. Theobald.

Electronic charge. W. N. Bond (Phil. Mag., 1931, [vii], **12**, 632—640; cf. this vol., 143).—The previous method has been applied to more extensive data, with the following results: $e=(4{\cdot}779_4\pm0{\cdot}001_1)\times10^{-10}$ abs. e.s. units, $h=(6{\cdot}558_6\pm0{\cdot}003_1)\times10^{-27}$ erg sec., $e/m=(1{\cdot}769_0\pm0{\cdot}004_6)\times10^7$ abs. em. unit g.$^{-1}$; $M_P/m=1846{\cdot}5_7\pm0{\cdot}4_8$, which differs from Eddington's val. of $(136)^2/10$ by more than six times the probable error. The val. of $hc/2\pi e^2$ is $137{\cdot}01\pm(0{\cdot}05_9\pm0{\cdot}00_5)$, agreeing with Eddington's val. of 137.
F. J. Wilkins.

Diffraction of electrons by single crystals. G. P. Thomson (Proc. Roy. Soc., 1931, **A**, **133**, 1—25).—A detailed investigation has been made of the diffraction of electrons of 30—50 kv. by single crystals of Cu and Ag. The usual wave theory is extended to account for the diffraction patterns observed by assuming the etched surface of the crystal to consist of a series of lumps, through which the electrons can pass, of the order of 10^{-6} cm. in linear dimensions. Close agreement exists between theory and experiment, even in the case of certain irregular "exceptional" patterns. There is a complete absence of forbidden reflexions and half orders. Experiments with Cu electrolytically deposited on the etched surface of single crystals of Cu showed that the spacing of part at least of the added substance is larger than that of normal Cu, although the structure is roughly similar; that the deposited surface usually follows the orientation of the original crystal; and that certain spots appear which would correspond with "forbidden" planes of Cu. Diffraction patterns are produced from a cleavage face of rock-salt, and also strong Kikuchi lines. The depth of penetration of the rays is of the order of 10^{-7} cm.
L. L. Bircumshaw.

Focussing method for producing electron diffraction patterns. A. A. Lebedeff (Nature, 1931, **128**, 491).—Details are given and electron diffraction patterns for NaCl, Au leaf, paraffin, and a Au film produced by cathodic sputtering are reproduced. L. S. Theobald.

Diffraction of electrons by thin films of nickel and copper oxide. J. A. Darbyshire (Trans. Faraday Soc., 1931, **27**, 675—678).—The electron diffraction spectra of the oxide films formed on the surface of Ni and Cu by heating correspond with those of the usual cryst. forms of NiO and Cu_2O. There is no evidence of the presence of metal. R. Cuthill.

Ageing of ions in air and nitrogen. J. Zeleny (Physical Rev., 1931, [ii], **38**, 969—976; cf. A., 1930, 1231).—The mobilities of ions at different short ages in air and N_2 were investigated. With increase of age the negative ions of short age and high mobility transform into slower ions. The slow decrease of mobility with age, and the large effect of slight changes of gas composition on the rate of this decrease, indicate a gradual change of size of the ions.
N. M. Bligh.

Reflexion of mercury from alkali halide crystals. H. A. Zahl and A. Ellett (Physical Rev., 1931, [ii], **38**, 977—997).—The distribution of Hg atoms scattered from NaCl, KCl, KBr, and KI was investigated as a function of the angle of incidence and temp. of the scatterer and incident beam.
N. M. Bligh.

Structure of films from molecular rays. K. Coper, L. Frommer, and H. Zocher (Z. Elektrochem., 1931, **37**, 571—577).—A description is given of the appearance and structure of thin films of Ag, Au, Cu, Pt, Cd, PbO, B_2O_3, NaCl, AgCl, CaF_2, and $CrCl_3$ prepared by the rapid condensation of the vapours of these substances in vac. In general, the films consist of inhomogeneous, non-spherical particles.
E. S. Hedges.

Density of ions at a polarised electrode. K. Teige (Chem. Listy, 1931, **25**, 277—278).
R. Truszkowski.

Properties of atomic layers. P. Lukirski, A. Sosina, S. Vekschinski, and T. Zareva (Z. Physik, 1931, **71**, 306—324).—Two methods of determining surface potentials by means of electron emission are described. Qual. measurements indicate that unimol. layers of Ba and Th lower the work function of the surface, and that the work function for any greater thickness is the same as that for a bimol. layer. Evaporation to a unimol. layer is much more readily attained than evaporation of the unimol. layer itself. A. B. D. Cassie.

Relative abundances of isotopes. H. C. Urey and C. A. Bradley, jun. (Physical Rev., 1931, [ii], **38**, 718—724).—To distinguish two types of nuclear stability, thermodynamic calculations are made for certain isotopic transmutation reactions. Results indicate that at. nuclei on earth do not represent an equilibrium mixture at any temp. N. M. Bligh.

Relative amounts of lithium isotopes, Li^7 and Li^6. H. Schüler (Naturwiss., 1931, **19**, 772).—The ratio of Li^7 to Li^6 isotopes is calc. from the intensities of hyperfine structure of the components of the Li^+ line at 5485 Å. The val. 10·5 is in good agreement with Aston's val. of 10·2±0·5. W. R. Angus.

Isotope separation in the spectra of Li I. D. S. Hughes (Physical Rev., 1931, [ii], **38**, 857—861; cf. A., 1930, 1328).—A faint isotope component was found on the long wave-length side of the lines 6708 and 3232 Å., the measured separation of this component and the doublet being in good agreement with the calc. separation of the Li^6 and Li^7 lines. The line 6104 Å. showed no components other than the regular doublet. N. M. Bligh.

Isotopes of lithium, sodium, and potassium. K. T. Bainbridge (J. Franklin Inst., 1931, **212**, 317—339).—Magnetic analysis of the positive rays of Li from a heated spodumene source shows no change with temp. in the relative abundance of Li^7 and Li^6. The isotopes Na^{21}, Na^{22}, Na^{25}, K^{40}, K^{42}, and K^{43} were found to occur only in very small amounts, if at all.
H. J. Emeléus.

At. wt. of fluorine. H. S. Patterson, R. Whytlaw-Gray, and W. Cawood (Nature, 1931, **128**, 375).—The at. wt. of F obtained from density measurements on MeF by the method used for Xe (this vol., 890) is 19·013 (C 12·010). The presence of small quantities of a higher isotope of F is suspected. The compressibility coeff. $1+\lambda$ of MeF at 21° is 1·00823. Moles and Batuecas' vals. for this coeff. and for density are too high. L. S. Theobald.

Isotopic constitution and at. wt. of selenium, bromine, boron, tungsten, antimony, osmium, ruthenium, tellurium, germanium, rhenium, and chlorine. F. W. Aston (Proc. Roy. Soc., 1931, **A**, **132**, 487—498).—By means of photometry of the mass spectra of a no. of elements, the no. and relative abundance of their isotopes have been obtained. Twenty new isotopes were discovered and the magnitude of many new packing fractions has been determined, including that of Si. At. wts. obtained by correcting the mean mass no. for the packing fraction and change to the chemical scale are: Se 78·96±0·04, Br $79{\cdot}916_5$±0·002, B 10·806±0·01, W 183·96, Sb 121·79, Os 190·31±0·06, Ru 101·1, Te 128·03±0·1, Ge 72·65±0·05, Rh 186·22±0·07. Most of these are in good agreement with the accepted chemical vals. but in the case of Se, Te, and Os the discrepancies are serious. L. L. Bircumshaw.

Fundamental at. wts. X. At. wt. of iodine. O. Hönigschmid and H. Striebel (Z. physikal. Chem., Bodenstein Festband, 1931, 283—290).—Determination of the ratio AgI : AgCl yielded for the at. wt. of I 126·917 (O=16). The AgI was prepared by heating Ag in I vapour and decanting the liquid salt from the excess of metal; the conversion into AgCl was effected by Cl_2 at 80—100°. H. F. Gillbe.

Apparatus for preparing Ra-*B*+*C* sources. L. F. Curtiss (Bur. Stand. J. Res., 1931, 7, 215—218).—In the "emanation pipette" Hg has to pass through the capillaries of glass stop-cocks and through rubber tubing. These defects are remedied in an all-glass apparatus which is described and has been used for prep. of Ra-*B* and Ra-*C* from radon. W. R. Angus.

Purification of radon. J. Bannon (J. Cancer Res. Comm. Sydney, 1931, 3, 86—89).—A liquid-air radon purification apparatus is described in which H_2 and O_2 are first removed by sparking, and the H_2O is absorbed by P_2O_5. C. C. N. Vass.

Radioactivity of potassium. G. von Hevesy, W. Seith, and M. Pahl (Z. physikal. Chem., Bodenstein Festband, 1931, 309—318).—Comparison of the activities of normal and "heavy" KCl demonstrates that the radioactivity of K cannot be ascribed to an isotope of at. wt. 40. The degradation of K is discussed. H. F. Gillbe.

Structure of atomic nuclei. H. Becker and W. Bothe (Naturwiss., 1931, **19**, 753).—The calculation of the energy of Be γ-radiation (A., 1930, 1086) is made. E_γ, the energy of a γ quantum, is equal to $E_C-E_{Be}+3{\cdot}6$ (10^6 e-volts) in agreement with the Gamow scheme of mass defects and quantum-mechanical theory of at. nuclei. W. R. Angus.

Properties of the electron and the behaviour of radioactive substances. R. D. Kleeman (Z. anorg. Chem., 1931, **199**, 225—234). H. F. Gillbe.

Theory of the effect of resonance levels on artificial disintegration. N. F. Mott (Proc. Roy. Soc., 1931, **A**, **133**, 228—240).—Calculations are made of the effective area a (E) that an α-particle must hit to eject a proton, being itself captured, and the area that it must hit in order that it shall be scattered into a given solid angle. The circumstances in which a resonance level should occur are investigated, and its breadth is estimated. L. L. Bircumshaw.

Ionisation produced by radon in spherical vessels. G. Glockler and G. B. Heisig (J. Physical Chem., 1931, **35**, 2478—2491; cf. A., 1927, 1003).—Theoretical. L. S. Theobald.

Protoactinium. O. Hahn and L. Meitner (Naturwiss., 1931, **19**, 738).—Attention is directed to the early work of Hahn and Meitner and of Soddy and Cranston. W. O. Kermack.

Position of uranium-*Z* in the uranium disintegration series. E. Walling (Z. physikal. Chem., 1931, **B**, **14**, 290—296).—Hahn's conclusions (A., 1921, ii, 478; 1923, ii, 111) as to the parent substance and its dual disintegration are confirmed, and his view that the product is U II is supported. N. H. Hartshorne.

Destruction of zinc sulphide phosphors by α-rays. P. M. Wolf and N. Riehl (Ann. Physik, 1931, [v], 11, 103—112).—The diminution of the luminescence of ZnS phosphors by the action of α-rays is examined for different phosphors. The rate of change of the phosphor is independent of the source or method of prep. It is rather a sp. property of the compound ZnS. Dry ZnS is unaffected by β- or γ-rays. The destruction of a Lenard centre is not a result of the process of scintillation. The centre can be excited many times by α-particles without destruction taking place. A. J. Mee.

Hard component of the β-radiation of potassium. D. Bocciarelli (Nature, 1931, **128**, 374—375).—Data obtained for KCl and KBr by Occhialini's method indicate the existence of a less intense, hard component of the β-radiation of K. L. S. Theobald.

Contribution to the study of β-rays by the method of magnetic spectra. J. d'Espine [with (in part) D. K. Yovanovitch and (Mlle.) I. Curie] (Ann. Physique, 1931, [x], **16**, 5—70).—The apparatus and technique for the investigation of the magnetic spectra of β-rays from different sources are described and discussed. Magnetic spectra of β-rays from Ra-*B*+*C*, Ra-*E*, mesothorium 2, and Th-*B* and -*C* have been obtained. Thin-walled glass ampoules of radon were used as source of Ra-*B*+*C* and the spectra of β-rays of different velocities are given. The results are considered in the light of different theories of at. structure and the mechanism of radioactive transformation is discussed. W. R. Angus.

Biological effects of cosmic and γ-radiation. J. H. Orton and S. T. Burfield (Nature, 1931, **128**, 376).—Speculative. L. S. Theobald.

Origin of the γ-rays. (Lord) Rutherford and C. D. Ellis (Proc. Roy. Soc., 1931, **A**, **132**, 667—688).—Measurements of the energies of the long-range α-particles from Ra-*C* render it almost certain

that the γ-rays are associated with transitions of α-particles in the nucleus. It is assumed that the α-particles form a normal quantum-mechanical system capable of existing temporarily in a series of stationary states, the energy differences of which are shown by the γ-rays and groups in the β-ray spectrum. Using a nuclear model in which different nos. of α-particles are excited to the same quantum state, an equation is deduced for the energies set free in transitions. This receives support from experiment.
L. L. Bircumshaw.

Quantum-mechanical models of a nucleus. R. H. Fowler (Nature, 1931, **128**, 453—454).—A theoretical investigation of models of a nucleus consisting of some 50 α-particles. L. S. Theobald.

Effect of γ-rays on velocity of radioactive disintegration. O. Reinkober (Z. Physik, 1931, **71**, 460—464).—No effect was found. A. J. Mee.

Nuclear absorption of hard γ-rays. C. Y. Chao (Naturwiss., 1931, **19**, 752).—Investigations on the scattering of the γ-radiation of Th-C'' have demonstrated a new scattered radiation in heavy elements accompanied by a change in wave-length. This results from a nuclear process.
W. R. Angus.

Scattering law for short wave γ-radiation. (Frl.) L. Meitner and H. H. Hupfeld (Naturwiss., 1931, **19**, 775—776).—A preliminary account of an extension of earlier work (A., 1930, 976).
W. R. Angus.

Absorption of penetrating γ-rays by lead screens of 12 to 30 cm. thickness. A. Piccard, E. Stahel, and F. Dony (Compt. rend., 1931, **193**, 526—527).—Comparison of the γ-radiation of Ra-C passed through Pb screens of thickness of 12—30 cm., before and after subsequent passage through a Pb filter 1·5 cm. thick, shows the same relative difference irrespective of the screen thickness. There is therefore no ultra-penetrating component in this radiation, and the explanation of cosmic radiation thereby is negatived. C. A. Silberrad.

Photo-electric effect for γ-rays. H. R. Hulme (Proc. Roy. Soc., 1931, **A**, **133**, 381—406).—Mathematical.

Oxidisable "active nitrogen." E. J. B. Willey and S. G. Foord (Nature, 1931, **128**, 493).—Experiments with N_2 and N_2–O_2 mixtures failed to reveal any oxidisable modification of N_2 or any nitrogen oxide which reacts only with O_3 and not with O_2. Increased yields of NO_2 do result, however, when the air is ozonised before or treated with O_3 after it is sparked (cf. J.C.S., 1912, **101**, 1152).
L. S. Theobald.

Absorption and diffusion of penetrating corpuscular radiation in lead and in iron. B. Rossi (Atti R. Accad. Lincei, 1931, [vi], **13**, 600—606).

Value of the cosmical constant. (Sir) A. Eddington (Proc. Roy. Soc., 1931, **A**, **133**, 605—615).

Corpuscular explanation of cosmic rays. F. Soddy (Nature, 1931, **128**, 408).—A criticism.
L. S. Theobald.

Measurements on the absorption of the penetrating corpuscular rays coming from inclined directions. B. Rossi (Nature, 1931, **128**, 408).—The inclined appear to be softer than the vertical rays.
L. S. Theobald.

Atmosphere of the planet Venus. E. Schoenberg (Sitzungsber. preuss. Akad. Wiss., 1931, **21**, 1—36).—The distribution of luminosity in the atm. of Venus has been determined, and from the results a method of estimating the constitution of the planetary atm. is obtained. W. R. Angus.

Light of the night sky. J. Kaplan (Physical Rev., 1931, [ii], **38**, 1048—1051).—The lines 4416 and 4168 Å. reported by Rayleigh are identified as O II lines. An explanation of the green auroral line in the night sky and aurora borealis, and of the above lines of the night sky, is proposed. N. M. Bligh.

Schrödinger potential function. R. M. Langer (Physical Rev., 1931, [ii], 38, 779—796).—The theory that the fundamental potential between charges is an even operator is developed and applied.
N. M. Bligh.

Quantised singularities in the electromagnetic field. P. A. M. Dirac (Proc. Roy. Soc., 1931, **A**, **133**, 60—72). L. L. Bircumshaw.

Quantum theory of dispersion in metallic conductors. II. R. de L. Kronig (Proc. Roy. Soc., 1931, **A**, **133**, 255—265; cf. A., 1929, 871).
L. L. Bircumshaw.

Conversion of energy into matter. F. G. Donnan (Z. physikal. Chem., Bodenstein Festband, 1931, 131—134).—Since at a temp. in the neighbourhood of 10^{12}° an equilibrium of the type proton$+$electron$\rightleftharpoons$photon (radiation energy) is conceivable, it is suggested that the reaction from right to left could be observed if a sufficiently dense stream of protons of frequency of the order of 10^{23} emerged into a cold space. The relation between this hypothesis and photochemical reactions is discussed.
H. F. Gillbe.

Life of metastable mercury and evidence for a long-lived metastable vibrating nitrogen molecule. M. L. Pool (Physical Rev., 1931, [ii], **38**, 955—966).—Rate of decay curves are discussed. An expression is found for the no. of metastable atoms. Consts. obtained are: for the excited vibrating metastable mol., max. observed life $0\cdot52\times10^{-3}$ sec.; natural life, ∞; distance between centres at impact, $0\cdot85\times10^{-8}$ cm.; probability of dissipative impact, 80×10^{-6}; diffusion coeff., 2·4. Corresponding vals. for the metastable atom are: $2\cdot54\times10^{-3}$ sec.; ∞; $3\cdot2\times10^{-8}$ cm.; $3\cdot3\times10^{-6}$; 0·129, respectively.
N. M. Bligh.

Primary and secondary absorption bands and their relation to optical activity. W. Kuhn and H. L. Lehmann (Z. Elektrochem., 1931, **37**, 549—552).—A comparison of absorption spectrum, optical rotation, dichroism, and anisotropy of some org. compounds. E. S. Hedges.

Emission spectra and predissociation in OH and NH. J. R. Bates (Z. physikal. Chem., Bodenstein Festband, 1931, 329—332).—The heats of dissociation of OH and NH, calc. from the vibrational levels deduced from the emission spectra, having regard to the predissociation, are 116·05 and 102·2 kg.-cal., respectively. H. F. Gillbe.

Dissociation of water in the glow discharge. E. G. Linder (Physical Rev., 1931, [ii], **38**, 679—692). —Ionisation in the dark space increasing exponentially with distance from the cathode leads to results in satisfactory agreement with experimental data for the dissociation of H_2O vapour. N. M. Bligh.

Absorption of light by flames containing sodium. C. D. Child (Physical Rev., 1931, [ii], **38**, 699—708; cf. Locher, A., 1928, 449).—The relation between the light transmitted by a series of flames into which NaCl is being introduced, the no. of flames, and concentration of the NaCl is investigated. An expression connecting these quantities is deduced showing a square root variation in satisfactory agreement with experiment. N. M. Bligh.

Total radiation of some oxides. G. Liebmann (Z. Physik, 1931, **71**, 416—421).—The total radiation of Pt, some pure oxides, and a mixture of oxides was determined in its relationship to temp., composition, and nuclear size. A. J. Mee.

Ultra-violet emission of calcium oxide phosphors. O. Schellenberg (Ann. Physik, 1931, [v], **11**, 94—102).—The effect of temp. on the ultra-violet emission range differs from that on the visible emission. With the latter the greater intensity and duration of emission are obtained at comparatively high temp. (200—300°), whereas for the ultra-violet emission optimum conditions are obtained at room temp.
A. J. Mee.

Band spectrum of yttrium oxide. With a note on the scandium and lanthanum oxide systems. L. W. Johnson and R. C. Johnson (Proc. Roy. Soc., 1931, **A**, **133**, 207—219).—About 100 band heads in the spectrum of YO have been measured and assigned to 2 systems, having a common ground state. A vibrational analysis is given and the mol. consts. are evaluated. The band systems of YO, ScO, and LaO are very similar, and closely resemble those of CaF, SaF, and BaF. L. L. Bircumshaw.

Ultra-violet bands of phosphorous oxide. P. N. Ghosh and G. N. Ball (Z. Physik, 1931, **71**, 362—370).—A band system of PO ascribed to $^2\Sigma\longrightarrow{}^2\Pi$ transitions was investigated under high dispersion; the heat of dissociation of the ground state is 7·4 volts.
A. B. D. Cassie.

Spectrum of the hydrogen–nitrous oxide flame. A. Fowler and J. S. Bodami (Proc. Roy. Soc., 1931, **A**, **133**, 325—332).—Observations of the bright cone near the base of the H_2–N_2O flame in a mixed jet show that the spectrum is identical with that of the flame of NH_3 burning in O_2, apart from differences in intensities of certain bands in the spectra. The Schuster bands are not observed.
L. L. Bircumshaw.

Interpretation of the spectra of CaF and SrF. A. Harvey (Proc. Roy. Soc., 1931, **A**, **133**, 336—350). —A comparison of the spectra in emission and absorption under high dispersion confirm the designations $^2\Sigma\longrightarrow{}^2\Sigma$ and $^2\Pi\longrightarrow{}^2\Sigma$ for the more, and less, refrangible band systems of CaF and SrF. For CaF, $I_0''=86\times10^{-40}$ g.-cm.^{2}, and $r_0''=2{\cdot}0\times10^{-8}$ cm. for the lower $^2\Sigma$ state. The isotope effect for Sr^{88}, Sr^{86} is found in the SrF bands. L. L. Bircumshaw.

Diffuse bands occurring in mixtures of ammonia and excited mercury vapour. A. C. G. Mitchell (J. Franklin Inst., 1931, **212**, 341—342).—The spectrum of the fluorescence on illuminating NH_3–Hg mixtures with a cooled Hg arc consists of a very diffuse band between λ 2700 and 5600 Å. (max. intensity at λ 3400 Å.). H. J. Emeléus.

Absorption of light in single crystals. R. Hilsch and R. W. Pohl (Physikal. Z., 1931, **32**, 734—735).—The absorption of a single crystal of KBr and of the photochemical reaction product are given and discussed. W. R. Angus.

Measurement of absorption spectra in the ultra-violet. H. Conrad-Billroth (Z. physikal. Chem., 1931, **B**, **14**, 122—134).—Apparatus is described by which the ultra-violet absorption spectrum of a solution is photographed simultaneously with that of the pure solvent, using as light source an under-water Al arc. The method gives results in good agreement with previous work, but has certain limitations. N. H. Hartshorne.

Energy levels of gadolinium IV in the crystal lattice as obtained from the ultra-violet absorption spectra of $GdCl_3,6H_2O$ and $GdBr_3,6H_2O$. S. Freed and F. H. Spedding (Physical Rev., 1931, [ii], **38**, 670—678; cf. A., 1929, 1362).—Wave-lengths, intervals, and magnetic decomps. are tabulated, and discussed in relation to lattice structure.
N. M. Bligh.

Spectroscopic investigation of dissociation relations of metal halides in solution. H. Fromherz (Z. Elektrochem., 1931, **37**, 553—558).—A discussion of published work (cf. A., 1929, 626; 1930, 853, 1234). E. S. Hedges.

Spectrum and photochemical behaviour of chlorine dioxide. W. Finkelnburg and H. J. Schumacher (Z. physikal. Chem., Bodenstein Festband, 1931, 704—716).—The band spectrum of ClO_2 between 5225 and 2700 Å. has been examined. Fine structure is apparent in the longer wave-length bands, but at 3750 Å. predissociation commences; the extrapolated convergence frequency is 39,000±1000 cm.$^{-1}$ The predissociation is ascribed to dissociation into ClO and O (^3P), whilst the convergence corresponds with the production of ClO and O (^1O). The dissociation energy of ClO is 45±5 g.-cal. ClO_2 has probably a cyclic structure. The photochemical reactions of ClO_2 are discussed and possible mechanisms of the formation of ClO_3 are described.
H. F. Gillbe.

Visible absorption spectrum and specific vibration of the permanganate ion. K. Schnetzler (Z. physikal. Chem., 1931, **B**, **14**, 241—248).—The absorption spectrum of $KMnO_4$ in solid solution in $KClO_4$ shows seven equidistant bands between 5600 and 4400 Å., each band having a short-wave satellite of about half its strength. The band max. occur at longer wave-lengths than those previously found for solutions of $KMnO_4$. Modifications occur in single bands when light vibrating in the α, β, or γ

directions is used. The no. of oscillators is of the same order as the no. of mols. present.
N. H. HARTSHORNE.

Absorption band spectra of silver bromide and silver iodide vapours. B. A. BRICE (Physical Rev., 1931, [ii], **38**, 658—669; cf. A., 1930, 838).—Band heads were measured in the region 3165—3501 for AgBr, and 3016—3556 Å. for AgI; absorption was continuous below 3350, with a max. at 3170 Å. A vibrational analysis is given. Heats of dissociation for the normal state are: AgBr 2·77, AgI 3·02, and for the excited states, AgBr 0·21, AgI, 0·10 volt, respectively. The vibrational isotope effect for AgBr confirms two Ag and two Br isotopes; no evidence for an I isotope was found. N. M. BLIGH.

Absorption spectra of sulphur compounds. I. L. LORENZ and R. SAMUEL (Z. physikal. Chem., 1931, B, **14**, 219—231).—The ultra-violet absorption spectra of $SOCl_2$, SCl_2, Na_2SO_3, $NaHSO_3$, $Na_2S_2O_4$, Na_2SO_4, $NaHSO_4$, $NaMeSO_4$, Me_2SO_4, SO_2Cl_2, Na_2SO_3, $Na_2S_2O_6$, $K_2S_3O_6$, $K_2S_4O_6$, $K_2S_5O_6$, and Na_2SeO_3, mostly in solution, have been determined. The results are discussed in relation to the mol. constitution of the substances. N. H. HARTSHORNE.

Rotation vibration spectrum of gaseous, liquid, and dissolved ammonia. G. JUNG and H. GUDE (Z. Elektrochem., 1931, **37**, 545—548).—The changes brought about by liquefaction of NH_3 and by dissolution in H_2O and some alcohols are described. E. S. HEDGES.

Influence of dissolved substances on the infra-red absorption spectrum of water. R. SUHRMANN and F. BREYER (Naturwiss., 1931, **19**, 772—773).—LiCl, NaCl, and KCl have been studied. Dissolved substances cause an intensification of H_2O bands. The sharpening increases with concentration, but does not follow the sequence of hydration. It is suggested that the greater ion exerts a bigger influence on the polymerised H_2O complex than the smaller. Undissociated dissolved substances give a slight sharpening of the bands. W. R. ANGUS.

Polymerides and new infra-red absorption bands of water. J. W. ELLIS (Physical Rev., 1931, [ii], **38**, 693—698).—New absorption bands at 1·79 and 1·74 μ and the bands at 19·5 and 4·7 μ are interpreted. The closely analogous bands of selenite are compared. Definite polymerides are indicated. N. M. BLIGH.

Double band of solid hydrogen chloride. G. HETTNER (Naturwiss., 1931, **19**, 815).—At approx. 90° abs. the HCl spectrum consists of a double band with max. at 3·63 and 3·70 μ, *i.e.*, at rather longer wave-length than the corresponding band of gaseous HCl. No fine structure is obtained. Preliminary investigations of liquid HCl give one band with max. at 3·61 μ. W. R. ANGUS.

Doppler effect in light scattering. (SIR) C. V. RAMAN (Nature, 1931, **128**, 636). L. S. THEOBALD.

Lines of large frequency shift in the Raman spectra of crystals. R. TOMASCHEK (Nature, 1931, **128**, 495).—The lines showing a large shift in the Raman spectrum of fluorite and calcite (this vol., 668) can be explained as phosphorescence lines of Gd.
L. S. THEOBALD.

Fine structure of spectral lines of light scattered by liquids. S. RAFALOWSKI (Nature, 1931, **128**, 495).—The phenomenon previously described (A., 1930, 1498) could not be confirmed under different experimental conditions. L. S. THEOBALD.

Widening of diffuse lines without change of frequency in the Raman effect. (MLLE.) M. J. NEY (Bull. Acad. Polonaise, 1931, A, 106—111).—From studies with C_6H_6 and quartz (at 18° and 500°) evidence is adduced in favour of the hypothesis that the widening of diffuse lines without change of frequency is due to mol. rotation. W. R. ANGUS.

Effect of varying concentrations of certain electrolytes on the violet band of the Raman spectra of water. C. C. HATLEY and D. CALLIHAN (Physical Rev., 1931, [ii], **38**, 909—913).—The Raman scattering by pure H_2O excited by the 3650 Å. group of the Hg arc showed a violet band of 3 components at 4150 Å.; the effect on this band of various concentrations of aq. KCl, NaOH, and KOH solutions was examined, and in all cases showed an energy shift towards the long wave-length side. N. M. BLIGH.

Raman spectra and catalysis. I. H. VON EULER and H. HELLSTRÖM (Z. physikal. Chem., Bodenstein Festband, 1931, 731—736).—Raman spectra of a homogeneous reacting mixture of KOH, EtOAc, and H_2O, and of the interfacial layer between a conc. solution of KOH and a mixture of EtOH and EtOAc were photographed. The second type shows faintly the normal lines, but two strong lines of frequencies 1050 and 1110 cm.$^{-1}$ appear; these undergo displacements towards lower frequencies on passing from the upper to the lower layer. The effect may correspond with activation of the reactant mols.
H. F. GILLBE.

Influence of exciting frequency on the intensities of lines in Raman spectra. S. C. SIRKAR (Indian J. Physics, 1931, 6, 133—146).—The ratios of the intensities of Raman lines due to C_6H_6 and CCl_4 to those of the exciting Hg lines in the visible and ultra-violet have been measured. The intensities of the Raman lines in the ultra-violet increase more rapidly than is indicated by the fourth power law and the deviation is the greater the greater is the shift of the Raman from the exciting line. These deviations are satisfactorily accounted for by Placzek's theory of the Raman effect. F. J. WILKINS.

Raman spectra of glycol and some organic chlorine compounds. V. N. THATTE and S. M. SHAHANE (Indian J. Physics, 1931, 6, 155—163).—The Raman spectra of glycol, chloral, C_2HCl_5, $C_2H_2Cl_4$, and $C_2H_2Cl_2$ have been studied. Increase in the number of Cl atoms in Cl-substituted ethanes causes an increase in the val. of a given Raman displacement. F. J. WILKINS.

Raman spectrum and chemical constitution of some chloroethylenes. G. B. BONINO and L. BRÜLL (Atti R. Accad. Lincei, 1931, [vi], **13**, 275—281).—The Raman spectra of *cis*- and *trans*-$\alpha\beta$-dichloroethylene have been measured. The characteristic oscillation and deformation frequencies of these mols. are compared with those of C_2H_4 and of C_2Cl_4 (cf. A., 1930, 1236). O. J. WALKER.

Retarded luminescence in carbon dioxide. (MLLE.) M. KACZYNSKA (Bull. Acad. Polonaise, 1931, A, 16—19).—A retarded luminescence has been shown in the case of CO_2. This varies with the intensity of the exciting discharge and with the pressure of the gas. A. J. MEE.

Colour and intensity of the chemiluminescence of solid sodium. R. M. BOWIE (J. Opt. Soc. Amer., 1931, 21, 507—512).—An investigation of the light by means of a Cs photo-electric cell gave a max. about 5100 Å. J. LEWKOWITSCH.

Galvano-luminescence. R. R. SULLIVAN and R. T. DUFFORD (J. Opt. Soc. Amer., 1931, 21, 513—523; cf. A., 1927, 918; 1929, 378, 1364).—Various metals in typical Grignard solutions were examined. A solution of $MgBr_2,2Et_2O$ has the highest efficiency so far found. J. LEWKOWITSCH.

Permanent changes in the fluorescence of hæmatoporphyrin. S. RAFALOWSKI (Z. Physik, 1931, 71, 798—806).—The fluorescence spectrum in aq. NH_3 and glycerol has been investigated. The irreversible changes which occur in the fluorescence spectrum as the effect of temp. changes, concentration differences, and irradiation of the solution are due to oxidation. A. J. MEE.

Spectral fluorescence efficiencies of certain substances with applications to heterochromatic photographic photometry. G. R. HARRISON and P. A. LEIGHTON (Physical Rev., 1931, [ii], 38, 899—908).—The efficiency of fluorescence in the visible and ultra-violet regions was investigated for fluorescein, chlorophyll, quinine sulphate, light and heavy fluorescent oil, aesculin, and U glass, and results are applied to the development of a simplified method of heterochromatic photographic photometry in the range 3900—2000 Å., with possible extension to the Schumann region. N. M. BLIGH.

Absorption of metastable and ionised nitrogen by magnesium. P. I. LUKIRSKY and S. W. PTIZYN (Z. Physik, 1931, 71, 339—349).—Neutral N_2 is absorbed only by a rapid evaporation of Mg, but ionised N mols. and metastable mols. of 8 volts energy are absorbed by a Mg layer to form Mg_3N_2. A. B. D. CASSIE.

"Sperrschicht" photo-effect. E. DUHME (Z. Elektrochem., 1931, 37, 682—683).—An electric current is produced when dry-plate rectifiers of the detector type (*e.g.*, Cu/Cu_2O) are illuminated. E. S. HEDGES.

New photo-electric researches. Q. MAJORANA (Atti R. Accad. Lincei, 1931, [vi], 13, 318—323).—Phenomena produced by intermittent light on triode valves and photo-electric cells are described. O. J. WALKER.

Photo-electric effect in thin metallic films. W. G. PENNEY (Proc. Roy. Soc., 1931, A, 133, 407—417).—Mathematical.

Preparation of sensitive vacuum thermo-elements and vacuum thermo-relays by cathodic sputtering. Z. KLEMENSIEWICZ and (MISS) Z. WASOWICZ (Z. Physik, 1931, 71, 817—820).—The deposition of thin layers of conductors on insulating material by cathodic sputtering provides a method of making vac. thermo-elements and relays of high sensitivity and reproducible characteristics. A. J. MEE.

Laws of the Becquerel effect at bismuth oxide electrodes. A. COEHN and R. MYKOLAJEVYCZ (Z. physikal. Chem., Bodenstein Festband, 1931, 641—655).—The photosensitive constituent of the Bi oxide electrode, viz., Bi_2O_4, behaves when deposited on an insol. electrode as an electrode of high O pressure. The electrode potential varies with the nature of the base, probably because of local action. Illumination causes at first a decrease of potential, but at lower potentials the effect reverses. The magnitude of the Becquerel effect, for const. absorption and quantum yield, falls rapidly with increase of the wave-length of the incident light from 4500 to 6700 Å. The effect can be fully explained on the assumption that light exerts a reducing influence on Bi_2O_4. H. F. GILLBE.

Becquerel effect. III. C. WINTHER (Z. physikal. Chem., Bodenstein Festband, 1931, 341—351).—An artificial Becquerel electrode has been prepared, and comparison of its behaviour with that of the Cu/CuO electrode shows that the conductivity of the CuO film of the latter increases proportionately with the intensity of the incident light. H. F. GILLBE.

Becquerel effect. IV. C. WINTHER (Z. physikal. Chem., 1931, 155, 225—237; cf. preceding abstract).—In support of the theory that the Becquerel effect is a photo-electric conductivity phenomenon the prep. of CuO electrodes having the properties of the Becquerel cell is described. R. CUTHILL.

Mobility in crystalline solid bodies. A. SMEKAL (Z. physikal. Chem., Bodenstein Festband, 1931, 443—452; cf. A., 1928, 1330).—Theoretical. An equation is developed for the general case to express the temp. variation of the fraction of the total ionic conductivity in a solid which is due to each type of mobile ion; one term of the equation is concerned with the fraction which is dependent on the structure of the substance. The true conductivity is influenced by structure, and by chemical, mechanical, and electric disturbances. The conductivity of the high-temp. modifications of AgI and Ag_2S is discussed. H. F. GILLBE.

Electrical conductivity and the structure of thin metal films. III. Specific resistance and structure as a function of temperature. L. HAMBURGER (Ann. Physik, 1931, [v], 10, 905—926).—An extension of previous work (this vol., 1112). W. R. ANGUS.

Electrical properties of dilute metallic mixed crystals. J. O. LINDE (Ann. Physik, 1931, [v], 10, 52—70).—The at. resistance increases of Cu, Ni, Co, Fe, Mn, Cr, Ag, Pd, Pt, Rh, In, and Sn in Au at temp. between +20° and −190° have been determined. Results concerning the solubility relationships in alloys of Au with Rh, Ru, Ir, Os, and In are given. W. GOOD.

Conductivity of silver sulphide. C. Tubandt and H. Reinhold (Z. Elektrochem., 1931, 37, 589—593).—The electrical conductivity of Ag_2S has been measured between 200° and 500° both in the pure state and in presence of excess of S. The conductivity of α-Ag_2S above 197° is electrolytic in character and has a negative temp. coeff. In presence of S vapour the conductivity falls, following the v. p. of the S and reaching a const. value for the saturated vapour. This effect is reversible and the saturated vapour has a positive temp. coeff. H_2S has a similar effect to that of S vapour. It appears that two kinds of conducting Ag ions are involved: (*a*) a large no. of ions of small mobility, consistent with the ordinary diffusion velocity, and (*b*) a small no. of ions of abnormally high mobility, which no longer exert their effect when excess of S is present.

E. S. Hedges.

Density, inner friction, dielectric constant, dipole moment, dissolving power, and dissociating power of hydrocyanic acid. K. Fredenhagen (Trans. Amer. Electrochem. Soc., 1931, 60, 223—232).—The results of the author's recent experimental work (A., 1929, 498; 1930, 1501) are summarised and discussed (cf. this vol., 430).

H. J. T. Ellingham.

Determination of dielectric constants. E. Cohn (Physikal. Z., 1931, 32, 687—688).—The ellipsoid method does not give an abs. determination. A comparison method is suggested. A. J. Mee.

Dipole moments of inorganic compounds. H. Ulich and W. Nespital (Z. Elektrochem., 1931, 37, 559—562).—In agreement with Hund's theory (A., 1925, ii, 479), the symmetrical halides CCl_4, SnI_4, BCl_3, $SnCl_4$, $AlBr_3$, $BeCl_2$, $BeBr_2$, $SiCl_4$, and $GeCl_4$ have no dipole moment. Exceptions occur in $SbCl_3$ and $AsCl_3$. In some cases the dipole moment is traced to the formation of a compound between the halide and the solvent. E. S. Hedges.

Dielectric constant and dipole moment of hydrogen cyanide and cyanogen. H. Braune and T. Asche (Z. physikal. Chem., 1931, **B**, **14**, 18—26; cf. A., 1929, 1217).—From measurements of the dielectric consts. of the gases at various temp. the dipole moments of HCN and $(CN)_2$ are calc. as $2{\cdot}88 \times 10^{-18}$ and $0{\cdot}3 \times 10^{-18}$, respectively. J. W. Smith.

Dipole moment of hydrogen cyanide. H. Lütgert (Z. physikal. Chem., 1931, **B**, **14**, 27—30; cf. A., 1929, 1217, and preceding abstract).—From measurement of the dielectric consts. of dil. solutions in C_6H_6 at various temp. the dipole moment of HCN is calc. to be $2{\cdot}53 \times 10^{-18}$ and from the dielectric consts. of solutions in xylene at one temp. combined with existing electron and at. polarisation data $2{\cdot}60 \times 10^{-18}$.

J. W. Smith.

Dipole moment and molecular orientation at a liquid–gas interface. B. I. Tamamushi (Bull. Chem. Soc. Japan, 1931, 6, 207—209).—The dipole moments of a number of fatty acids, alcohols, and esters have been calc. The consistent difference between the calc. and observed vals. indicates that other factors besides the electric moments of single mols., such as form of mol., position of natural electric moment, dielectric polarisation, and mol. association are of importance. H. F. Gillbe.

Electric moment of symmetrically hexa-substituted benzenes. Spatial requirements of substituents. H. Lütgert (Z. physikal. Chem., 1931, **B**, **14**, 31—36).—From measurements of the dielectric const. of dil. solutions in CCl_4 and C_6H_6 at two different temp. it has been shown that three symmetrical hexa-substituted C_6H_6 derivatives (tribromomesitylene, trinitromesitylene, and tribromotrinitrobenzene) each have zero dipole moment. This is discussed with reference to the spatial arrangement of the C_6H_6 ring. J. W. Smith.

Dipole measurements with benzene derivatives. I. Regularities with halogen, nitro-, and methyl derivatives. L. Tiganik (Z. physikal. Chem., 1931, **B**, **13**, 425—461).—From the dielectric consts. of dil. solutions in C_6H_6, combined with refractivity data, the dipole moments of 47 C_6H_6 derivatives have been calc. The data confirm the hypothesis that the total induced polarisation of simple C_6H_6 derivatives is equal to the mol. refraction for Na light $+0{\cdot}4$. Almost const. ratios exist between the dipole moments of *m*-di- and mono-, *p*-di- and mono-, and *s*-tri- and mono-derivatives. From the behaviour of hexa-substituted derivatives it is concluded that the moments of *s*-tri-derivatives are perpendicular to the C_6H_6 ring. J. W. Smith.

Dipole measurements in benzene derivatives. II. Amino-derivatives. L. Tiganik (Z. physikal. Chem., 1931, **B**, **14**, 135—148; cf. preceding abstract). —The following vals. of $\mu_D \times 10^{18}$ have been obtained by extrapolation to infinite dilution in C_6H_6 solution, mostly at 20°: NH_2Ph 1·52; $C_6H_4(NH_2)_2$, *o*- 1·44, *m*- 1·79, *p*- 1·56; $C_6H_4Me{\cdot}NH_2$, *o*- 1·58, *m*- 1·44, *p*- 1·31; $C_6H_4Cl{\cdot}NH_2$, *o*- 1·77, *m*- 2·66, *p*- 2·97; $C_6H_4Br{\cdot}NH_2$, *o*- 1·77, *m*- 2·65, *p*- 2·99; $C_6H_4(NO_2){\cdot}NH_2$, *o*- 4·25, *m*- 4·94, *p*- 6·4. These show that the NH_2 and Me group moments act in the same direction. An expression is deduced for the moment of a mol. containing two freely rotating dipole groups, one or both of which have moments inclined to the valencies binding them to the rest of the mol. The inclination of the moment of the NH_2 group to its valency with the C_6H_6 nucleus is estimated to be about 40°.

N. H. Hartshorne.

Dielectric constants of certain organic liquids at medium frequency. W. R. Pyle (Physical Rev., 1931, [ii], **38**, 1057—1070).—At 85·8 kilocycles frequency the respective vals. of the dielectric const. and temp. are: C_6H_6 2·279, 22·9°; cinnamaldehyde 16·918, 24·2°; Et_2O 4·197, 26·9°; methyl*cyclo*hexane 2·071, 24·8°; Me *o*-nitrobenzoate 27·756, 26·9°; PhNO 34·369, 26·1°; oxalyl chloride 3·470, 21·2°; Pr^{α}_2O 3·394, 25·7°; Pr^{β}_2O 4·449, 25·9°; propylene chloride 8·925, 26·1°. At the same frequency the temp. coeffs. of the dielectric consts. for *o*-, *m*-, and *p*-xylenes were determined over a temp. range of about 30°. N. M. Bligh.

Electric moments of hydrobenzoin and *iso*-hydrobenzoin. O. Hassel and E. Næshagen (Z. physikal. Chem., 1931, **B**, **14**, 232—236; cf. A., 1930, 1347).—Redeterminations at 60° and 18°

confirm previous conclusions (this vol., 894) that there is a marked difference, the present results being: hydrobenzoin $2·3\times10^{-18}$, *iso*hydrobenzoin $2·7\times10^{-18}$. N. H. HARTSHORNE.

Molecular and atomic volume. XXXIII. Atomic volume and atomic models. W. BILTZ (Z. physikal. Chem., Bodenstein Festband, 1931, 198—210).—Theoretical. For approx. half the elements, $v_0=11·3n/N$, where v_0 is the zero at. vol., n the quantum no. of the outermost electron orbit, and N the group no. of the element in the periodic table. H. F. GILLBE.

Refraction and dispersion of some gaseous compounds. H. LOWERY (Proc. Roy. Soc., 1931, A, **133**, 188—207; cf. A., 1928, 220).—Using a Jamin interferometer, the refractivities of a number of gaseous compounds have been measured for the green Hg line 5461 Å., and the dispersion has been determined over the range 4358—6708 Å. The following vals. of $(\mu-1)_d$ (referring to the same no. of mols. d as 1 c.c. of H_2 contains at n.t.p.) were obtained: $SiCl_4$ 0·001969, $SiBr_4$ 0·002725, BCl_3 0·001404, BBr_3 0·002012, $COCl_2$ 0·001149, $COMe_2$ 0·001096, Et_2O 0·001509, C_2H_2 0·0005936, C_2H_4 0·0007192, C_2H_6 0·0007648, MeCl 0·0007804, CH_2Cl_2 0·001112, CH_2Br_2 0·001435. L. L. BIRCUMSHAW.

Refractive power of organic halogen compounds. W. LEITHE (Z. Elektrochem., 1931, **37**, 623—625).—The mol. refractions of several series of org. halogen compounds have been measured and deviations from the law of additivity are discussed. The increase due to each halogen atom substituted for H rises with the no. of halogen atoms in the mol. In general, in a series increasing refraction due to a linking is associated with increasing chemical reactivity. E. S. HEDGES.

Refractive dispersion of organic compounds. I. Experimental methods. II. *cyclo*Hexane. III. Benzene. T. M. LOWRY and C. B. ALLSOPP (Proc. Roy. Soc., 1931, A, **133**, 26—36, 36—47, 48—59).—I. Details are given of an interferometric method for measuring the refractive indices of thin films of liquid to four decimal places over a wavelength range from 5000 Å. up to the limit of transparency of the film in the ultra-violet.

II. Vals. are given for n of *cyclo*hexane for 21 wave-lengths from 6708 to 4358 Å., as measured with a refractometer, and for 97 wave-lengths from 5410 to 2452 Å., as deduced from photographic observations with an etalon. The results at 20° can be expressed by $n^2=2·00519+[0·0098035/(\lambda^2-0·011923)]$. Deviations of ±0·001 are found between 2800 and 3950 Å., but outside this range the mean deviation is ±0·0002.

III. Vals. are given for n of C_6H_6 at 20° for 22 wave-lengths from 6707 to 4358 Å. with a refractometer, and for 122 wave-lengths from 4900 to 2700 Å. deduced from photographic observations with an etalon. The vals. in the visible region of the spectrum are less accurate than those determined by Gifford (A., 1923, ii, 705). Gifford's data in the visible region, the authors' in the violet and ultra-violet, and Rubens' in the infra-red (Ann. Physik, 1892, **45**, 238) corr. to 20°, can be expressed by $n^2=1·51304+0·66992\lambda^2/(\lambda^2-0·030170)+0·06143(\lambda^2-0·070171)\lambda^2/[(\lambda^2-0·070171)^2+0·0003448\lambda^2]-0·0027\lambda^2$. L. L. BIRCUMSHAW.

Crystal form and optical constants of acetylsalicylic acid. R. NIINI (Z. Krist., 1931, **79**, 532—536). — Monoclinic holohedral, $a:b:c=1·7322:1:1·7322$, β 95° 42·5′; differences in faces which should be similar preclude rhombohedral symmetry in spite of the equality of a and c. For λ 5760, 5460, and 4360, respectively, n_α is 1·5042, 1·6424, 1·6554; n_β 1·5066, 1·6464, 1·6604; and n_γ 1·5216, 1·6720, 1·6914. C. A. SILBERRAD.

Dispersion of ammonium bromide. M. HAASE (Z. Krist., 1931, **80**, 132—133; cf. A., 1929, 754).—n_F^{25}, n_D^{25}, and n_C^{25} for NH_4Br are respectively 1·729, 1·712, and 1·705 (all ±0·001), giving $\nu=(n_D-1)/(n_F-n_C)=29·7$. C. A. SILBERRAD.

Theory of optical activity and anomalous rotation dispersion. W. KUHN and H. L. LEHMANN (Chem. Weekblad, 1931, **28**, 517—520)—A reply to Scheringa (this vol., 895). H. F. GILLBE.

Mutarotation and rotatory dispersion of galactonic acid and lactone. T. M. LOWRY and V. K. KRIEBLE (Z. physikal. Chem., Bodenstein Festband, 1931, 881—889).—*γ*-Galactonolactone has m. p. 112°, $[\alpha]_{5461}^{20}$ (1—2% solution) −93·1°. The rotatory dispersion between 6708 and 4358 Å. has been determined, and corresponds with characteristic absorption at 2420 Å. Na galactonate is dextrorotatory, and exhibits complex and anomalous dispersion, min. at 5700—5780 Å. Galactonic acid has $[\alpha]_{5461}$ −9·78°; rotatory dispersion is normal but complex. Equilibrium between the acid and *γ*-lactone occurs at 25·2% of the former. The mutarotation curves for the formation of the lactone in 0·109*N*-HCl and 0·0653*N*-NaCl are unimol. for all wave-lengths, the velocity coeff. being 0·0087 and the catalytic coeff. of the acid 0·080; in 0·2—0·4*N*-HCl the catalytic coeff. is 0·0132—0·0136. H. F. GILLBE.

Influence of salts on the optical rotation of gelatin. II. D. C. CARPENTER and J. J. KUCERA (J. Physical Chem., 1931, **35**, 2619—2626; cf. A., 1928, 125).—The characteristic lowering of the optical activity of 0·7% K gelatinate (calfskin) between p_H 6 and 7 by K salts is in the order $KCNS > KI > KClO_3 > KNO_3 > KBr > KCl$, KOAc, $EtCO_2K$, and HCO_2K. The effect of the salts of the org. acids is very small. Uni-bivalent salts follow the order $K_2SO_4 > (CO_2K)_2 > K_2CrO_4$, and their effect passes through a max. at concentrations between 0·1 and 0·3*M*. The changes in rotation are attributed to the equilibrium between the gel and sol forms of gelatin. L. S. THEOBALD.

Magnetic rotation dispersion of sulphur in solution. T. HORI and A. OKAZAKI (Z. Physik, 1931, **71**, 350—361).—The magnetic rotatory power of CCl_4 and of S_2 in solution was determined by means of a Savart plate. A. B. D. CASSIE.

Electro-optical Kerr constants of liquid and dissolved substances and the nature and cause of the mutual influence and orientation of mole-

cules in the liquid state. I. G. Briegleb (Z. physikal. Chem., 1931, **B**, **14**, 97—121).—The Kerr consts. of several liquid org. compounds and the Kerr consts., dielectric consts., refractivities, and densities of $COMe_2$, Et_2O, $CHCl_3$, CS_2, and C_6H_6 dissolved in heptane have been measured. The mol. Kerr const. decreases with concentration, which in the case of the polar substances is attributable to association, as is the concentration effect on the mol. refractivities and mol. polarisation. The Kerr consts. extrapolated to infinite dilution are all lower than those of the substances in the gaseous state.

N. H. Hartshorne.

Molecular theory of electro-optic phenomena. R. de Mallemann (Compt. rend., 1931, **193**, 523—526).—Theoretical. Mol. polarisation in a mol. possessing at least two planes of symmetry reduces to a single vector passing through a fixed point, (centre of polarisation) irrespective of the direction of the field. In an asymmetric mol. it consists of two vectors, a resultant and a couple with axis along the resultant and not in general passing through a fixed point. C. A. Silberrad.

Affinity. VI. T. de Donder (Bull. Acad. roy. Belg., 1931, [v], **17**, 780—787, 874—887).—Mathematical.

Possible existence of the free hydroxyl radical. K. F. Bonhoeffer and T. G. Pearson (Z. physikal. Chem., 1931, **B**, **14**, 1—8).—A discharge in H_2O vapour gave OH bands the intensity of which increased linearly with the discharge current; H_2O therefore dissociates into an excited OH radical and a non-excited H atom. The OH radicals recombine to form H_2O and O within 10^{-3} sec., and isolation of OH is impossible. A. B. D. Cassie.

Free methyl and ethyl. F. Paneth and K. Herzfeld (Z. Elektrochem., 1931, **37**, 577—582).—The duration of existence of free Me and Et (A., 1929, 788) is increased by replacing H_2 as the carrying gas by He or N_2. The free radicals combine completely with a Pb mirror. The kinetics of the processes are treated mathematically. E. S. Hedges.

Formation of para-hydrogen under pressure at low temperatures. A. Farkas and K. F. Bonhoeffer (Z. physikal. Chem., Bodenstein Festband, 1931, 638—640).—The formation of para-H_2 in a brass vessel at the temp. of liquid air and pressures up to 110 atm. was homogeneous. H. F. Gillbe.

Decomposition of molecules through collisions of the second kind. H. Beutler and W. Eisenschimmel (Z. Elektrochem., 1931, **37**, 582—584).—Theoretical. E. S. Hedges.

Electronic structure of nitrogen dioxide. W. A. Noyes (Z. Elektrochem., 1931, **37**, 569—571).—The electronic structure $\overset{\cdot\cdot}{\underset{\cdot\cdot}{\mathrm{O}}}::\overset{\cdot\,+}{\mathrm{N}}:\overset{\cdot\cdot\,-}{\underset{\cdot\cdot}{\mathrm{O}}}:$ is used to explain numerous reactions of NO_2. E. S. Hedges.

Determination of molecular structure from optical and electrical data. E. Bergmann and L. Engel (Z. Elektrochem., 1931, **37**, 563—569).—A lecture. E. S. Hedges.

Relation between heat of activation and molecular structure. H. Dohse (Z. physikal. Chem., Bodenstein Festband, 1931, 533—540).—The activation heats of dehydration, *Q*, of EtOH, $Bu^{\beta}OH$, and *tert*.-amyl alcohol in contact with bauxite are 31, 26, and 17·5 kg.-cal., respectively. An α-Me group thus lowers *Q* by 5500 g.-cal., a β-Me group by 2500, and a γ-Me group by 500 g.-cal. The calc. distances between the groups in the mol. are in moderate agreement with those deduced from spatial considerations, but the agreement is closer if it is assumed that the mols. are readily deformed when adsorbed on the catalyst.

H. F. Gillbe.

Compounds of the transition elements with metalloids of small atomic dimensions. G. Hägg (Svensk Kem. Tidskr., 1931, **43**, 187—198; cf. A., 1930, 1351).—A discussion of the at. structure of the borides, carbides, nitrides, and hydrides of Bohr's transition elements. Compounds in which the ratio of the at. radius of the metalloid to that of the metal is less than 0·59 exhibit a simple type of "insertion" lattice, whilst for greater ratios complicated structures result. Most of the former compounds contain a simple lattice, either the face-centred cube or close-packed hexagonal lattice, composed of the metal atoms, the atoms of the metalloids occupying positions in the lattice such that they are co-ordinated with either 6 or 4 metal atoms. Less common are the centred cube and simple hexagonal lattices; in these cases the metalloid atom is co-ordinated with 4 and 6 metal atoms, respectively. Structures in which the co-ordination no. of the metal is 12 predominate largely, but the actual factors which determine the particular type of metal atom lattice present in a compound are still unknown.

H. F. Harwood.

Structure of hexammino- and hexaquo-salts. O. Hassel (Z. Krist., 1931, **79**, 531—532).—The author's views (cf. A., 1927, 1014; 1928, 974; 1929, 1222) are elaborated as against those of Pauling (cf. this vol., 151). C. A. Silberrad.

Stereochemistry of crystal compounds. VI. Compounds AB_2. Geometrical deduction of probable structure type. P. Niggli and E. Brandenburger (Z. Krist., 1931, **79**, 379—429; cf. this vol., 411, 670).—The geometrically probable structures of such compounds, based on their classification according to at. distances (d_A, d_B, d_{AB}) and co-ordination nos. of the constituent atoms, are deduced with examples. In most cases $d_A \geq d_B > d_{AB}$, but where A is an anion and B a cation, or with a complex bivalent anion, d_B may be $\leq d_{AB}$.

C. A. Silberrad.

Group rotation in solid ammonium and calcium nitrates. F. C. Kracek, S. B. Hendricks, and E. Posnjak (Nature, 1931, **128**, 410—411).—Mol. rotations in the solid state have been detected in NH_4NO_3. At 105° the tetragonal modification of NH_4NO_3 has *a* 5·77, *c* 5·00 Å. with 2 mols. of NH_4NO_3 per unit structure. The separations of the rotating NH_4^+ and NO_3^- groups in the plane of the NO_3^- groups are 3·80 Å. At 155°, the cubic modification has *a* 4·40 Å. with 1 mol. of NH_4NO_3 per unit. The separation of the rotating NH_4^+ and NO_3^- groups is

3·79 Å. In solid NH_4NO_3 above 125° probably all the rotational degrees of freedom of both $NH_4^{\cdot}$ and NO_3' are fully excited. Rotation of NO_3' is often to be found in cryst. nitrates and many of the previously published crystal structures are probably incorrect.
L. S. Theobald.

Constitution and isomerism of thiosulphuric acid. P. Rây (J. Indian Chem. Soc., 1931, **8**, 307—310).—The yellow to orange solutions of thiosulphatopentacobaltic acid (I), $H_4[(CN)_5CoS_2O_3]$ (A., 1928, 35), yield H_2SO_3 and S when heated; the Ba and Ca salts decompose similarly. The orange-red cryst. acid, obtained by evaporating the solution in vac. over H_2SO_4, dissolves in H_2O with separation of a little S and H_2S to give a yellow to orange solution, which, when warmed, liberates H_2SO_4 and more H_2S, the colour changing to dark red; SO_2 is not evolved, even on boiling. The Mg, Ca, and NH_4 salts from the solid acid are reddish-brown, and evolve H_2S, but not SO_2, on treatment with mineral acid. Isomerism is thus proved for the complex acid, and it is assumed that thiosulphuric acid can exist in two forms, $S{:}SO(OH)_2$ (α) and $HS{\cdot}SO_2{\cdot}OH$ (β), the former being present in solutions of (I), the latter in the solid (cf. A., 1924, ii, 103).
R. S. Cahn.

Principle of free rotation in molecules with single carbon linkings. C. Wagner (Z. physikal. Chem., 1931, **B**, **14**, 166—168).—From a consideration of the sp. heat of C_2H_6 it is concluded that a kind of twisting oscillation instead of free rotation takes place between the Me groups.
N. H. Hartshorne.

Low-temperature rotational heat capacities and the relative amounts of the nuclear singlet, triplet, and quintuplet symmetry modifications of methane. D. S. Villars and G. Schultze (Physical Rev., 1931, [ii], **38**, 998—1010).—Mainly mathematical. There should be 3 non-combining varieties of CH_4. Heat capacities of each variety, of the true equilibrium mixture, and of the "frozen equilibrium" mixture are calc. N. M. Bligh.

Magneto-electric saturation effect. O. E. Frivold and S. Koch (Nature, 1931, **128**, 675).—The effect, required by classical magnetic theory, of the addition of a strong electrolyte on the apparent magnetic moment of mols. which possess fixed magnetic as well as electric moments could not be detected in magnetic susceptibility measurements on a solution of $Cr(NH_3)_3(CNS)_3$ in $COMe_2$ with KCNS as the added electrolyte. L. S. Theobald.

Gyromagnetic effect for paramagnetic substances. II. Results on salts of the iron group. W. Sucksmith (Proc. Roy. Soc., 1931, **A**, **133**, 179—188).—The means used to increase the sensitivity of the apparatus previously used for Dy_2O_3 (A., 1930, 1100) are described, together with results obtained for the paramagnetic salts from $MnCO_3$, $MnSO_4$, $CrCl_3$, $CoSO_4$, $CoCl_2$, and $FeSO_4$. L. L. Bircumshaw.

Transition of ferromagnetic manganese arsenide into the paramagnetic form. A. Smits, H. Gerding, and F. Vermast (Z. physikal. Chem., Bodenstein Festband, 1931, 357—368).—The course of the vol.-temp. curve of MnAs between 15° and 50° resembles those of the intensity of magnetisation–temp. and the sp. heat–temp. curves. The transition from the para- to the ferro-magnetic form involves a series of irreversible metastable conditions; the density change is from 6·26 to 6·2. No vol. change results from the application of a magnetic field.
H. F. Gillbe.

Displacement of the Curie point for nickel by pressure. D. P. Ray-Chaudhuri (Z. Physik, 1931, **71**, 473—477).—In the Curie point of a Ni wire under tension agreement with the Heisenberg theory of ferromagnetism is found. There is agreement between the curves of temp. against temp. coeff. of resistance, and against extension, and there is also similarity with the curve obtained between temp. and sp. heat for a ferromagnetic body. A. J. Mee.

Molecular forces. III. Derivation of the van der Waals expression a/v^2. A. Eucken (Z. physikal. Chem., Bodenstein Festband, 1931, 432—436).—The van der Waals expression a/v^2 has been deduced without making the assumption that the sphere of action of the forces of attraction is large compared with the mean distance between the mols. The so-called swarming effect of mols. at low temp., which requires a variation with temp. of the attraction term, consists merely of the formation of double mols. as a result of collisions between 3 mols., and possibly of the formation of triple mols. after further collisions.
H. F. Gillbe.

Molecular sphere of action of the metals. C. Benedicks (Z. physikal. Chem., Bodenstein Festband, 1931, 379—384).—The radii r of the mol. spheres of action of 13 metals, calc. from the equation $r{=}nH/K$ on the assumption that $n{=}2$, are of the same order as the apparent at. radii ρ of Bragg. r is a periodic function of the at. no., but the fluctuations are much greater than those of ρ and resemble those of the square of the at. vol. To a first approximation $r{=}$ const.$\times\rho^6$. H. F. Gillbe.

Empirical evaluation of the potential due to van der Waals forces surrounding molecules. K. Wohl (Z. physikal. Chem., 1931, **B**, **14**, 36—65).—The variation with temp. of the second virial coeff. for gases is more accurately described when a repulsive force characteristic of each atom replaces the rigid sphere (cf. London, this vol., 149; Slater and Kirkwood, *ibid.*, 675). The coeff. of the repulsive term, and the power of the reciprocal of the distance from the centre of the atom or mol. required to fit the experimental curves, are given for He, H_2, Ne, Ar, N_2, O_2, and CO_2. A. B. D. Cassie.

Energy of C–C and C–H linkings in saturated hydrocarbons. M. Rebek (Arh. Hemiju, 1931, **5**, 192—196).—A review of the results obtained by various authors for the above vals. indicates that they are of the same order. R. Truszkowski.

Quadrupole forces in van der Waals attractions. H. Margenau (Physical Rev., 1931, [ii], **38**, 747—756).—For van der Waals forces between non-polar atoms at distances apart of the order of the kinetic theory radius the contribution of the interactions between higher poles must be taken into account. Calculations are made for the interactions: dipole–

dipole, dipole–quadrupole, and quadrupole–quadrupole for H and He atoms. N. M. Bligh.

Avogadro's number and "mean free path." S. Ray (Proc. XV Indian Sci. Cong., 1928, 141).—If the usual expression, $\lambda=1/(2\pi N\sigma^2)^{\frac{1}{2}}$ is correct, the mean free path is not intimately related to vol., pressure, temp., or entropy; since Avogadro's no. is approx. the same for different atoms, the expression $\lambda=(N/3)^{\frac{1}{3}}-\sigma$ is preferred. Chemical Abstracts.

Effect of the application of a field of attraction to a gas. R. D. Kleeman (Science, 1931, 74, 290). L. S. Theobald.

Abstracting schemes for X-ray structure determinations. J. D. Bernal, P. P. Ewald, and C. Mauguin (Z. Krist., 1931, 79, 495—530).—A complete synoptical table of the nomenclatures of Schwonflies, Wyckoff, and Mauguin is appended. C. A. Silberrad.

Accurate determination of lattice constants of polycrystalline materials. F. Regler (Physikal. Z., 1931, 32, 680—687).—The usual correction applied in the accurate determination of lattice consts. is not sufficient. A. J. Mee.

Kinematographic representation of the recrystallisation of rock-salt. K. Przibram (Z. Elektrochem., 1931, 37, 535—536).—When rock-salt is subjected to a pressure of 2000 kg. per sq. cm. and subjected to Ra radiations it darkens, but slowly becomes lighter when pressure and radiation are removed. A kinematographic record of the process supports the view that the darkening is due to distortion of the space-lattice and the brightening to recrystallisation. E. S. Hedges.

Theory of the oriented superimposition of ionic crystals; formation of Grimm mixed crystals. I. N. Stranski (Z. physikal. Chem., Bodenstein Festband, 1931, 230—238).—The upper limit of supersaturation at which a given type of crystal will deposit on an isomorphous crystal of a different compound has been calc. for the case in which both the substances are binary compounds and differ only in the charges on the component ions. The deposition of NaBr on PbS is considered in detail. H. F. Gillbe.

Recrystallisation. G. Tammann (Z. Elektrochem., 1931, 37, 429—436).—A summary of the author's views on the formation and growth of crystallisation nuclei, especially as influenced by cold work. E. S. Hedges.

Atomic states in metal lattices on the basis of magnetic measurements. E. Vogt (Z. Elektrochem., 1931, 37, 460—466).—A lecture. E. S. Hedges.

Isomorphism considered in relation to X-ray investigations. A. Ferrari (Gazzetta, 1931, 61, 358—369).—The conditions which determine the occurrence of isomorphism between compounds are discussed. Complete miscibility can always occur when two lattices are made up of unit cells which have the same shape, and only slightly different vols. O. J. Walker.

Constitutional formulæ of crystalline substances. H. Rheinboldt (Z. anorg. Chem., 1931, 200, 168—172).—The formulæ of the occupants of the lattice points are enclosed in [ ], and there are added numbers representing the no. of immediately adjacent and equidistant or approx. equidistant groups. The NaCl lattice, for instance, is represented by $[Na]^6[Cl]^6$. R. Cuthill.

Lattice constants. M. C. Neuburger (Z. Krist., 1931, 80, 103—131).

Accurate determination of dimensions of crystal lattices. N. H. Kolkmeijer and A. L. T. Moesveld (Z. Krist., 1931, 80, 63—90).

Increase in surface area due to crystal faces developed by etching. L. Tonks (Physical Rev., 1931, [ii], 38, 1030—1039).—The actual surface of an etched cryst. body, being made up of cryst. faces, is greater than the apparent surface; the ratio of increase in area to apparent area is the face excess. Criteria for determining those faces which give min. face excess, and two methods for calculating face excess, are deduced for various types of faces. N. M. Bligh.

Why crystals exist. F. Zwicky (Proc. Nat. Acad. Sci., 1931, 17, 524—532).—It is suggested that the cohesive forces having radii of action of the order of at. dimensions are responsible for the condensed state of matter, but not for the cryst. state. C. W. Gibby.

Method of investigating fibre structure and of showing strains in pieces of metal. F. Regler (Z. Physik, 1931, 71, 371—388).—An X-ray method of determining structure and strains is fully described. A. B. D. Cassie.

X-Ray fibre diagram as a quantitative measure of the change in the structure of the cellulose fibre by chemical processes. I. Quantitative relation between the intensities of the equatorial interference lines for fibre preparations of natural and mercerised cellulose of known composition. W. Schramek (Z. physikal. Chem., 1931, B, 13, 462—474).—The observation made by previous investigators that technical mercerisation produces only an incomplete mercerisation effect is confirmed by X-ray investigation. It is possible to obtain a quant. relationship between the X-ray diagram and the degree of mercerisation. J. W. Smith.

X-Ray investigation of space-lattice distortion in light metals. J. Hengstenberg and H. Mark (Z. Elektrochem., 1931, 37, 524—528).—Changes in the X-ray spectrum of duralumin and "electron metal" on cold-working are described. E. S. Hedges.

Hexagonal nickel. G. Bredig and E. S. von Bergkampf (Z. physikal. Chem., Bodenstein Festband, 1931, 172—176).—By cathodic dispersion of Ni in N_2 or H_2 a metallic mirror of non-magnetic, hexagonal Ni, having *a* 2·60—2·66, *c* 4·15—4·22 Å., is obtained. The metal passes into the ordinary cubic form on heating in H_2 at 300°. H. F. Gillbe.

Density and crystal structure of niobium. M. C. Neuburger (Z. Krist., 1931, 78, 164—167).—A re-examination of the purest of Meisel's three samples of Nb (cf. A., 1930, 983) gave *d* 8·55 (calc.

8·56). The unit cell has *a* 3·303±0·002 Å., and contains 2 mols.; space-group O_h^9; at. radius 1·430 Å.
C. A. SILBERRAD.

Crystal structure of some carbides and borides. M. VON STACKELBERG (Z. Elektrochem., 1931, **37**, 542—544).—A summary of work on carbides (cf. A., 1930, 672, 1351) shows that derivatives of CH_4 have a single C atom in the space lattice, whilst derivatives of C_2H_2 contain the lattice group C_2. A preliminary *X*-ray examination of borides of the type CaB_6, SrB_6, BaB_6, etc. shows them to possess a cubic lattice of the CsCl type, composed of metal atoms and B_6 groups. The B atoms in the B_6 group are arranged at the angles of a regular octahedron, having an edge of 1·17 Å. in the case of CaB_6. The method of linking is discussed. E. S. HEDGES.

Crystal structure of N_2O_4. L. VEGARD (Z. Physik, 1931, **71**, 299—300; this vol., 548, 1115).—Experimental evidence is insufficient to confirm an N_2O_4 crystal unit, and is not inconsistent with a linear NO_2 unit. A. B. D. CASSIE.

Formation of mixed crystals in molecular lattices through exchange of molecules. L. VEGARD (Z. Physik, 1931, **71**, 465—472).—Substances like solid N_2O and CO_2 which possess typical mol. lattices can form mixed crystals through the interchange of mols. The change in length of the elementary cube obeys the additive law. A. J. MEE.

Crystal structure of ammonium chromate. D. J. BUJOR (Z. Krist., 1931, **78**, 1—15).—$(NH_4)_2CrO_4$ crystals (cf. A., 1889, 1117) are twinned about $(00\bar{1})$ and the *b* axis, a fact confirmed by etch figures. The unit cell has *a* 6·15, *b* 5·27, *c* 7·66 Å., β 115° 13′, and contains 2 mols.; space-group C_s^1.
C. A. SILBERRAD.

Crystal structure or potassium chromate. M. Y. COLBY (Z. Krist., 1931, **78**, 168).—K_2CrO_4 has *a* 5·92, *b* 10·39, *c* 7·68 Å., with 4 mols. in the unit cell; space-group V_h^{16}; d^{18} 2·732. C. A. SILBERRAD.

Structure of beryllium sulphate tetrahydrate. P. SCHONEFELD (Z. Krist., 1931, **78**, 16—41).—Previous results (cf. A., 1928, 463) are confirmed save that *a* should be 8·02±0·02 Å. The connexion between the structure, properties, and polarisation of the constituents is discussed. C. A. SILBERRAD.

Crystal structure of sodium nitrite, $NaNO_2$. G. E. ZIEGLER (Physical Rev., 1931, [ii], **38**, 1040—1047).—The lattice is body-centered, orthorhombic, space-group C_{2v}^{20}, unit cell containing 2 mols. *a* 3·55, *b* 5·56, *c* 5·37 Å. The positions of the atoms and distances between atoms are recorded. The angle between the N–O linkings is 132°. N. M. BLIGH.

Crystal structure of eulytite. G. MENZER (Z. Krist., 1931, **78**, 136—163).—A detailed account of work already noted (this vol., 550).
C. A. SILBERRAD.

Crystal structures of parisite, synchysite, and kordylite. I. OFTEDAL (Z. Krist., 1931, **79**, 437—464).—Parisite, $2RFCO_3,CaCO_3$, and synchysite, $RFCO_3,CaCO_3$, (R=La, Ce, etc.), although very closely related, are distinct species; some reputed parisite is really synchysite. Their structures, as also that of kordylite, $2RFCO_3,BaCO_3$, are very approx. represented by hexagonal pseudo-cells having *a* 4·094, 4·094, 4·35 and *c* 27·93, 18·20, 22·8 Å., respectively, each cell containing 2 mols. For accurate description an *a* $\sqrt{3}$ times as great, or approx. 7 Å., is required, the unit cell containing 6 mols. and the symmetry being lower. Probable structures are deduced closely resembling that of bastnasite (cf. this vol., 1116). Parisite is very weakly, if at all, piezo-electric, and it and synchysite show parallel growths. The recorded density of kordylite is probably too low.
C. A. SILBERRAD.

Roentgenography of liquids. I. Diffraction of *X*-rays by organic liquids. G. E. MUCHIN and I. I. TSCHALENKO (Ukrain. Chem. J., 1931, **6**, [Sci.], 9—51).—A review of the literature.
R. TRUSZKOWSKI.

Diffraction of *X*-rays in liquids and ionic solutions. J. A. PRINS (Z. Physik, 1931, **71**, 445—449).—The continuous spectrum is greatly interrupted in certain circumstances by the scattering of *X*-rays on passing through liquids. The results of earlier work on aliphatic compounds are corrected and extended. A. J. MEE.

Two-dimensional crystals. N. FUCHS (Z. physikal. Chem., 1931, **B**, **14**, 285—289).—Crystals of $C_{31}H_{70}$ formed on the surface of its slightly supersaturated solution in non-volatile liquid paraffin may be only 1 mol. thick. N. H. HARTSHORNE.

Crystal structure of the hydrates of copper formate. I. Copper formate tetrahydrate. II. Copper formate dihydrate. K. J. KABRAJI (Indian J. Physics, 1931, **6**, 81—114, 115—132).—The space-group of both dihydrate and tetrahydrate is C_{2h}^3: the former has 16 mols. per cell and the latter 8. In the tetrahydrate the H_2O mols. lie entirely between consecutive (010) planes through the centres of the atoms of $(HCO_2)_2Cu$. The length of the H_2O mol. in both hydrates is 4·22 Å. F. J. WILKINS.

***X*-Ray study of the magnetic character of liquid crystalline *p*-azoxyanisole and a comparison with the isotropic liquid.** G. W. STEWART (Physical Rev., 1931, [ii], **38**, 931—942).—The effect of a magnetic field on the orientation of the large groups of mols. in the liquid-cryst. state was measured, and the data are applied to an interpretation of the magnetic character, and to a comparison of the liquid-cryst. and transparent liquid states. In the former the *X*-ray diffraction intensity is 10% greater than in the latter state, in which the existence of cybotactic groups is thus supported.
N. M. BLIGH.

Transformations in the crystal lattice. E. HERTEL (Z. Elektrochem., 1931, **37**, 536—538).—The mol. compound formed of 4-bromo-α-naphthylamine with 2 : 6-dinitrophenol exists in two forms, which differ in m. p., solubility, colour, cryst. habit, and cryst. space lattice. The stable yellow modification (m. p. 91°) contains a linking between the OH of the nitrophenol and the NH_2 of the naphthylamine, which is absent in the metastable form (m. p. 85°), where the residual affinities of the benzenoid components are involved. Yellow *o*-bromoaniline picrate changes to a red modification at 95°. Changes in the lattice are discussed. E. S. HEDGES.

X-Ray investigation of *cyclo*hexane derivatives. I. General survey. II. Quebrachitol. III. *l*-Inositol, *i*-inositol, and quercitol. IV. *i*-Inositol dihydrate. A. L. PATTERSON and T. N. WHITE (Z. Krist., 1931, **78**, 76—100, and **80**, 1—4).—I. Previous investigations are discussed, and a table of possible and known *cyclo*hexanols is given. As working hypotheses the puckered ring and dextrose relationship theories are adopted with Lespieau's nomenclature (cf. A., 1895, i, 489; 1927, 98; 1928, 465; this vol., 69). II.—IV. The following data (in this order) are given: crystal class, dimensions of unit cell (a, b, c in Å.), β, density, no. of mols. in unit cell, probable space-group: quebrachitol, monoclinic sphenoidal, 6·60, 7·15, 8·65, not 90°, 1·54, 2, C_2^2 (C_2p2); *l*-inositol, monoclinic sphenoidal, 6·17, 9·11, 6·83, 106·6°, 1·598, 2, C_2^2 (C_2p2), $[\alpha]_D$ $-65{\cdot}8°$, no hydrate was obtainable; *i*-inositol, monoclinic prismatic, 6·64, 12·0, 19·7, 105·8°, 1·61 (not 1·752; cf. A., 1881, 1022), 8, C_{2h}^5 ($C_{2h}p\alpha2$); *i*-inositol dihydrate, monoclinic prismatic, 8·98, 16·59, 6·49, 109·8°, 1·58, 4, C_{2h}^5 ($C_{2h}p\alpha2$); quercitol, monoclinic sphenoidal, 6·83, 8·53, 6·45, 110° 57′, 1·5806, 2, C_2^2 (C_2p2). Distances between atoms, *e. g.*, of C, in different mols. are much greater, in the same mol. much less, than would be expected from inorg. data, pointing to such mols. being tightly bound structures, but forming comparatively open crystal structures. Quebrachitol from *Hevea brasiliensis* is identical with that from *Heterodendron oleæifolium*. C. A. SILBERRAD.

X-Ray investigation of *cyclo*hexane derivatives. V. α- and γ-*cyclo*Hexane-1 : 2-diol, β-*cyclo*hexane-1 : 4-diol, and β-*cyclo*hexanediol 1 : 4-diacetate. T. N. WHITE (Z. Krist., 1931, **80**, 5—17).—α-*cyclo*Hexane-1 : 2-diol (cf. A., 1899, i, 22), m. p. 97—98°, d^{25} 1·182, orthorhombic, unit cell, a 7·62, b 8·55, c 19·57 Å., with 8 mols.; space-group V_h^{15} ($D_{2h}p\gamma\alpha\beta$). γ-*cyclo*Hexane-1 : 2-diol prepared according to Brunel's method for the β-isomeride (cf. A., 1903, i, 338; 1905, i, 869) differed from his account thereof, and is hence designated γ; m. p. 104°, d^{24} 1·147, monoclinic prismatic, $a:b:c=1{\cdot}954:1:0{\cdot}716$, β 103·9°; unit cell a 19·13, b 9·92, c 7·23 Å., with 8 mols., space-group C_{2h}^6 ($C_{2h}b\alpha1$). β-*cyclo*Hexane-1 : 4-diol, or *trans*-quinitol (cf. A., 1894, i, 174), d^{20} 1·18, monoclinic prismatic, $a:b:c=0{\cdot}293:1:0{\cdot}339$, β 96°; unit cell a 6·32, b 21·2, c 7·27 Å., with 6 mols., space-group C_{2h}^5 ($C_{2h}p\alpha2$). β-*cyclo*Hexanediol 1 : 4-diacetate, d 1·18 (approx.), monoclinic prismatic, $a:b:c=2{\cdot}344:1:1{\cdot}168$, β 107·4°; unit cell a 13·56, b 5·83, c 6·72 Å., with 2 mols., space-group C_{2h}^5 ($C_{2h}p\alpha2$). C. A. SILBERRAD.

***cyclo*Hexane problem.** O. HASSEL (Z. Elektrochem., 1931, **37**, 540—542).—The structure of *cyclo*hexane and its derivatives is reviewed in the light of crystallographic data. E. S. HEDGES.

Structure of the molecular compound veramon [pyramidone+veronal]. E. HERTEL (Z. physikal. Chem., Bodenstein Festband, 1931, 267—272).—Comparison of the X-ray diagrams of the mol. compound of pyramidone and veronal with those of the components shows that the substance conforms to the definition previously suggested for a true mol. compound. The crystals are rhombic; 4 mols. of each of the components in the unit cell; space-group C_{2v}^2 or C_{2v}^4. The identity periods of the triclinic crystals of pyramidone are 7·4, 18·1, and 10·8 Å.; 4 mols. in the unit cell. H. F. GILLBE.

Crystal structure of hexabromobutylenes. W. EISSNER and R. BRILL (Z. Krist., 1931, **79**, 430—436).—The isomeride of m. p. 185° (cf. A., 1926, 1120), d 3·30, is monoclinic prismatic, $a:b:c=1{\cdot}57:1:2{\cdot}75$, β 68° 35′, n 1·75; variations indicate impurities in spite of recrystallisation. The unit cell has a $11{\cdot}5_5$, b 6·40, c $10{\cdot}0_6$, β 44° 27′, containing 2 symmetrical mols., space-group C_{2h}^3. This is consequently the symmetrical isomeride $[CHBr_2{\cdot}CBr{:}]_2$, that of m. p. 114° being $CHBr_2{\cdot}CBr_2{\cdot}CBr{:}CHBr$. The atoms in the mol. are almost coplanar. C. A. SILBERRAD.

Crystallographic study of some organic substances. A. FERRARI and A. SCHERILLO (Z. Krist., 1931, **80**, 45—53).—2 : 5′-Di*iso*oxazolyl ketone (this vol., 968), d 1·48, is monoclinic prismatic, $a:b:c=1{\cdot}038:1:0{\cdot}8646$, β 91° 37′; unit cell a 15·31, b 14·75, c 12·77 Å., with 16 mols. The ketone $C_{12}H_8O_6N_4$ (*loc. cit.*), d 1·492, is rhombic, $a:b:c=1{\cdot}18:1:0{\cdot}87$; unit cell a 12·98, b 11·00, c 9·57 Å., with 4 mols. The compound $C_4H_2O_3N_4$ (this vol., 1170) is monoclinic prismatic, $a:b:c=1{\cdot}500:1:3{\cdot}546$, β 105° 34′; unit cell a 7·38, b 4·92, c 17·45 Å., with 4 mols. 2 : 2′-Naphthacarbazole (cf. A., 1929, 1172), d 1·312, is monoclinic prismatic, $a:b:c=1{\cdot}169:1:0{\cdot}6989$, β 114° 14′; unit cell a 14·05, b 12·02, c 8·40 Å., with 4 mols. C. A. SILBERRAD.

Space-groups of carbohydrates. J. YOUNG and F. W. SPIERS (Z. Krist., 1931, **78**, 101—110).—The following data are given: crystal system, dimensions of unit cell (a, b, c) in Å., (if monoclinic) β, density, no. of mols. in unit cell, space-group: γ-*d*-mannonolactone, orthorhombic, 14·0, 11·1, 4·73, 1·61, 4, V^4; 2 : 3 : 5 : 6-tetramethyl-γ-*d*-mannonolactone, monoclinic, 9·79, 13·8, 4·50, 93·3°, 1·26, 2, C_2^2; 2 : 3 : 5-trimethyl-γ-*l*-rhamnonolactone, orthorhombic, 12·2, 18·3, 4·65, 1·27, 4, V^1; 2 : 3 : 4-trimethyl-δ-*l*-arabonolactone, orthorhombic, 10·8, 12·2, 7·30, 1·30, 4, V^4; 2 : 3 : 4-trimethyl-α-*d*-xylopyranose, monoclinic, 8·68, 8·31, 6·65, 91·0°, 1·30, 2, C_2^2; 1 : 3 : 4 : 5-tetramethyl-β-*d*-fructopyranose, orthorhombic, 9·22, 8·97, 14·8, 1·30, 4, V^4; 1 : 3 : 4 : 5-tetra-acetyl-β-*d*-fructopyranose, monoclinic, 10·7, 7·98, 17·0, 144·5°, 1·36, 2, C_2^1. C. A. SILBERRAD.

X-Ray investigations of cellulose derivatives. X. Fibre period of cellulose derivatives. K. HESS and C. TROGUS (Z. physikal. Chem., Bodenstein Festband, 1931, 385—391).—The fibre periods of numerous cellulose derivatives are $n \times 5{\cdot}15$ Å., where n is 2, 3, 4, or 5. This dimension, which is the length of a glucose group, is thus more closely related to the constitution of cellulose than is the length of the cellobiose group (10·3 Å.). H. F. GILLBE.

Calculation of characteristic atomic frequencies. A. MAGNUS (Z. physikal. Chem., Bodenstein Festband, 1931, 273—282).—For cryst. substances the formula $\nu=\sqrt{6v_M/Mr_0^2x}/2\pi$, where ν is the characteristic frequency, v_M the arithmetic mean at. vol. and M the harmonic mean at. wt. of the com-

ponents, r_0 the normal inter-at. distance, and x the compressibility, has been derived. The calc. characteristic temp. of various binary ionic compounds agrees well with the experimental vals., but for the elements the calc. vals. are frequently much too high. Although the discrepancy may in many cases be attributed to the Schottky transition, this does not hold for the alkali metals and Ca.
H. F. Gillbe.

Electric glow emission of iron. G. Siljeholm (Ann. Physik, 1931, [v], **10**, 178—222).—The dependence of the positive emission of Fe on temp. and its behaviour at the transition point A3, the influence of lattice change at A3 on the emission, and the alteration of thermo-power and electrical resistance with temp. have been studied. W. Good.

Physics and metallography of magnesium. E. Schmid (Z. Elektrochem., 1931, **37**, 447—459).—A lecture on the physical anisotropy of Mg crystals, elastic parameter, thermal expansion, electrical conductivity, plastic deformation, and the formation of mixed crystals in the systems Al–Mg, Zn–Mg, and Mn–Mg. E. S. Hedges.

Electric and magnetic properties of metals. R. Becker (Z. Elektrochem., 1931, **37**, 403—414).—A lecture. E. S. Hedges.

Elasticity of single crystals of iron. E. Goens and E. Schmid (Z. Elektrochem., 1931, **37**, 539—540).—In elastic properties the Fe crystal is strongly anisotropic. E. S. Hedges.

Magnetic properties of copper–nickel alloys. E. H. Williams (Physical Rev., 1931, [ii], **38**, 828—831).—The change of susceptibility with temp. and composition for alloys containing 0·1—70% Ni was investigated. N. M. Bligh.

Magnetisation of single crystals of cobalt at high temperatures. K. Honda and H. Masumoto (Sci. Rep. Tôhoku, 1931, **20**, 323—341).—Magnetisation is easiest in the direction of the [0001] axis and in weak fields reaches a max. at 230°. Magnetisation is difficult in the direction of the $[10\bar{1}0]$ and $[11\bar{2}0]$ axes, increases with rise of temp. up to 300°, and then remains const. The saturation val. at 0° abs. is 1446 c.g.s. A. R. Powell.

Relation between Barkhausen effect and intensity of magnetisation. S. Procopiu and T. Farcas (Ann. Sci. Univ. Jassy, 1930, **16**, 344—351).—For cast steel the Barkhausen effect is proportional to the intensity of magnetisation. H. F. Gillbe.

Barkhausen effect. S. Procopiu (Ann. Sci. Univ. Jassy, 1930, **16**, 352—374).—The Barkhausen effect with Fe is due to the orientation of the particles and is proportional to the variation of the intensity of magnetisation. H. F. Gillbe.

Kerr constant of nitrobenzene. R. Möller (Physikal. Z., 1931, **32**, 697—718).—The non-linear potential decrease in $PhNO_2$ is confirmed. $PhNO_2$ ($\Omega=3\times10^{-11}$) shows a Kerr const. of $3{\cdot}74\times10^{-5}$.
W. R. Angus.

Physics of the nitrobenzene "Kerr" cell. I. Distribution of a strong electrostatic field in the nitrobenzene Kerr cell. F. Hehlgans (Physikal. Z., 1931, **32**, 718—727).—The inhomogeneity of a strong electrostatic field in the $PhNO_2$ Kerr cell is produced by impurities. W. R. Angus.

Hall effect in liquid metals. J. Kikoin and I. Fakidov (Z. Physik, 1931, **71**, 393—402).—Hg showed a negligible Hall effect and K–Na alloys an effect in agreement with theory. A. B. D. Cassie.

Dilatometric investigation of the vitreous state. O. Koerner and H. Salmang (Z. anorg. Chem., 1931, **199**, 235—240).—The abrupt change of length of a cryst. material at the transition point is independent of the rate of heating, but with silicate glasses the reverse is true. The temp. at which softening commences falls as the rate of heating is diminished. Glass is thus merely a supercooled liquid, and there is no justification for the assumption that the vitreous condition represents a fourth state of matter. H. F. Gillbe.

Transitions of crystalline substances at high pressures. G. Tammann and R. Kohlhaas (Z. anorg. Chem., 1931, **199**, 209—224).—When pressure is applied to a graduated piston operating in a cylinder containing a cryst. material the occurrence of a transition is apparent from the pressure–vol. curve. An approx. val. only of the transition pressure can be obtained, since the pressure is not uniform throughout the material. Data are given for PhOH, AgI, FeS, borneol, and Sn. H. F. Gillbe.

Elastic anisotropy of iron. D. A. G. Bruggeman (Naturwiss., 1931, **19**, 814—815).

Sintering of powdered iron by heat and pressure treatment. L. Schlecht, W. Schubardt, and F. Duftschmid (Z. Elektrochem., 1931, **37**, 485—491).—The structure of pure Fe powder, formed by the thermal decomp. of Fe carbonyl, is described and the sintering brought about by heating at various temp., with or without increased pressure, is illustrated by means of photomicrographs.
E. S. Hedges.

Vibration method for investigating strength of crystals. V. D. Kusnetzov and E. V. Lavrentjeva (Z. Krist., 1931, **80**, 54—62).

Dependence of crystal plasticity on temperature. III. Aluminium. W. Boas and E. Schmid (Z. Physik, 1931, **71**, 703—714).—The investigation of the extension of Al crystals in the temp. range −185° to 600° shows a very marked alteration of properties at about 400°. Above the latter temp. the crystals have different properties according to their orientation. A. J. Mee.

Vaporisation of magnesium in a vacuum. W. Kaufmann and P. Siedler (Z. Elektrochem., 1931, **37**, 492—497).—Mg can be distilled at 650°/2 mm. and can be sublimed at 500—650°/0·05—2·0 mm. Mg. of 99·99% purity can be obtained by a single distillation, and on repeated distillation a product is obtained in which impurities cannot be recognised chemically or spectroscopically.
E. S. Hedges.

Velocity of evaporation of crystals. G. Tammann and K. L. Dreyer (Z. physikal. Chem., Bodenstein Festband, 1931, 1—18).—The velocity of evaporation of volatile crystals increases with increase of the difference between the v. p. of the substance and the external pressure, and, unlike that of liquids, rises to a limiting val. with rise of temp. The temp. at the surface of the solid has been calc. from the temp. coeffs. of the evaporation velocity and the v. p.; for camphor and $C_{10}H_8$ the difference between the surrounding temp. and the surface temp. is of the order of 4—20°. H. F. GILLBE.

Determination of the mol. wt. of vapours at very low pressures by the method of Heller and Neumann. M. VOLMER (Z. physikal. Chem., Bodenstein Festband, 1931, 863—873).—The (solid) substance is placed in a rectangular box containing two small holes so placed that when the box is suspended by a thread and placed in a high vac. the issuing vapour produces a couple which causes the box to take up a definite position relative to its initial position. By measurement of the displacement angle the mol. wt. of the vapour may be calc. Owing to some difficulties the error is about 3·4%. Typical measurements with $COPh_2$ and NPh:NPh are described. Metaldehyde has the formula $(MeCHO)_4$, whilst the vapour of quinhydrone at room temp. has mol. wt. 109. H. F. GILLBE.

Molecular size and phase partition. J. N. BRÖNSTED (Z. physikal. Chem., Bodenstein Festband, 1931, 257—266).—On the assumption that the relative potential energies of chemically similar compounds are proportional to the sizes of the mols., *i.e.*, to the mol. wt. in the case of ordinary systems, equations are derived for calculating the v. p. of one compound from that of a similar compound, and for the solubility equilibria in two-phase systems. The theory appears to be applicable also to colloidal substances such as proteins. H. F. GILLBE.

Dependence of the Kirchhoff constant on temperature. F. RECHEL (Ann. Physik, 1931, [v], 10, 1—14).—The velocity of sound in air, CO_2, O_2, N_2, and NH_3 was investigated from 16° to 910°. The deviations from theory in the variation of the Kirchhoff const. with temp. are confirmed. W. GOOD.

Behaviour of pulverised metals under pressure. F. SKAUPY and O. KANTOROWICZ (Z. Elektrochem., 1931, 37, 482—485).—The variation of electrical resistance, R, of powdered metals with the pressure, P, is represented by the equation $1/R=c\sqrt{P}+C$, where c and C are consts. depending on the material and its previous treatment. The resistivities of powdered soft metals (Zn, Sn, Pb, Ag, graphite) in the pressed state are lower than those of the compact metals, whilst the resistivities of compressed powders of hard metals (Fe, Wo, Ni) are higher than in the compact state. The results are discussed in relation to sintering. E. S. HEDGES.

Resistance of lead to high-frequency currents at superconducting temperatures. J. C. MCLENNAN, A. C. BURTON, A. PITT, and J. O. WILHELM (Phil. Mag., 1931, [vii], 12, 707—719).—The superconductivity of Pb which appears with direct current abruptly at 7·2° abs. does not appear when high-frequency currents of frequency 11×10^6 per sec. are used. A decrease is not obtained until 4·2° abs. F. J. WILKINS.

Resistivity of single-crystal zinc. E. P. T. TYNDALL and A. G. HOYEM (Physical Rev., 1931, [ii], 38, 820—827; cf. Ware, A., 1930, 844).—Measurements of sp. resistance ρ as a function of orientation support the Voigt–Thomson symmetry relation. Vals. obtained were $\rho_{\parallel}$ 6·2 and $\rho_{\perp}$ $5{\cdot}86\times10^{-6}$ ohm per c.c. for Kahlbaum Zn, and vals. each about 0·6% lower for spectroscopically pure Zn. A few crystals of the latter gave anomalous results as found by Bridgman (cf. A., 1929, 1136). N. M. BLIGH.

Electrical conductivity of metals. C. D. NIVEN (Canad. J. Res., 1931, 5, 79—86).—When electrical resistance vanishes at low temp. it does so suddenly. It is suggested that a metallic atom is one with an incomplete electron configuration, and that in ordinary conduction an electron jumps from one atom to another, where it remains until it is in a type of equilibrium with the electrons already on that atom. In the superconducting state the electronic orbits of different atoms become synchronised, and when an electron leaves an atom another automatically replaces it. J. W. SMITH.

Electrical conductivity and structure of thin metallic layers. IV. E. HAMBURGER (Ann. Physik, 1931, [v], 11, 40—52).—The applications of the relation between electrical conductivity and structure of thin metallic layers previously found (cf. this vol., 1112) are discussed. A. J. MEE.

Triple points of nitrogen and of oxygen as standard temperatures. E. JUSTI (Ann. Physik, 1931, [v], 10, 983—992).—A resistance thermometer capable of reproducing the m. p. of N_2 or O_2 to ±0·002° is described. Data are: O_2, m. p. 54·24±0·04° abs., v. p. 1·20±0·05 mm.; N_2, m. p. 63·09±0·01° abs., v. p. 93·91±0·05 mm. W. R. ANGUS.

Discontinuities at the m. p. of bismuth. W. L. WEBSTER (Proc. Roy. Soc., 1931, A, 133, 162—172).—Measurements of the temp. of emission of latent heat, the loss of rigidity, and the anomalous diamagnetic discontinuity coincide within an experimental error of 0·3°. Heating curves show that the melting of Bi takes place over several degrees. L. L. BIRCUMSHAW.

Preliminary determination of the latent heat of fusion and density of helium between 15° and 20° abs. F. SIMON and F. STECKEL (Z. physikal. Chem., Bodenstein Festband, 1931, 737—744).—An evaporation calorimeter for use at low temp. is described. The latent heat of fusion of He at 17° abs. is of the order of 40 g.-cal. per g.-atom, *i.e.*, about double the val. at the b.p. At 14·9° and 20·4° abs. liquid He has d 0·31 and 0·35, respectively, and solid He $d_{\text{calc.}}$ 0·32 and 0·37, respectively. H. F. GILLBE.

Nature of latent heat of fusion. K. HONDA and H. MASUMOTO (Sci. Rep. Tôhoku, 1931, 20, 342—352).—Assuming that the atoms of a solid element are making a simple harmonic motion, the dynamic internal pressure p_i (ratio of the internal work to the expansion in vol. caused by a rise in temp. of 1°) of numerous elements has been calc., and it is shown that the latent heat of fusion is the product of p_i and the change in sp. vol. at the m. p. For elements with a cubic lattice p_i at the m. p. is directly, and the vol. increase of 1 g.-atom due to rise in temp. of 1° at the m. p. inversely, proportional to the abs. m. p., and the at. heat of fusion is proportional to the product of the vol. change during melting and the square of the abs. m. p. A. R. Powell.

Fusion under pressure and value of interpolation formulæ. E. Jänecke (Z. physikal. Chem., 1931, **156**, 161—175).—Theoretical. The equations $(p+a)(b-t)=c^2$ and $(p+a)^r(b-t)=c$ give the pressure-temp. vals. for the fusion of certain substances under pressure; the second equation also agrees with the data for change of vol. difference with temp. and pressure. The equations can be used as interpolation formulæ and the second gives approx. the equation of state for solid–liquid at high pressures (cf. A., 1925, ii, 495; 1926, 570, 894; 1927, 1031). M. S. Burr.

Calculation of the lattice energies and heats of sublimation of the alkali halides. K. Fajans and E. Schwartz (Z. physikal. Chem., Bodenstein Festband, 1931, 717—730).—Calculation of the lattice energy of the alkali halides, employing 9 as the exponent of the repulsion potential in the Born equation, leads to discrepancies as great as 15 kg.-cal. Although the anomalies in the b. p. and sublimation heats are not entirely explicable in terms of the relative sizes of the ions, quant. agreement with the observed vals. is obtained if the deformation of the ions in the vapour phase is taken into consideration. H. F. Gillbe.

General theory of b.-p. rules. T. S. Wheeler (Phil. Mag., 1931, [vii], **12**, 685—689).—The general theory of b.-p. rules for temp. of equal v. p. and of rules involving v.-p. relations other than that of equality is discussed. F. J. Wilkins.

Heat of dissociation of iodine. W. G. Brown (Physical Rev., 1931, [ii], **38**, 709—711).—Measurements of the visible absorption bands of I in the neighbourhood of their convergence are tabulated, and lead to the val. 1·535±0·001 volts for the heat of dissociation. N. M. Bligh.

Heats of vaporisation of organic compounds. J. H. Mathews and P. R. Fehlandt (J. Amer. Chem. Soc., 1931, **53**, 3212—3217; cf. A., 1926, 462).—The method previously described has been modified so that only 30 c.c. of liquid are required for determining the heat of vaporisation, L. Vals. of L for 22 org. compounds are recorded. J. G. A. Griffiths.

Metastability of elements and compounds as a result of enantiotropy or monotropy. XV. Study of mercuric iodide with the aid of the differential gas dilatometer. E. Cohen and H. L. Bradée (Z. physikal. Chem., Bodenstein Festband, 1931, 481—493).—HgI_2 (red` has d (X-ray) 6·31, d_4^{18} (pyknometer) 6·38, coeff. of expansion (18° to 125·1°) 0·000140, transition temp. 127°, vol. change on transition (1 atm.) 0·00349±0·00005 c.c. per g. When physically "pure," the red form has d_4^{18} 6·32, and the higher val. ordinarily obtained is ascribed to the presence of a previously unknown monotropic form of red HgI_2. H. F. Gillbe.

Chemical constants of the vapours of hydrogen and of hydrogen chloride, and the entropy change accompanying the reaction $H_2 + Cl_2 \rightleftharpoons 2HCl$. T. E. Stern (Proc. Roy. Soc., 1931, A, **133**, 303—310).—Theoretical. A mistake in the author's recent calculations of the chemical const. i' of H_2 vapour (this vol., 295) is rectified. The val. for HCl vapour is calc. to be —0·42. Using the values for the entropies at 0° abs. of g.-mols. of H_2, Cl_2, and HCl, the entropy change accompanying the reaction $H_2+Cl_2 \rightleftharpoons 2HCl$ between the cryst. phases at 0° abs. is calc. to be 1·63 g.-cal. per 1°. This value follows from the supposition that H_2 mols. rotate, whilst Cl_2 mols. do not, in the cryst. phase at the lowest temp. L. L. Bircumshaw.

Theory of corresponding states and the new theory of van der Waals forces. K. Wohl (Z. physikal. Chem., Bodenstein Festband, 1931, 807—816).—A discussion, particularly of London's theory. The apparent anomaly of H_2 and He is due to the disturbing influence of the zero energy on the crit. data. The approximation formula of Slater and Kirkwood, in which only easily accessible data are involved, is more satisfactory than that of London. H. F. Gillbe.

Density of nitrous oxide. T. Batuecas (Z. physikal. Chem., Bodenstein Festband, 1931, 78—84). —The mean density of N_2O, prepared by different methods, is 1·9804±0·00005 g. per litre, a val. which is about 0·1% higher than those in the literature. H. F. Gillbe.

Generalised thermodynamic properties of higher hydrocarbon vapours. J. Q. Cope, W. K. Lewis, and H. C. Weber (Ind. Eng. Chem., 1931, **23**, 887—892).—If vals. of PV/RT for the saturated vapours of hydrocarbons having more than two C atoms are plotted against P_r/T_r all the points obtained for all hydrocarbons lie on the same curve; the max. deviation is 3%. Further, for hydrocarbons with more than three C atoms the deviations from the gas laws are approx. equal for equal values of P_r and T_r whether the vapours are saturated or not if RT/P_cV is not greater than 4. It is therefore possible to determine graphically the vol. and thermal properties of the vapour of any higher hydrocarbon up to and somewhat beyond its crit. point. F. J. Wilkins.

Polarity and vapour pressure. A. R. Martin (Nature, 1931, 128, 456). L. S. Theobald.

Change of density of carbon disulphide with temperature. J. Mazur (Nature, 1931, **128**, 673).—The density of CS_2 increases from 1·2628 at —20° to 1·4363 at —90° when the increase in d with a fall in temp. becomes more rapid; near the f. p. (—112°) d is 1·4751. L. S. Theobald.

Comparison of viscosities of liquids by oscillating columns. G. Subrahmaniam (Proc. XV Indian Sci. Cong., 1928, 86).—The rate of decay of small, steady oscillations of a liquid in a U-tube is related to the coeff. of viscosity by the expression $\nu=b^2\lambda/2\tau$, where ν is the kinematic coeff., λ is the logarithmic decrement, τ the free period, and b a const. assumed to be the same for the same tube and different wetting liquids. The relation has been verified for H_2O, EtOH, Et_2O, C_6H_6, xylene, turpentine, and CS_2. Chemical Abstracts.

Viscosity, heat conductivity, and diffusion in gas mixtures. XIX. Temperature coefficient, numerical and calculated values of the gas viscosity from the chemical formula and the critical temperature. M. Trautz (Ann. Physik, 1931, [v], 11, 190—226).—Temp. coeffs. of many vapours have been evaluated and are discussed. Experimental and theoretical vals. of η are compared.

W. R. Angus.

Densities of aqueous solutions of per-rhenic acid. W. Feit (Z. anorg. Chem., 1931, 199, 271—272).—Vals. for solutions containing up to 65·12% $HReO_4$ are given.

H. F. Gillbe.

Dielectric constants of mixtures of ethyl alcohol and water from −5° to 40°. J. Wyman, jun. (J. Amer. Chem. Soc., 1931, 53, 3292—3301).—The method previously described (A., 1930, 666) is applied for frequencies $2·15—4·1\times10^8$ to EtOH–H_2O mixtures. The polarisation at 20° is almost a linear function of the mol. fraction of EtOH. The dielectric const. (24·35) of pure EtOH at 25° is independent of wave-lengths between 3·97 and 17 m.

J. G. A. Griffiths.

Diamagnetism of liquid mixtures. H. Buchner (Nature, 1931, 128, 301—302; cf. this vol., 900).—Mixtures of $COMe_2$ and $CHCl_3$ obey the mixture law to within 2%, and show no trace of paramagnetism. Trichlorotrimethylcarbinol is diamagnetic with $\chi=-0·65\times10^{-6}$ (in the hydrated form $\chi=-0·67\times10^{-6}$); *d* 1·5, m. p. 96·5° or 97° (76° for the hydrate) (cf. this vol., 676). For $COMe_2$ χ is $-0·58\times10^{-6}$ and for $CHCl_3$ $-0·485\times10^{-6}$.

L. S. Theobald.

Diamagnetism of liquid mixtures. E. van Aubel (Nature, 1931, 128, 455; cf. this vol., 900).—Attention is directed to other liquid mixtures which show no max. magnetic susceptibility (A., 1918, ii. 388).

L. S. Theobald.

Supposed diphasic nature of glass. F. W. Preston (J. Soc. Glass Tech., 1930, 14, 349—350T; cf. B., 1921, 116A; 1923, 774A).—Heating for a short time close to the annealing point is suggested as a means of testing hypotheses previously put forward.

M. Parkin.

Theory of orderly structure of solid solutions. II. Diffusion. C. Wagner (Z. physikal. Chem., Bodenstein Festband, 1931, 177—186).—Formulæ are derived for the diffusion of the components in solid solutions of orderly structure, the γ' phase in the Fe–N system being taken as an example of the type in which the atoms of one component are so small that any excess occupies a position between the lattice atoms, whereas an excess of the other component causes the appearance of spaces in the lattice. The formulæ provide a means of determining the fractions of interstitial diffusion and of diffusion by movement through empty places in the lattice.

H. F. Gillbe.

Interdiffusion of two metals with compound formation. G. Tammann and H. J. Rocha (Z. anorg. Chem., 1931, 199, 289—305).—If the diffusion layer between two metals is composed of a single type of crystal its rate of growth follows a linear law, whereas if mixed crystals are formed the growth obeys a parabolic law. Measurements have been made of the rate of diffusion of Sn into Au, of Cd from the Cd–Cu eutectics into Cu, and of Zn into Fe, Cu, and β-Cu–Zn mixed crystals. In all cases the parabolic law is valid. The state of aggregation of the metals is of importance for the formation of new cryst. forms, since the number of crystallisation centres in a cooling melt may be much greater than in the contact surface between two types of crystals capable of interdiffusion.

H. F. Gillbe.

Aluminium–chromium alloys. M. Goto and G. Dogane (Nihon Kogyokwaishi, 1927, No. 512, 931—936).—The system Al–Cr up to 36·63% Cr has been studied.

Chemical Abstracts.

***X*-Ray study of the alloys of silver with bismuth, antimony, and arsenic. I.** S. J. Broderick and W. F. Ehret (J. Physical Chem., 1931, 35, 2627—2636).—No compound is formed in the system Ag–Bi (cf. Pogg. Ann., 1860, 110, 21). The max. solubility of Bi in Ag is approx. 5·5 wt.-%, and within this phase *a* increases from 4·076 Å. for pure Ag to 4·087 Å. for the saturated phase. The max. solubility of Sb in Ag is approx. 6 wt.-%, and *a* increases from 4·076 to 4·109 Å. A homogeneous, hexagonal close-packed phase exists between 11 and 16% Sb; at 89% Ag, a_1 is 2·920 Å., a_3 4·774 Å., and a_3/a_1 1·632. Another homogeneous phase, either rhombic or deformed cubic, is present between 72 and 78% Ag; at 74·2% Ag, a_1 is 3·000 Å., a_2 5·178 Å., and a_3 4·830 Å. The *X*-ray examination of the system Ag–Bi, but not that of Ag–Sb, supports the thermal diagrams of Petrenko (A., 1906, ii, 667).

L. S. Theobald.

Röntgen analysis of the systems gold–antimony and silver–tin. O. Nial, A. Almin, and A. Westgren (Z. physikal. Chem., 1931, B, 14, 81—90).—The results for the system Au–Sb agree with previous work (A., 1906, ii, 679; 1928, 1079). An improved val. of *a* for $AuSb_2$ is 6·647±0·005 Å. Results for the system Ag–Sn agree with the thermal diagram (B., 1926, 792). The phase fields at 400° in passing from pure Ag to pure Sn are: α solid solution, face-centred cubic, *a* 4·077—4·125 Å.; α+ε; ε solid solution, close-packed hexagonal, *a* 2·925 to 2·953, *c* 4·774—4·771 Å.; ε+ε′; ε′ solid solution, orthorhombic, *a* 2·985—2·994, *b* 5·144—5·154, *c* 4·771 Å.; ε′+Sn.

N. H. Hartshorne.

Röntgen analysis of gold–tin alloys. S. Stenbeck and A. Westgren (Z. physikal. Chem., 1931, B, 14, 91—96).—The compounds found by Vogel (A., 1905, ii, 640) are confirmed. Solid solutions are formed in the range 12—16 at.-% Sn, and these are close-packed hexagonal with *a* 2·896—2·932 and *c* 4·776—4·761 Å. Previous measurements (A., 1927, 815) of the lattice dimensions of AuSn are confirmed within narrow limits.

N. H. Hartshorne.

***X*-Ray analysis of copper–silicon alloys.** S. Arrhenius and A. Westgren (Z. physikal. Chem., 1931, B, 14, 66—79).—Cu–Si alloys show at least five intermediate phases: β, 14·5% Si, appears at higher temp. and shows hexagonal packing; γ, 17% Si, appears at lower temp., and is like β-Mn; δ, 18% Si, appears at higher temp.; ε, 21% Si, appears at lower temp., and has a face-centred cubic lattice,

a 9·694 Å.; η appears on solidification of the alloy, and contains 25% Si. A. B. D. Cassie.

Copper–magnesium alloys. IV. Equilibrium diagram. W. R. D. Jones (Inst. Metals, Sept., 1931, Advance copy, 25 pp.).—The equilibria were determined by thermal and micrographic examination using electrolytic Cu and Mg purified by sublimation in vac. The system contains two compounds Cu_2Mg, m. p. 820°, and $CuMg_2$, m. p. 567·5°, which yield a eutectic mixture (65·4% Cu, 552°). The solubility of Cu in Mg rises from 0·02% at 20° to 0·03% at 485°, and that of Mg in Cu from 2—2·2% at 20° to about 2·6% at 700°. $MgCu_2$ forms a eutectic with the Cu-rich solid solution (90·3% Cu, 722°) and Mg_2Cu forms a eutectic with the Mg-rich solid solution (30·7% Cu, 485°). There are no fields of solid solutions in the neighbourhood of either compound. No evidence for the compound MgCu could be obtained. A. R. Powell.

Physico-chemical study of the gold–copper solid solutions. N. S. Kurnakov and N. V. Ageev (Inst. Metals, Sept., 1931, Advance copy, 17 pp.).—Resistivity measurements at temp. up to 600° show that $AuCu_3$ forms solid solutions with 22—40 at.-% Au and AuCu solid solutions with 42·5—70 at.-% Au. The formation of both compounds is retarded by rapid chilling, but under normal rates of cooling the transformations occur at 425—450° and are accompanied by a marked fall in vol. Work-hardening of the quenched alloys assists the preservation of the metastable supercooled solid solution during tempering at 150—350° (cf. following abstract). A. R. Powell.

Transformations in the gold–copper alloys. J. L. Haughton and R. J. M. Payne. **X-Ray examination of gold–copper alloys.** G. D. Preston (Inst. Metals, Sept., 1931, Advance copy, 24 pp.).—Measurements have been made between 18 and 70 at.-% Au of the electrical resistance with changing temp., and of the sp. resistance of slowly cooled alloys, supplemented by micrographic examination and by X-ray analysis. The results confirm the existence of AuCu and $AuCu_3$ and the presence of another transformation in alloys approximating to the composition Au_2Cu_3 has been established. The transformation temp. of AuCu rises steeply from 20° at 29 at.-% Cu to 323° at 38·2% Cu, then more slowly to a flat max. at 422° with 50 at.-% Cu, falling again slowly to a min. at 58·8 at.-% Cu, at which point the transformation curve of Au_2Cu_3 commences. This curve reaches a max. of 360° with 60 at.-% Cu, then falls sharply to a min. at 297° with 63 at.-% Cu. The transformation curve for $AuCu_3$ rises slowly from this point to a flat max. at 395° with 75 at.-% Cu, then falls steeply to room temp. with 82 at.-% Cu. In the AuCu group of alloys marked hysteresis in the transformation temps. occurs. The resistivity of slowly cooled alloys indicates that the Cu-rich limit of the transformation at 20° occurs at 17·5 at.-% Au and the Au-rich limit at 71 at.-% Au. Alloys quenched from above the transformation points have a homogeneous solid solution structure, whilst those cooled through these points have a more or less martensitic structure. The alloy AuCu when annealed at 400° for 20 hr. and quenched has a face-centred cubic structure, a 3·94 Å., with random orientation of the Cu and Au atoms, but when slowly cooled from 700° it has a body-centred tetragonal lattice, a 2·79 Å., c/a 1·31, the Au and Cu atoms being arranged regularly at the points of the lattice. The alloy Au_2Cu_3 has a body-centred tetragonal lattice, a 2·73 Å., c/a 1·36. No two-phase field could be detected by X-rays. A. R. Powell.

Constitution of the alloys of silver and mercury. A. J. Murphy. **X-Ray examination of the alloys.** G. D. Preston (Inst. Metals, Sept., 1931, Advance copy, 21 pp.).—Progressive additions of Hg produce a continual reduction of the initial f. p. down to −38·8° and no alloy has a f. p. below that of Hg. The solidus falls in a smooth curve from the m. p. of Ag to 55% Ag at 276° and to about 51% Ag at 0°. Two intermediate phases of restricted composition are formed; the β-phase contains 40% Ag and has a close-packed hexagonal lattice, a 2·98 Å., c/a 1·62, whilst the γ-phase contains 29—30% Ag and has a body-centred cubic lattice, a 10·0 Å. Above 276° β dissociates into α+liquid and above 127° γ dissociates into β+liquid. Increase of pressure has practically no effect on the equilibria in the system. A. R. Powell.

System copper–lead and related heterogeneous systems. W. Claus (Kolloid-Z., 1931, 57, 14—16).—Consideration of the separation of a melt of Cu and Pb into two phases on cooling in the light of Stokes' law provides an explanation of the different vals. obtained by various observers for the temp. at which the separation occurs. The explanation holds for other systems of a similar type, where discordant results have been obtained by different methods. E. S. Hedges.

Macro-etching of aluminium–silicon alloys. W. Hume-Rothery (Inst. Metals, Sept., 1931, Advance copy, 4 pp.).—The specimen is immersed in 15—16% solution of $CuCl_2$ for 5—10 sec., washed, and wiped with a woollen cloth to remove Cu. The procedure is repeated 3—4 times and the specimen finally brightened by immersion in dil. H_2CrO_4 solution. Oblique illumination is recommended for photographing the macrostructure revealed in this manner. A. R. Powell.

Electrical conductivity of gold–nickel alloys. G. Grube and F. Vaupel (Z. physikal. Chem., Bodenstein Festband, 1931, 187—197).—The resistance–temp. curves for a series of Au–Ni alloys between 20° and 900° show that the reduction of the mutual solubility of the components as the temp. falls causes the separation of Au-rich and Ni-rich mixed crystals. The segregation–temp. curve is in fair agreement with that of Fraenkel and Stern. The temp. of the magnetic transition of Ni falls as the Au content is increased up to about 15%, and thereafter remains const. The resistance of Au is increased considerably by addition of small quantities of Ni, but at 400—800° the resistance of alloys containing from 60 to 95% Ni is practically const. H. F. Gillbe.

Superconductivity of gold–bismuth alloys. W. J. de Haas and F. Jurriaanse (Naturwiss., 1931, 19, 706).—When the eutectic mixture of Au–Bi alloys is dissolved in HNO_3, some crystals remain which are completely insol. These are tetragonal Au_2Bi and are responsible for the superconductivity of Au–Bi alloys at 1·84° abs. The form of the crystal lattice appears to play an important rôle in superconductivity phenomena. W. R. Angus.

Solutions of ethyl alcohol in benzene, water, and in benzene and water. E. R. Washburn, V. Hnizda, and R. Vold (J. Amer. Chem. Soc., 1931, **53**, 3237—3244).—Miscibility data for the system $EtOH–H_2O–C_6H_6$ at 25° and the depression of the f. p. of C_6H_6 by 1·1—96·9 wt.-% EtOH have been determined. It is suggested that the addition of H_2O to C_6H_6–EtOH mixtures leads to a predominance of simple EtOH mols. by shifting the polymerisation equilibrium. J. G. A. Griffiths.

Effects of dissolved substances on the solution temperature of a phenol–water system. J. L. Culbertson and E. S. Palmer (J. Physical Chem., 1931, **35**, 3063—3069).—For K salts the lyotropic series is $SO_4 > Cl > Br > NO_3 > I > CNS$. The crit. solution temp. appears to depend on the surface tension of the aq. solution. L. S. Theobald.

Solubility of naphthols in water. G. E. Muchin and I. I. Tschalenko (Ukrain. Chem. J., 1931, **6**, [Sci.], 117—119).—The crit. solution temp. for α-naphthol is 210·5°, and β-naphthol 192·0°.

R. Truszkowski.

Solubilities and solubility products of metallic sulphides in water. I. M. Kolthoff (J. Physical Chem., 1931, **35**, 2711—2721).—A crit. survey of the literature. The solubilities in pure H_2O and in equilibrium H_2O have been calc., but the vals. are too small to be of practical significance. The relation between solubility and $[H^{\cdot}]$ and $[H_2S]$ should be expressed by the reaction const. Weigel's solubility data are untrustworthy. L. S. Theobald.

Iodine pentoxide and its hydrate. E. Moles and A. Perez-Vitoria (Z. physikal. Chem., Bodenstein Festband, 1931, 583—590).—The solubility of I_2O_5 in 20—65% HNO_3 at 25° has been determined. Isobars of the thermal decomp. of HIO_3 show that HI_3O_8 is formed at 70°, and I_2O_5 at 200°. When heated in air I_2O_5 commences to decompose at 275°. The coloration usually observed at lower temp. appears only if H_2SO_4 is used during the prep. of the material. H. F. Gillbe.

Solubility of oxalic acid in aqueous solutions of hydrochloric acid. E. M. Chapin and J. M. Bell (J. Amer. Chem. Soc., 1931, **53**, 3284—3287; cf. A., 1924, i, 368).—The data refer to 0—34·5% HCl at 0°, 50°, and 80°. The solubility of oxalic acid is minimal in 10% HCl at 80°, 18% HCl at 50°, and 20% HCl at 0°. A solid phase other than $H_2C_2O_4,2H_2O$ was not detected. J. G. A. Griffiths.

Calcium sulphate in sea-water. Y. Tanaka, K. Nakamura, and R. Hara (J. Soc. Chem. Ind. Japan, 1931, **34**, 284—287B).—The solubility of $CaSO_4,2H_2O$ at 0—100° and of $CaSO_4$ up to 200° in aq. NaCl has been determined interferometrically. With very fine crystals abnormal vals. are obtained for both salts and discordant results with $CaSO_4$ can be avoided only by using natural anhydrite. The data indicate the gypsum transition point for any given NaCl solution. The greater part of the $CaSO_4$ may be removed from brine by heating the latter at 200°. C. Irwin.

Solubility influences (couple pyramidone–veronal). L. Irrera (Gazzetta, 1931, **61**, 614—618).—The solubility of veronal in H_2O is increased by the presence of pyramidone between 14° and 27°. For small concentrations of the latter the solubility coeff. is independent of temp., but at higher concentrations it increases with the temp. From calculations of the heat of dissolution by means of the van 't Hoff isochore it is shown that veronal and pyramidone form complex compounds only in conc. solutions.

O. J. Walker.

Solubilities of alkali bromides and fluorides in anhydrous methyl, ethyl, and butyl alcohols. F. G. Germuth (J. Franklin Inst., 1931, **212**, 343—349).—Solubility data for NaBr, KBr, NaF, and KF in MeOH, EtOH, and $Bu^{\alpha}OH$ between 20° and 55° are given. The solubility of each decreases with increasing mol. wt. of the solvent. NaBr in EtOH and BuOH shows a max. on the solubility–temp. curve. NaBr, KBr, and KF in MeOH, and KF in EtOH have a negative temp. coeff.

H. J. Emeléus.

Iodine. II. J. Lanza (Anal. Fis. Quím., 1931, **29**, 470—489).—The partition of iodine between CS_2 and H_2O and the influence of halides on the distribution have been examined. H. F. Gillbe.

Laws governing the separation of traces of substances entering into the composition of mixed crystals. R. Mumbrauer (Z. physikal. Chem., 1931, **156**, 113—134).—The crystallisation of solutions of Ba salts containing Th-*B* or Th-*X* has been studied. On slow crystallisation of supersaturated solutions the active substance is distributed between the solid solution and the liquid phase in accordance with the law of simple distribution (cf. A., 1927, 431), and is homogeneously dispersed in the mixed crystal. On rapid crystallisation from supersaturated solution or crystallisation by evaporation of the saturated solution, the distribution follows, however, a logarithmic law (cf. A., 1925, ii, 381). The observations recorded by Chlopin (A., 1930, 27) seem to have been complicated by recrystallisation effects. R. Cuthill.

Discontinuities in adsorption isotherms. A. F. Benton and T. A. White (J. Amer. Chem. Soc., 1931, **53**, 3301—3314; cf. A., 1930, 990; this vol., 902, 1005).—Details are given of results outlined previously. The adsorption of H_2 at −183° by sintered Cu, and by Ni, Cu, or Fe poisoned with CO is less than that by the unpoisoned metals, but the isotherms exhibit similar discontinuities. H_2 is adsorbed on the top of the CO as well as on the bare metal. Fe alone affords discontinuous adsorption at −78·5°; the other metals afford the "chemical" or "activated" type. Differential heats of adsorption between −195° and −183° are <1800 g.-cal. per mol. Stepwise adsorption has no relation to catalytically active patches. The results support the theory that adsorption occurs in successive rows, that neighbouring mols. evaporate from the surface less readily than isolated mols. and that physically adsorbed mols. possess mobility in the plane of the surface. J. G. A. Griffiths.

Activated adsorption. W. E. Garner (Nature, 1931, 128, 583—584).—Theory and experiment support the view that in certain transitional regions the heat of adsorption increases with a rise in temp.
L. S. Theobald.

Activated adsorption of hydrogen by zinc and chromium oxides. H. S. Taylor (Nature, 1931, 128, 636).—At 0° and above, H_2 is slowly and reversibly adsorbed on ZnO prepared by igniting ZnC_2O_4 at 400°. All the H_2 is recovered by evacuation at 450°. The activation energy is 14 kg.-cal. for the main surface covered, with smaller vals. for the more active areas. The heat of adsorption (calc. by D. V. Sickman) is 21 kg.-cal. per mol. Below 0°, another type of adsorption occurs which reaches equilibrium almost instantaneously with no activation energy. The heat of adsorption in this case is 1100 g.-cal. per mol. At 0°, this type of adsorption is negligible.
L. S. Theobald.

Adsorption and specific reactions at surfaces. H. S. Taylor (Z. physikal. Chem., Bodenstein Festband, 1931, 475—480).—The activation energy of adsorption processes is discussed in relation to the problem of sp. reactions at surfaces. The adsorption of H_2 on Al_2O_3 is slow but measurable at 445°, and its velocity increases seven-fold on raising the temp. to 525°; the activation energy of the process is thus about 27·5 kg.-cal. per mol. The adsorption is reversible and no H_2O is formed. In the dehydration range (200—300°), therefore, dehydrogenation cannot occur, and the dehydration activity is probably due to a rapid activated adsorption of H_2O. The velocity of adsorption of O_2 on Ag between 0° and 184° has been determined; the activation energy, calc. from the results at 0° and 56°, is 15 kg.-cal. per mol.
H. F. Gillbe.

Adsorption of hydrogen by a zinc oxide–chromium oxide catalyst. F. E. T. Kingman (Trans. Faraday Soc., 1931, 27, 654—661).—The rate of adsorption of H_2 by a ZnO–Cr_2O_3 catalyst at −80°, 0°, and 100° first falls and then rises again as the reduction of the catalyst progresses. It seems that the adsorption process involves a van der Waals type of adsorption, a type with a high heat of activation, but not causing reduction, and adsorption on the O atoms of the surface, leading to reduction. The speed of the last type of adsorption is appreciable only at 100°, and the speed of the second type increases as the temp. rises. R. Cuthill.

Energy transfer at adsorbed molecules. K. F. Herzfeld and M. G. Meyer (Z. physikal. Chem., Bodenstein Festband, 1931, 669—678).—Theoretical. The transfer of energy when a mol. is adsorbed on a cryst. surface is discussed on the assumption that such interaction may be regarded as taking place between two multipoles. In general the adsorbed mol. will be excited only if more than 1 energy quantum is transferred from the crystal.
H. F. Gillbe.

Adsorption from mixed solvents. I. Benzoic acid. G. E. Muchin, N. G. Gurski, and T. M. Polonski (Ukrain. Chem. J., 1931, 6, [Sci.], 135—145).—The adsorption by C of BzOH from EtOH–C_6H_6 and EtOH–$CHCl_3$ mixtures is smaller than from solutions in the pure solvents. R. Truszkowski.

Adsorption of electrolytes by crystalline surfaces. III. L. de Brouckère (Bull. Acad. roy. Belg., 1931, [v], 16, 1263—1274; cf. A., 1930, 850).—The adsorption of NaBr, KBr, NaI, KI, and CdI_2 by $BaSO_4$ is a reversible phenomenon unaffected by capillary effects and by adsorption of solvent. Anions and cations are adsorbed in equiv. quantities.
C. W. Gibby.

Adsorption on layers of barium fluoride sublimed in vacuum, and the structure of these layers. J. H. de Boer (Z. physikal. Chem., 1931, B, 14, 149—165).—The adsorption of I on BaF_2 sublimed in vac. is represented by the same isotherm as is its adsorption on CaF_2 (A., 1929, 875; this vol., 902), and in both cases the max. quantity of I adsorbed depends on the amount of salt sublimed, indicating that the latter has a lamellar structure. The results also show that the fall in polarity of the I with increasing distance from the salt surface is greater with BaF_2 than with CaF_2, and that the I is more strongly polarised by the former; this is confirmed by a comparison of the absorption spectra of the I on the two surfaces. It is suggested that the surfaces consist of F ions, and that the I atoms occupy more space on the BaF_2 than on CaF_2, in conformity with the greater distance between the F ions in the former.
N. H. Hartshorne.

Influence of hydrogen-ion concentration on the adsorption of weak electrolytes by pure charcoal. II. H. J. Phelps (Proc. Roy. Soc., 1931, A, 133, 155—161).—The quantity of base adsorbed by charcoal prepared from "ashless" filter-papers is for NH_2Pr^{α} and NH_2Bu^{α} proportional to the concentration of the non-ionised mols. at any given value of $[H^{\cdot}]$, and the adsorption is uninfluenced by acid treatment of the charcoal. Some impurity in the charcoal appears to prevent attainment of true equilibrium with solutions of $EtCO_2H$, but after acid treatment the adsorption is proportional to the concentration of non-ionised mols. It is concluded that a sufficiently purified charcoal presents a perfectly neutral surface to aq. solutions of weak acids and bases and adsorbs these only as non-ionised mols.
L. L. Bircumshaw.

Activated charcoal. I. S. Roychoudhury (J. Indian Chem. Soc., 1931, 8, 433—467).—Animal (*a*), sugar (*b*), and gelatin (*c*) charcoals were purified by Miller's method (A., 1926, 898) and then activated under differing conditions of temp., time of heating, and presence of air, N_2, or CO_2. The extent of activation, measured by the absorption of BzOH (*loc. cit.*), varies considerably; CO_2 generally causes greatest activity and (*a*) is the best absorbent. In many cases, particularly with samples of (*b*), the amount of acid adsorbed per g. of charcoal does not fall with decrease in the end concentration; foreign substances are probably present on the surface. Samples of (*b*) frequently show no adsorption when small amounts (0·125 g.) are used. Further purification of activated charcoals by repeated washing with conductivity

H_2O gives products having a + charge (in contact with H_2O), even when the original prep. has a — charge; this shows that adsorbed ions are responsible for the charge (cf. A., 1922, ii, 689). The order of adsorption of BzOH, AcOH, formic, propionic, butyric, and mono-, di-, and tri-chloroacetic acids varies with different charcoals; dissimilar curves are obtained with differing amounts of the same sample. The orders resemble the mixed series of Dubinin (A., 1930, 1364) but they also depend on the mass of the absorbent. The amount of BzOH adsorbed by various charcoals is decreased to varying extents by EtOH.

Negatively charged (*a*) adsorbs alkali but not acid; in contact with aq. KCl, acid is liberated. Samples of (*b*) adsorb acid but not alkali; alkali is liberated in contact with KCl. The charges on (*a*), (*b*), (*c*), and active C (Merck) in presence of electrolytes are studied. The equiv. adsorption of the ions of HCl and H_2SO_4 found by previous workers is confirmed, and the theories of Frumkin (A., 1926, 1091, *et seq.*) and Schilov (A., 1928, 581, *et seq.*) are criticised.

H. BURTON.

Changes in sorption capacity of zinc oxide through pulverisation. G. F. HUTTIG and M. KANTOR (Z. anal. Chem., 1931, **86**, 95—98).—Finely-powdered ZnO adsorbs more Congo-red, Bordeaux-red R, and eosin than the coarser material, but the ratio of the adsorbent capacities of the two forms of ZnO is not const. E. S. HEDGES.

Adsorption of water and ethyl acetate vapours by silica gels. A. L. ELDER and O. L. BRANDES (J. Physical Chem., 1931, **35**, 3022—3024).—At relatively low partial pressures Patrick's commercial SiO_2 gel is more efficient than Holmes' chalky gel for adsorbing either H_2O or AcOEt from an air stream at 30°; at higher pressures the chalky gel has the larger adsorption capacity. L. S. THEOBALD.

Alumina as an ionising adsorbent. W. D. BANCROFT and J. W. ACKERMAN (J. Physical Chem., 1931, **35**, 2568—2580).—Adsorption experiments confirm the view (A., 1930, 28) that the colour of Al_2O_3–alizarin lakes is due to adsorption of the alizarate ion. These lakes coagulate and become lighter in colour when treated with aq. H_2O_2 owing to the reaction between unadsorbed Na alizarate and the acids present in the H_2O_2. Hydrous SnO adsorbs undissociated alizarin or Na alizarate giving an orange or purple lake, respectively, but it does not adsorb the alizarate ion. Hydrous ZnO adsorbs undissociated Na alizarate to form a purple lake. In the presence of silk or SiO_2, rhodamine is ionised and adsorbed, producing strong fluorescence, but Al_2O_3, ZnO, SnO, wool, and cotton show practically no fluorescence, indicating a different type of adsorption. Hydrous Al_2O_3 forms a violet lake with violuric acid, but adsorption is slight; hydrous Sn oxide adsorbs the undissociated acid to a slight extent, but gives no colour, whilst hydrous ZnO adsorbs neither the acid nor its Na salt. L. S. THEOBALD.

Study of adsorption processes in dilute non-aqueous solutions by the aid of dielectric measurements. L. EBERT and E. WALDSCHMIDT (Z. physikal. Chem., Bodenstein Festband, 1931, 101—112).—A general account is given of the applications of the method and of the experimental procedure. Measurements of the adsorption equilibria in the system C_6H_6–C–H_2O are described. Equilibrium between moist C and dry C_6H_6 is attained within about 1 hr., whereas if dry C is immersed in moist C_6H_6 the C_6H_6 blocks the active surface of the adsorbent and equilibrium is established only very slowly. The adsorption of EtOH from C_6H_6 by C is given approx. by $S=7{\cdot}15m$, where S is the quantity adsorbed, expressed as a percentage of the initial concentration, and m is the weight of the adsorbent. For feebly adsorbed substances the const. diminishes and the exponent of S becomes <1. The behaviour of different C and SiO_2 gel adsorbents after heating at various temp. has been studied; with some specimens of C the activity increases with rise in the temp. of heating and with others it decreases; with SiO_2 gel the activity appears always to diminish. H. F. GILLBE.

Calculation of equilibrium concentrations in adsorption from liquids. W. ROGERS, jun., and M. D. SCLAR (J. Physical Chem., 1931, **35**, 2758—2762).—A method is described by which the Freundlich isothermal may be used to calculate the equilibrium concentration and the amount of solute adsorbed when the initial concentration, vol. of solution, and wt. of adsorbent are known. The validity of the method is established by comparison with data for which Freundlich's isothermal holds.

L. S. THEOBALD.

"Anomalous" Kroeker curves. P. MEHL (Kolloid-Z., 1931, **56**, 299—305).—The variation of the adsorption function x/m with m (where x is the amount adsorbed and m the mass of adsorbent) has been studied at const. initial concentration and const. vol. with AcOH and picric acid in EtOH and H_2O, using blood charcoal and "carboraffin" as adsorbents. The form of this function (the Kroeker curve) varies regularly as the concentration and x diminish, the convexity towards the m axis becoming flatter and developing a marked max. in the region of small values of m. The so-called "anomalies" of the Kroeker curve are thus shown to be a characteristic feature of adsorption at low concentrations and for small amounts of adsorbent. An anomaly observed in the adsorption of AcOH in EtOH by C, the amount varying with the time during which the adsorbent is agitated with the solution, is traced to the formation of AcOEt under the catalytic influence of the C.

E. S. HEDGES.

Combination of gases with potassium permanganate. F. DURAU (Z. physikal. Chem., 1931, **156**, 195—209).—O_2 and N_2 are simply adsorbed, but only to a very small extent, by powdered $KMnO_4$. With H_2, CO_2, CO, and SO_2 chemosorption takes place in addition to a small adsorption which is not sufficient to cover the surface with a unimol. layer. There is little or no absorption. The adsorption of O_2 and N_2 is not influenced by previous treatment with one of the other gases. A comparison of the adsorption isotherms of C_3H_8 by NaCl (cf. A., 1928, 1317) and $KMnO_4$ shows that whilst the former is convex to the pressure axis, the latter is concave. This strengthens the theory (*loc. cit.*) that adsorption by the van der Waals attraction is due to lattice disturbances. A method is described for determining the sp. gr. of a powder without interference by adsorbed or chemosorbed gases. M. S. Burr.

Combination of gases with decomposed potassium permanganate. F. Durau (Z. physikal. Chem., 1931, **156**, 210—224; cf. preceding abstract).—By heating $KMnO_4$ under reduced pressure O_2 is given off and a product analogous to adsorbent charcoal is obtained. Simple adsorption of A and N_2 takes place, but N_2 is not adsorbed below a pressure of 1 mm. There is strong chemosorption of O_2, CO_2, and CO, but chemosorption of CH_4, C_2H_6, and C_3H_8 is small compared with the adsorption. Adsorption of N_2 is only slightly affected by change in surface properties, but in the case of other gases the effects of previous treatment, *e.g.*, with another gas, are more marked. A unimol. layer is probably formed by adsorption. Chemosorption appears to be due to the formation of more or less stable compounds which are slowly decomposed at high temp. and reduced pressure, hence the slow continuous evolution of gas from the glass or other walls of evacuated vessels. M. S. Burr.

Anomalous first heats of adsorption. G. M. Schwab and W. Brennecke (Z. physikal. Chem., Bodenstein Festband, 1931, 907—911).—Measurements with H_2 and He at low pressure demonstrate that systematic calorimetric errors may occur in the determination of heats of adsorption on activated metals owing to the poor conductivity of the adsorbent, and that fictitious max. may occur on the adsorption–adsorption heat curves.

H. F. Gillbe.

Coherer method of determining heats of adsorption. S. Lenher and G. H. Cameron (J. Physical Chem., 1931. **35**, 3082—3085).—Reproducible vals. for the cohering voltages of W filaments in H_2, O_2, N_2, or in a vac. could not be obtained, and hence the coherer method of determining heats of adsorption is regarded as untrustworthy (cf. A., 1926, 239). Palmer's assumed mechanism for the action of the coherer is criticised.

L. S. Theobald.

Kinetics of adsorption of vapours in an air stream. J. K. Syrkin and A. J. Kondraschov (Kolloid-Z., 1931, **56**, 295—299).—The velocity of adsorption of the vapours of CS_2, pyridine, $Bu^{\beta}OH$, and $CMe_2Et{\cdot}OH$ from an air stream by C between 10° and 100° may be expressed by the formula $\log A/(A-c)=0{\cdot}434Kt$, where A is the equilibrium concentration, c the adsorbed amount, t the time, and K a const. The val. of K varies with the temp.; the temp. coeff. is 1·06—1·32. The rate of adsorption is much slower than is to be expected from purely kinetic considerations. Probably, only those mols. are adsorbed which have their polar groups favourably oriented with respect to the adsorbent at the moment of striking the surface; mols. not so oriented act as inhibitors. E. S. Hedges.

Effect of mercuric iodide and ammonium chloride on glass. C. E. Miller (J. Physical Chem., 1931, **35**, 2985—2992).—Adsorption measurements with PhMe vapour show that fused pyrex glass is attacked when heated (450°) in contact with HgI_2 or NH_4Cl; considerable adsorption on the surface then results. With NH_4Cl the etching becomes visible, and HgI_2 leaves streaks of a black compound. Soft glass reacts with HgI_2 on heating to give a sol. iodide. The corrosive action is attributed to the existence of $Na^{\cdot}$ in the glass, and renders it unsuitable for use when the adsorption of polar compounds is studied.

L. S. Theobald.

Wetting and adsorption at the boundary of three phases. D. Talmud (Z. physikal. Chem., 1931, **156**, 237—238).—If, at the boundary of three phases, a fourth immiscible substance is placed, the latter spreads along the boundary line. The limiting condition is a unimol. adsorption thread. This represents unidimensional adsorption due to linear tension in the region of separation of the three phases. Point tension at the boundary point of four phases is also conceivable. M. S. Burr.

Method of measuring surface tension. J. H. Gaddum (Proc. Roy. Soc., 1931, **B**, **109**, 114—125).—The drop-wt. method has been modified by measuring the vol. of drops by means of the micrometer syringe. The procedure enables the surface tension of a liquid to be measured in abs. units and is especially suitable for following the slow fall of "static" surface tension in the newly-formed surface of a hydrophilic colloidal solution. The apparent viscous-elasticity of the surface of saponin solutions is shown by changes occurring in the shape of the drops. The rapid changes are due to concentration changes in the surface, and it is suggested that the slow changes are due to diffusion of saponin. Slow changes occurring in the tension of certain plastic bodies (*e.g.*, rubber and muscle) following a strain may also be due to the diffusion of mols. into positions where they affect the tension. E. S. Hedges.

Thermodynamic study of surface tension. VIII. Affinity and velocity of adsorption. R. Defay (Bull. Acad. roy. Belg., 1931, [v], **16**, 1249—1263; cf. A., 1930, 1247).—Mathematical. Surface tension is independent of curvature in the absence of adsorption, both for a drop of liquid in contact with a mixture of vapours, and for the meniscus between two pure immiscible liquids. C. W. Gibby.

Interfacial tension and hydrogen-ion concentration. R. A. Peters (Proc. Roy. Soc., 1931, **A**, **133**, 140—154).—The interfacial tension of C_6H_6 solutions of long-chain carboxylic acids against "buffered" aq. solutions begins to fall at p_H 5·5 and tends to vanish at p_H 9·3 approx. For a given p_H the results are the same for phosphate- and glycine-buffered solutions and also for all the acids investigated except decoic, which shows certain abnormalities with phosphate buffers. With hexadecylamine the interfacial tension rises over roughly the same p_H range. K_a and K_b for $\cdot CO_2H$ and $\cdot NH_2$ in the interface are calc. to be $3{\cdot}2\times10^{-8}$ and $1{\cdot}0\times10^{-7}$, respectively. Et palmitate shows a fall similar to that for the acids, but hexadecyl alcohol shows no change. Some biological aspects of the results are discussed.

L. L. Bircumshaw.

Effect of light on the surface tension of Boys' soap solution. L. D. Mahajan (Indian J. Physics, 1931, **6**, 147—154).—The surface tension of a soap solution decreases rapidly if it is exposed to sunlight or is boiled. Solutions kept in the dark show little change in surface tension. The fall in surface tension is not therefore an adsorption phenomenon, but is due to chemical changes which take place in the solution under the influence of light or heat rays.

F. J. WILKINS.

Effect of light on the surface tension of Boys' soap solution. P. L. DU NOÜY (Nature, 1931, **128**, 674).—A criticism (cf. preceding abstract).

L. S. THEOBALD.

Surface tension of molten glass at temperatures near the m. p. W. B. PIETENPOL and H. H. SCOTT (Physical Rev., 1930, [ii], 35, 296).—The surface tension of different glasses is approx. 250—350 dynes per cm. and varies only slightly with temp. up to approx. 200° above the softening point.

L. S. THEOBALD.

Formation of films at liquid–liquid interfaces. J. A. SERRALLACH and G. JONES (Ind. Eng. Chem., 1931, **23**, 1016—1019).—Solid films form at the interface of oil and aq. solutions of emulsifying agents when the two unagitated surfaces are kept in contact for some weeks. The properties of the film are due more to the influence of the oil than of the emulsifier. Olive oil, castor oil, cod-liver oil, and refined heavy mineral oil were studied with eight different emulsifying agents. Cod-liver oil is remarkable for forming tough, thick, opaque films and mineral oil has the least tendency. The observations are useful as a means of determining suitable conditions for preparing stable emulsions. They suggest, also, that in true emulsions the film of emulsifying agent may be thicker than 1 mol.

E. S. HEDGES.

Very thin films and their physical properties. H. E. DEVAUX (J. Phys. Radium, 1931, [vii], 2, 237—272).—A summary.

A. J. MEE.

Free electrical charges on droplets of insoluble liquids in water. R. DU BOIS and A. H. ROBERTS (J. Physical Chem., 1931, **35**, 3070—3081).—The charges per sq. cm. measured by the null-point method (A., 1930, 1366) on oleic acid–H_2O or stearic acid–H_2O interfaces are of the same order of magnitude as those found for cetylsulphonic acid (*loc. cit.*); the fraction of the surface covered by free charges is $1/10^5$. Drops of tetradecane or tetrahydronaphthalene in H_2O show practically the same charge as do the fatty acids. The addition of KCl to the H_2O increases the charges, and conductivity measurements reveal adsorption on the drops. Drops of H_2O in the hydrocarbons are unaffected by an electric field. Cataphoretic velocity measurements with a horizontal electric field give vals. for the charge densities which differ only slightly from those obtained by the null-point method. Charge densities increase rapidly with diminution in the radius of the drop.

L. S. THEOBALD.

Surface conductance at the cellulose–water interface. K. KANAMARU (J. Cellulose Inst. Tokyo, 1931, 7, 15—20).—A method has been evolved for calculating the sp. conducting capacity of the cellulose–H_2O interface from the data obtained in the measurement of ζ-potential by the streaming potential method (cf. this vol., 1232). A mathematical analysis of the method is given. The surface conductance of a diaphragm against H_2O is determined by the sp. conducting capacity F_s of the diaphragm, *i.e.*, the capacity to conduct current along the solid–liquid interface, and by the sp. surface s of the diaphragm. Electrodialysis, acid treatment, mercerisation, oxidation, and other similar modifications of cellulose cause an increase in F_s. Hydrolysis and esterification have the reverse effect.

T. T. POTTS.

Surface phenomena on gels of thorium and ferric oxides. O. HAHN and G. GRAUE (Z. physikal. Chem., Bodenstein Festband, 1931, 608—619).—The sp. surface of $Th(OH)_4$ gels, prepared either from the sol or by precipitation by aq. NH_3 from Th salt solutions, is about 30%, and is independent of the conditions of its formation. With $Fe(OH)_3$ gels, on the contrary, the surface varies considerably with change of the precipitation conditions. The dispersion is greater in gels prepared at 20° than in those prepared at 100°, and ageing is more rapid than with $Th(OH)_4$ sols and takes place more slowly in the more thoroughly purified gels; Cl′ thus catalyses the ageing. Dry $Fe(OH)_3$ gels, when heated at 280°, undergo considerable increase of particle size. Gels prepared from the sol are much coarser than those obtained by precipitation. If the sol is fresh, the gel ages but slowly, but the rate of ageing increases with the age of the original sol. The measurements were made by the emanation method, and no difference was discernible between gels on which the radio-Th was deposited after prep. and those on which it was precipitated simultaneously.

H. F. GILLBE.

Electro-osmosis and interfacial electrokinetic potentials. H. MURAOKA and K. HIRUMA (Res. Electro-Tech. Lab. Tokyo, 1930, No. 279, 18 pp.).—Determinations were made of the amount of liquid transported through diaphragms of earthenware or glass particles, and vals. obtained for the interfacial potential of Helmholtz' double layer.

CHEMICAL ABSTRACTS.

Molecular size of halides and of their complex compounds in indifferent solvents. I. H. ULICH (Z. physikal. Chem., Bodenstein Festband, 1931, 423—431).—Cryoscopic and ebullioscopic measurements with solutions of a variety of Al halides and complex halides in C_6H_6 and CS_2 show that no dissociation occurs at high dilutions. At higher concentrations typical dipole association takes place; in the case of $AlBr_3$ the association is attributable to the tendency of Al to a co-ordination number of 4, and results only in the dipole-free Al_2Br_6.

H. F. GILLBE.

Temperature of maximum refractivity of some aqueous solutions. N. GREGG-WILSON and R. WRIGHT (J. Physical Chem., 1931, **35**, 3011—3014).—The temp. of max. refractivity of 0·5 and 0·25N aq. solutions of the halides and nitrates of H, Li, Na, K, and NH_4, H_2SO_4, HCO_2H, AcOH, $EtCO_2H$ and of the corresponding Na salts have been determined by a graphical method which depends on the fact that the temp. coeff. of n decreases with a fall in temp. to zero at the temp. of max. refractivity. For aq. solutions this temp. lies below the f. p., and for any given solute the lowering of the temp. of max. refractivity increases with an increase in concentration.

L. S. THEOBALD.

Quantitative limiting law for the viscosity of strong binary electrolytes. H. Falkenhagen (Physikal. Z., 1931, 32, 745—764; cf. A., 1929, 1389; 1930, 155; this vol., 905).—The author's theory is extended to include any binary electrolyte, and yields results in good agreement with experiment.
J. W. Smith.

Apparatus for quantitative investigations of disperse systems with the photo-electric cell. N. N. Andréev (Kolloid-Z., 1931, 57, 39—42).—The construction and use of the apparatus are described.
E. S. Hedges.

Determination of the mean size of particle in disperse systems by means of the photo-electric cell. N. N. Andréev (Kolloid-Z., 1931, 57, 42—47).—The term A^2 in Rayleigh's equation can be measured by the strength of the photo-electric current and leads to the determination of particle size. The limiting particle size at which scattering of light is replaced by reflexion can be determined by observing the scattered light during coagulation by electrolytes.
E. S. Hedges.

Molecules in a strong centrifugal field. T. Svedberg (J. Phys. Radium, 1931, [vii], 2, 227—236).—The influence of the field on the mol. wt., speed of settling, and mol. symmetry has been examined. Results are given for several proteins. N. M. Bligh.

Depth and rigidity of sediment in flocculated clay suspensions. R. K. Schofield and G. W. S. Blair (Trans. Faraday Soc., 1931, 27, 629—632; cf. B , 1929, 446).—If a suspension of clay which has been treated with acid to replace metal ions with $H^{\cdot}$ is alternately allowed to settle for 16 hr. and shaken up, the vol. of sediment formed continually diminishes. Partial replacement of the exchangeable $H^{\cdot}$ by $Ca^{\cdot\cdot}$ or $Ba^{\cdot\cdot}$ does not affect the vol. of sediment, even if the solution is made $1N$ in regard to $CaCl_2$ or $BaCl_2$. A clay containing exchangeable $Na^{\cdot}$ or $K^{\cdot}$, however, passes into a thixotropic gel of larger vol. when suspended in a solution of the corresponding chloride of concentration exceeding about $1N$. The rigidity of the sediment depends both on the exchangeable ions present and on the nature and concentration of the added salt. R. Cuthill.

Osmometer for lyophilic colloids. R. O. Herzog and H. M. Spurlin (Z. physikal. Chem., Bodenstein Festband, 1931, 239—246).—The osmometer described is especially suitable for the study of cellulose esters; at 50° the max. osmotic pressure is attained within 6 hr. Measurements with 0·1—30% solutions of cellulose benzyl ether in Me glycol acetate at 18°, 35°, and 50° show that in dil. solutions (up to about 1%) the osmotic pressure is a linear function of the concentration, whereas at concentrations greater than about 5% it is proportional to the square of the concentration; extrapolation indicates a mol. wt. of 29,000. With rise of temp. the osmotic pressure at low concentrations increases, but the pressure at high concentrations, *i.e.*, in the swelling interval, falls. Freshly prepared solutions yield the same types of curves, but the abs. osmotic pressure is lower.
H. F. Gillbe.

Hydrocarbons as dispersion media : a review. B. S. Soyenkoff (J. Physical Chem., 1931, 35, 2993—3009).—A review of the prep. and the behaviour in an electric field of sols dispersed in hydrocarbons. It is shown that a p.d.$<$5 kv. per cm. has, in general, no effect on such sols, and that electric charge is not an important stability factor. L. S. Theobald.

Molecular structure and solvation. W. Haller (Kolloid-Z., 1931, 56, 257—267).—Theoretical. The different properties of lyophobic and lyophilic colloids are due to differences in solvation, which in turn depend on the mol. structure of the colloidal substance. Lyophilic colloids generally consist of long, thread-like mols., which must not be assumed to be straight, but rather curved or rolled. These structural units can bind H_2O or other solvents both by adsorption and by rendering the mols. of solvent inactive by steric influence. The parts played by these two processes in swelling and in viscosity are discussed.
E. S. Hedges.

Colloidal air. A. Krause and K. Kapitańczyk (Kolloid-Z., 1931, 57, 50—56).—When 1 vol. of distilled H_2O is added to 9 vols. of 16—17N-NaOH the air dissolved in the distilled water is " salted-out " in the form of microscopic bubbles, which condense on ultramicroscopic particles of Na_2CO_3. By ultrafiltration of the NaOH solution, all the Na_2CO_3 can be removed and a true colloidal dispersion of air can then be obtained; this remains stable for 1—2 hr. at room temp., but for longer intervals at lower temp. The stability of the sols is increased also by increasing the concentration of NaOH, and by the addition of glycerol, probably by reason of the higher viscosity; soap has a protective effect on the sol. By mixing glycerol with 18·35N-NaOH polymerisation takes place, giving a liquid of very high viscosity (1958 × H_2O) in which the air sol remains stable for 50 days. These sols show the Tyndall cone; the particles have a weak Brownian movement and appear to be negatively charged. E. S. Hedges.

Radio-colloids. O. Werner (Z. physikal. Chem., 1931, 156, 89—112).—No mol. groups can be detected in Th-X solutions by Chamié's photographic method (A., 1929, 620), but groups have been observed in Th-B and Th-C solutions, these disappearing on addition of HCl, NaCl, or mannitol. The groups are so large and formed in such dil. solution that it is probable that they consist of foreign particles which have adsorbed the active material, and that it is on such adsorption rather than merely on the possibility of the formation of sparingly sol. substances, *e.g.*, by hydrolysis, that the formation of radio-colloids depends (cf. A., 1930, 130). This view is supported by the observation that group formation, as measured by the amount of solute which can be removed by centifuging, is considerably reduced if the H_2O used for preparing the solution is first treated so as to remove suspended impurities. By addition of electrolytes the electric state of the carrier substance may be varied, owing to preferential adsorption effects, and the adsorption of the active substance influenced correspondingly. The adsorption of Th-B is affected quite differently from that of Th-C, for whereas Th-B is present in solution as cations, Th-C is mainly in the form of anions. At high electrolyte concentrations the small solubility of the adsorbate may commence to influence the colloid formation, whilst in weakly alkaline solutions of Th-*C* the presence of undissociated $Bi(OH)_3$ may have some effect.

R. CUTHILL.

Rôle of dielectric constants, polarisation, and dipole moment in colloid systems. VIII. Dielectric and related data in polymeric series of high-molecular substances. W. GALLAY (Kolloid-Z., 1931, 57, 1—7).—The mol. wt., *d*, *n*, and dielectric const. of some poly-indenes and -styrenes have been measured and the dielectric and refraction polarisation and dipole moment calc. In both series the dielectric polarisation has a max. and the refraction polarisation a min. in the region of high colloidal dispersion, whilst the dipole moment increases with increasing size of the mol. E. S. HEDGES.

Magnetism of colloidal gold. V. I. VAIDYANATHAN and B. SINGH (Nature, 1931, 128, 302—303; cf. A., 1930, 673).—The sp. susceptibility of a Zsigmondy Au sol was $0{\cdot}0804\times10^{-6}$ as against $0{\cdot}15\times10^{-6}$ for massive Au. The decrease may be due to the presence of amorphous material or to the difference of the cryst. structure in a small amount of the sol.

L. S. THEOBALD.

Electrolyte coagulation of colloids. X. Potentiometric titration of the coagulation process of aluminium hydroxide sols. P. S. VASSILIEV and A. J. RABINOVITSCH (Kolloid-Z., 1931, 56, 305—317).—The potentiometric titration of $Al(OH)_3$ sols with different electrolytes shows that coagulation is preceded by a displacement of Cl ions from the surface of the colloid particles into the intermicellar liquid. This displacement takes place through exchange adsorption, and there is a close relation between the valency of the added anions, the concentration required for coagulation, and the amount of liberated Cl′. After coagulation has set in the activity of the Cl′ generally falls. As coagulation proceeds the ζ-potential of the particles of $Al(OH)_3$ decreases. The colloidal micelle is represented by the formula $[mAl(OH)_3,nAlCl_3,pAl]^{3p+}+3pCl^-$. E. S. HEDGES.

Interaction of salts with inorganic compounds, and especially with hydrophilic colloids. K. H. MEYER and M. DUNKEL (Z. physikal Chem., Bodenstein Festband, 1931, 553—573).—The alkali halides are classified as aquo-acids and aquo-bases, the former being characterised by a large, slightly hydrated anion and a small, strongly hydrated cation. The two classes may be recognised by their mode of interaction with hydrophilic org. compounds and by their solubility relationships in different types of org. solvents; thus LiI, a typical aquo-acid, is soluble in pyridine, whereas CsF, a typical aquo-base, is insol. in pyridine, but is very sol. in PhOH. Similar relationships are exhibited by the relative influences of the halides on the solubility of acid and basic org. compounds in H_2O; the apparently anomalous effects observed in certain cases are due to complex formation, a view which is supported, *e.g.*, by the partition of LiI between BuOH and H_2O. H. F. GILLBE.

Preparation of chromic hydroxide gels. F. HEIN and H. BÄR (Kolloid-Z., 1931, 57, 47—49).—Compounds of the type $CrX_2{\cdot}OR,3NH_3$ (where X is a halogen and R an alkyl radical) are precipitated when NH_3 is added to a solution of CrX_2 in R_2O; they dissolve in H_2O with hydrolysis and at sufficient concentrations a gel of $Cr(OH)_3$ is formed. The gels are fairly stable and undergo syneresis.

E. S. HEDGES.

Water relationships in colloids. I. Vapour-pressure measurements on elastic gels. D. R. BRIGGS (J. Physical Chem., 1931, 35, 2914—2929).—The isotenoscope method provides a rapid means for determining the relative v. p. or activity coeff. of H_2O in colloids. Within certain limits, it is accurate to 1% and is preferable to the f. p. or the H_2SO_4 equilibrium method. V.-p. data for isoelectric casein and Na and Ca caseinates support the view that the change in H_2O-binding capacity (and swelling capacity) of a protein is the sum of the H_2O-binding capacities of the isoelectric protein and of the ionised atoms bound to the protein when salts are formed. The Na and Ca caseinates are practically 100% and 20% ionised respectively. L. S. THEOBALD.

Course of cooling curves of gelating systems. E. L. LEDERER (Kolloid-Z., 1931, 57, 16—22).—Theoretical. The evolution of heat on gelation is of the order of magnitude of the heat of solvation for both hydrosols and alcosols of soap. The temp. at which gelation begins is independent of the solvent. The thermal conductivities of soap gels and sols have been calc. from published data; the gel has in each case a val. of 60—80% of that of the sol.

E. S. HEDGES.

Gelatin in water-alcohol mixtures. H. SIEBOURG (J. Physical Chem., 1931, 35, 3015—3021).—The viscosity of standard gelatin solutions diluted with H_2O–EtOH mixtures has been measured, and the relative vol. of the disperse phase calc. by means of Einstein's formula. For isoelectric gelatin the vol. appears to be a linear function of the composition of the solvent and for strongly acid or basic gelatin it shows a max. in the highly alcoholic solutions. The results agree with Loeb's curves for swelling effects.

L. S. THEOBALD.

Gum arabic. I. Viscosity and adsorption measurements. G. L. RIDDELL and C. W. DAVIES (J. Physical Chem., 1931, 35, 2722—2731).—The viscosity of dil. aq. solutions of commercial gum arabic is practically unaffected by ageing treatments or by heating on a water-bath for 4 hr., and is insensitive to small changes in p_H. Adsorption of gum arabic, determined by changes in viscosity, by Zn, Al, lithographic stone, and bone charcoal increases rapidly at first with an increase in concentration and then falls more gradually to a const. value. This anomalous type of adsorption appears to be due to a change in the mol. condition of gum arabic. L. S. THEOBALD.

Viscosity of fibroin sol. I. Viscosity of fibroin dispersed in Loewe's reagent. M. HIRASAWA and K. KITAZAWA (Bull. Sericult., Japan, 1931, 4, 12—13).—η increases with the amount of fibroin in the reagent, and decreases with time.

H. DAVSON.

Measurements of structure-viscosity of cellulose derivatives in organic solvents and the influence of additions on their viscosity. III. Y. NISIZAWA (Kolloid-Z., 1931, 56, 317—324; cf.

this vol., 1124).—Addition of H_2O to solutions of cellulose acetate in $COMe_2$ or $CH_2Ph{\cdot}OH$ raises the viscosity, enlarges the region of structure-viscosity, and leads to coagulation. Light petroleum causes the systems to gelate, and the gel shows marked syneresis. The syneretic liquid also shows structure-viscosity and does not consist of the pure dispersion medium. AcOH produces a lowering of viscosity. Camphor and Ph_3PO_4 cause a lowering of relative viscosity, but enlarge the region of structure-viscosity. Cellulose acetate dissolves in a mixture of $CHCl_3$ and EtOH, although not in either of the single components; in this system, structure-viscosity varies greatly with the composition of the solvent.
E. S. HEDGES.

Swelling. I. Regularities in the taking up of acid dyes by cotton. A. LOTTERMOSER and A. CSALLNER (Kolloid-Z., 1931, **56**, 324—334).—The adsorption of naphthol-yellow and crystal-ponceau by cotton is negative and the desorption positive, but the discrepancy can be explained quantitatively by the swelling of the adsorbent. The adsorption of Congo-red is only partly reversible. In presence of electrolytes the amount of dye taken up increases, the effect produced by salts being in the order $NaCl>Na_2SO_4>$Na citrate. E. S. HEDGES.

Electrokinetic potential on cellulose. K. KANAMARU (J. Cellulose Inst. Tokyo, 1931, **7**, 3—13).—The ζ-potentials of pure and modified celluloses and cellulose esters have been measured against H_2O and against solutions of electrolytes, the streaming-potential method being employed. Acid hydrolysis causes an initial increase in ζ-potential followed by a fall, oxidation producing a regular decrease with increasing Cu no. The potential is increased on esterification. On mercerisation, the potential decreases with increasing concentration of mercerising solution, approaching a limit at 17 vol.-% NaOH. The ζ-potential of pulps decreases as hydration ability or degree of beating increases, is lower for acid-treated than for alkaline-treated pulps, and is higher for bleached than for unbleached pulps. The effect of lignin is problematical. T. T. POTTS.

Thixotropy as a means of structure research on colloids. E. HAUSER (Proc. Chem. Eng. Group, 1930, **12**, 137—141).

Thixotropy of bentonite suspensions. H. FREUNDLICH, O. SCHMIDT, and G. LINDAU (Z. physikal. Chem., Bodenstein Festband, 1931, 333—340).—Electrodialysed suspensions of bentonite are rendered markedly thixotropic by addition of KCl and, especially, of KOH. The effect is closely related to the base exchange which occurs between H of the suspensoid and the K of the electrolyte. With KOH the end-point of the exchange reaction coincides with the max. thixotropy, but with KCl an equilibrium is set up, and the considerable quantity of KCl which is always present explains the relatively small tendency to gel formation; the dependence of the latter process on time is due to the slow establishment of the equilibrium. The swelling of bentonite in KOH and KCl solutions attains a max. at the same concentrations as those at which the thixotropic effect is a max. A parallel effect with the sedimentation vol. indicates that the swelling of the particles, and not their charge, is the determining factor in the sedimentation process.
H. F. GILLBE.

Migration studies with ferric oxide sols. I. Positive sols. F. HAZEL and G. H. AYRES (J. Physical Chem., 1931, **35**, 2930—2942).—The effects of $[H^{\cdot}]$ and of the addition of electrolytes on the migration velocity of positive Fe_2O_3 sols. (0·006 g. Fe per litre) have been investigated by an ultramicroscopic method (A., 1928, 1323). Migration velocity falls with a rise in p_H, the isoelectric point lying at p_H 8·6 approx. For K_2CO_3, $CaSO_4$, K_2CrO_4, $K_2Cr_2O_7$, and KH_2PO_4 the velocity–log. concentration curves are linear. The discharging action of $Fe(CN)_6''''$ is the most pronounced, whilst that of Cl' is the least. Bi- and ter-valent ions occupy intermediate positions. For a sol of p_H 7·3, Cl' has no effect on migration velocity. It is unnecessary to deprive the particles completely of their charge in order to produce flocculation (A., 1915, ii, 138). L. S. THEOBALD.

Cataphoresis of suspended particles. I. Equation of cataphoresis. D. C. HENRY. **II. New experimental method and a confirmation of Smoluchowski's equation.** C. G. SUMNER and D. C. HENRY (Proc. Roy. Soc., 1931, **A**, **133**, 106—129, 130—140).—I. Smoluchowski's equation $U=cDX\zeta/\eta$ (where U is the velocity, X the field strength, ζ the potential difference across the double layer, D the dielectric const., η the viscosity of the medium, and $c=1/4\pi$) has been criticised on the ground that c varies with the shape of the particle. This conclusion is unsupported by most of the experimental evidence, and the theoretical relations have been re-examined without assuming that the applied potential gradient is everywhere parallel to the x axis and is undisturbed by the presence of the particle (which is the case only when the conductivity of the particle is the same as that of the medium). The results indicate that, subject to Smoluchowski's theoretical restrictions, his equation holds for spheres and cylinders (in both the axial and transverse positions), also for the electro-osmotic velocity at a plane surface or in a cylindrical channel of any cross-section. When the size of the particles is not large compared with the thickness of the double layer, U tends to a value $DX\zeta/6\pi\eta$ for very small particles. The dimension range includes most colloidal solutions.

II. By a modification of the experimental method of Billiter (Ann. Physik, 1903, **11**, 902) Smoluchowski's equation has been confirmed for the cataphoresis of cylindrical fibres. L. L. BIRCUMSHAW.

Energy exchange in gas mixtures. G. KORNFELD and K. HILFERDING (Z. physikal. Chem., Bodenstein Festband, 1931, 792—800).—Measurements of the heat conductivities of a variety of binary gas mixtures have been made with the object of ascertaining whether the inhibition of energy exchange required by the theory of Rice and Ramsperger actually occurs. The results suggest that such inhibition takes place only when H_2 is one of the components. H. F. GILLBE.

Equilibrium between chlorine, nitric oxide, and nitrosyl chloride. J. K. DIXON (Z. physikal. Chem., Bodenstein Festband, 1931, 679—686).—The reaction has been studied between 196° and 465°. The equilibrium const. (atm.) is given by $\log_{10} K_p = -3860/T + 3{\cdot}348 \log_{10} T - 0{\cdot}002457T - 1{\cdot}8275$. The heat effect (25°) is 18,600±100 g.-cal., the free energy change 8600±200 g.-cal., and the entropy change 33·6±1·0 g.-cal. per degree.

H. F. Gillbe.

Calculations on water-gas equilibrium. Choice of suitable molecular-heat equations. Heat of reaction and free energy as a function of temperature. W. M. D. Bryant (Ind. Eng. Chem., 1931, **23**, 1019—1024).—Available thermal and equilibrium data for the water-gas reaction are discussed. The heat of reaction for $CO_2+H_2=CO+H_2O$ (all gases) is calc. to be 9751 g.-cal. Combined with mol.-heat equations from various sources, the val. gives expressions for the variation of heat of reaction with temp. The sp.-heat equations of Lewis and Randall and of Eastman give similar results, but Partington and Shilling's equations do not agree with these results. Expressions are derived for the free-energy change, its temp. coeff., and for the corresponding reaction isochores. The mol.-heat equations of Lewis and Randall, of Eucken, and of Eastman, but not those of Partington and Shilling, reproduce satisfactorily the experimental equilibrium consts. in the water-gas reaction. For the free-energy change numerical results between 6828 and 6750 g.-cal. are obtained, depending on the sp. heats used.

E. S. Hedges.

Thermodynamic calculation of the affinities of some technically important gas reactions. H. Scheibel (Monatsh., 1931, **58**, 183—208).—Theoretical. Short general methods are developed for calculating the equilibrium consts. of gas reactions according to (1) classical thermodynamics, and (2) the Nernst heat theorem, using (*a*) conventional and (*b*) "true" chemical consts. The formulæ derived are tested for the combustion of C to CO_2 and to CO, the water-gas reaction, Deacon's Cl_2 process, and the formation of NH_3 from N_2 and H_2. Method (1) gives the best agreement with experiment, probably because it uses empirical consts. Simplified formulæ for methods (2*a*) and (2*b*) give as good results as the full formulæ. Method (2*b*) will probably be most accurate when the variation of *c* with temp. is fully understood.

R. S. Cahn.

General theory of solutions of strong electrolytes. T. S. Wheeler (Physikal. Z., 1931, **32**, 674—680).—The electrical dilution work of a dil. solution of a strong electrolyte, the ions of which are governed by a special law of force, a modification of the Coulomb law, can be expressed in the form of a series each member of which represents a static potential energy raised to a power given by the ratio of the potential energy to the kinetic. The Clausius virial equation can be derived from the expression. The general form of thermodynamic functions which can be derived from the equation is shown. Several of the special expressions relating to the theory of strong electrolytes can be derived.

A. J. Mee.

Apparent dissociation constants of carbon dioxide in sea-water of different salt contents. K. Buch, H. Wattenberg, and H. W. Harvey (Nature, 1931, **128**, 411—412, and Naturwiss., 1931, **19**, 773).—The apparent dissociation const. of H_2CO_3 in sea-water has been measured. The variation of K_1 with neutral salt content can be represented by $-\log K_1 = 6{\cdot}518 - 0{\cdot}588C^{\frac{1}{2}}$ at 18°, where C is the normality of all the cations present.

L. S. Theobald.

Apparent dissociation constants of methionine and *iso*serine. O. H. Emerson, P. L. Kirk, and C. L. A. Schmidt (J. Biol. Chem., 1931, **92**, 449—452).—For methionine (cf. A., 1930, 1026), $K_a' = 6{\cdot}17 \times 10^{-10}$, $K_b' = 1{\cdot}91 \times 10^{-12}$; for *iso*serine $K_a' = 5{\cdot}37 \times 10^{-10}$, $K_b' = 6{\cdot}03 \times 10^{-12}$. Their isoelectric points are at p_H 5·74 and 6·02, respectively.

A. Cohen.

Apparent dissociation constants of hydroxyvaline. E. J. Czarnetzky and C. L. A. Schmidt (J. Biol. Chem., 1931, **92**, 453—454).—The consts. recorded are $K_a' = 1{\cdot}97 \times 10^{-10}$ and $K_b' = 4{\cdot}05 \times 10^{-12}$; the isoelectric point is at p_H 6·15.

A. Cohen.

Relative hydration of sulphuric acid and alkali sulphates and its relation to catalytic activity. J. B. Senderens (Bull. Soc. chim., 1931, [iv], **49**, 1138—1147).—The absorption of H_2O from air, under comparable conditions, by H_2SO_4, $NaHSO_4$, $KHSO_4$, Na_2SO_4, and K_2SO_4 decreases in the order given. The catalytic activity of the three first named in dehydration reactions runs parallel with their avidity for H_2O, and is attributed to the formation of temporary hydrates.

C. W. Davies.

Physico-chemical studies of complex formation involving weak acids. I. Hydrolysis of complex cyanides. H. T. S. Britton and E. N. Dodd (J.C.S., 1931, 2332—2336).—By measuring the free HCN present in dil. aq. solutions of $KAg(CN)_2$, $K_4Fe(CN)_6$, $K_2Ni(CN)_4$, $K_2Zn(CN)_4$, and $K_2Cd(CN)_4$ it is found that the first three are stable, but that the last two are partly decomposed. $K_3Fe(CN)_6$ and $K_3Co(CN)_6$, although stable in H_2O, are markedly hydrolysed in KCN solutions.

C. W. Davies.

Electro-neutral dissociation of onium salts in the solution phase. G. Schwarzenbach (Helv. Chim. Acta, 1931, **14**, 1071—1080).—The decomp. of onium salts in certain solvents to give free acid and free base is usually due to hydrolysis in H_2O and to a change in the activity coeffs. of the ions in org. solvents. The latter change has been studied colorimetrically in solutions of the NH_4 salt of *m*-nitrophenol, phenol-red, and bromocresol-purple in EtOH on addition of known amounts of LiCl to regulate the activity coeffs. Brucine salts of *p*-nitrophenol, bromocresol-purple, and bromophenol-blue were similarly investigated in $CHCl_3$ solution with the addition of $NPhMe_3Cl$. The results are shown in tables and curves.

F. L. Usher.

Aluminium phosphates. I. Formation of complexes in acid solutions. N. Bjerrum and C. R. Dahm (Z. physikal. Chem., Bodenstein Festband, 1931, 627—637).—Conductivity measurements and electrometric $[H^{\cdot}]$ determinations have been made with solutions containing $AlCl_3$ and H_3PO_4 or NaH_2PO_4, and the approx. complex and acid dissociation consts. of the phosphato-alumino-complexes have been calc. It is improbable that only one complex is present in any given solution. H. F. Gillbe.

Problems of organic chemistry. III. Equilibrium in the system acetic acid–acetic anhydride–water. W. Mühlhäusser and M. Trautz (Z. physikal. Chem., Bodenstein Festband, 1931, 319—328).—The equilibrium $AcOH \rightleftharpoons Ac_2O+H_2O$ has been studied from both sides, at temp. between 400° and 640°, in presence of catalysts consisting of a mixture of $Ca_2P_2O_7$ and $Al_4(P_2O_7)_3$ or of the same mixture containing 10% of free H_3PO_4. The percentage decomp. of the acid at 360°, 680°, 720° is 1·64, 87, and 92, respectively. The calc. heat effect of the reaction, viz., about 42 kg.-cal., is practically const. at 400—520°, but at higher temp. smaller vals. are obtained owing to the occurrence of side reactions. H. F. Gillbe.

Determination of tautomeric equilibria in various solvents by absorption measurements. Two forms of *s*-2-triquinolylmethane. G. Scheibe and G. Kilian (Z. physikal. Chem., Bodenstein Festband, 1931, 468—474).—For the determination by extinction coeff. measurements of the concentration in different solvents of one form of a tautomeric substance it is necessary to establish both the magnitude and the extent of displacement of the absorption band in each solvent. Measurements with C_6H_6 solutions of *s*-2-triquinolylmethane show that the velocity coeff. of the tautomeric change is $9\cdot6\times10^{-3}$ at 18° and $3\cdot8\times10^{-2}$ at 40·6°. The position of the absorption max. varies with the equilibrium const. in a regular manner for the alcohols, but there is no regularity in the case of unrelated solvents. In C_6H_6 solution the transformation into the red form is endothermic, but in alcoholic solution it is exothermic. H. F. Gillbe.

Dissociation of acid–base indicators in ethyl alcohol with a discussion of the medium effect on the indicator properties. I. M. Kolthoff (J. Physical Chem., 1931, **35**, 2732—2748).—From the work of previous investigators it is calc. that H_2O is approx. 400 times as strong a base as is EtOH. The dissociation consts. of various indicators in pure EtOH have been determined using alcoholic buffer solutions. The effect of traces of H_2O on the colour of indicators in alcoholic solutions of various types of acid–base systems is discussed. The colour of pentamethoxytriphenylcarbinol changes towards the alkaline side when traces of H_2O are added, and this exceptional behaviour is attributed to the *ψ*-base character of the indicator. The effect of EtOH on the colour of an indicator in aq. solutions of various acid–base systems is discussed. The colour of an indicator acid in an aq. buffer solution of an uncharged acid and its salt is scarcely affected by EtOH, but the colour of an indicator base changes strongly to the alkaline side. The titration of weak, uncharged acids or bases in EtOH has no advantages over titration in aq. solution. Other titrations in EtOH are discussed. L. S. Theobald.

Acid–base reactions in pyridine solution. L. E. Krohn and V. K. LaMer (J. Amer. Chem. Soc., 1931, **53**, 3563—3565).—The colorimetrically determined changes of apparent "p_H" of pyridine with variation of concentration of added $NHEt_2$ or $CCl_3\cdot CO_2H$ between $10^{-5}M$ and $1\cdot0M$ are independent of the indicators used. The rapid decrease of apparent "p_H" on addition of pyridine to aq. $0\cdot1M$-$NHEt_2$ suggests that pyridine has some acidic properties. Acids and bases of different strengths are not so sharply differentiated in pyridine as in aq. solution. The change of apparent "p_H" of an acid or base as the solvent is progressively changed from H_2O to pyridine is irregular with mol. fractions of pyridine $<0\cdot2$. J. G. A. Griffiths.

Activity coefficient of hydrochloric acid in aluminium chloride solutions. H. S. Harned and C. M. Mason (J. Amer. Chem. Soc., 1931, **53**, 3377—3380).—The e.m.f. of the cell $H_2|HCl(m_1)$, $0\cdot0-0\cdot45M$-$AlCl_3|AgCl|Ag$ has been determined at 25°. The activity coeffs. of HCl in $AlCl_3$ and alkali chloride solutions vary similarly with the ionic strength. At const. ionic strength of 1μ, $\log\gamma=1\cdot8495+0\cdot0605m_1$, where $m_1=0\cdot05-1\cdot0M$. J. G. A. Griffiths.

Effect of neutral electrolytes on the activity of water towards calcium carbonate. J. E. Orlov (Z. anorg. Chem., 1931, **200**, 87—104; cf. A., 1930, 1130).—The expression previously given for the activity of H_2O in presence of $H^{\cdot}$ and HCO_3' ions holds also when neutral electrolytes are present in the solution. The coeffs. change in conc. electrolyte solutions, but a simple expression can be derived which holds for any added electrolyte. A reply is made to criticisms of the former paper (cf. this vol., 707). O. J. Walker.

Thermodynamic properties of fused salt solutions. IV. Potassium bromide in silver bromide. E. J. Salstrom (J. Amer. Chem. Soc., 1931, **53**, 3385—3389; cf. this vol., 309).—Density data are given. From the e.m.f. of $Ag(s)|0\cdot35-1\cdot0$ mol. fraction $AgBr(l)+KBr(l)|Br_2(g)$, graphite, between 465° and 620° the free energies of formation and of dilution, heats of formation, entropy changes, activities, and activity coeffs. of AgBr at 500°, 550°, and 600° have been computed. The activity exhibits a large negative deviation from Raoult's law. J. G. A. Griffiths.

Proton and electron activity in any solvent. G. Schwarzenbach (Helv. Chim. Acta, 1931, **14**, 1069—1071).—Further discussion of a point raised in an earlier paper (A., 1930, 1526). F. L. Usher.

Equilibria existing in gas–water systems forming electrolytes. O. M. Morgan and O. Maass (Canad. J. Res., 1931, **5**, 162—199).—The v. p. and conductivities of aq. solutions of SO_2, CO_2, and NH_3 have been determined at 0—25° at concentrations up to those corresponding with a v. p. of 1 atm. NH_3 in aq. solution is almost entirely combined with H_2O. SO_2 is only partly combined, and the amount not combined increases rapidly as the temp. rises; approx. values of the true dissociation const. have been calc. CO_2 is combined only to a small extent, the amount uncombined increasing with rise in temp. R. Cuthill.

Transition point of potassium ferrocyanide. E. Fabris (Gazzetta, 1931, **61**, 527—537).—Measurements of the rate of dehydration of $K_4Fe(CN)_6,3H_2O$

with and without a current of dry air, and of the heating and cooling curves of saturated $K_4Fe(CN)_6$ solutions in contact with the solid phase between 80° and 90°, show the existence of a transition point at 87·3°. O. J. WALKER.

Equilibrium of certain non-metallic systems. I. FeO–MnO. II. MnS–MnO, MnS–$MnSiO_3$, and MnS–Fe_2SiO_4. J. H. ANDREW, W. R. MADDOCKS, and (I) D. HOWAT, (II) E. A. FOWLER (Iron and Steel Inst., Sept., 1931, Advance copy, 1—13, 13—26).—I. Pure FeO is obtained by heating FeC_2O_4 at 700° in vac. and pure MnO by heating MnC_2O_4 at 850° in vac. The two oxides form a complete series of solid solutions, the m. p. rising almost linearly from the m. p. of FeO, 1410°, to the m. p. of MnO, 1585°; throughout the range the liquidus is within 20° of the solidus.

II. The systems MnS–MnO, MnS–$MnSiO_3$, and MnS–Fe_2SiO_4 are of the simple eutectiferous type with limited solid solubility at both ends. The MnS–MnO eutectic (1285°) contains 50% MnS; the MnS–$MnSiO_3$ eutectic (1250°) contains 10% MnS, and the MnS–Fe_2SiO_4 eutectic (1055°) also contains 10% MnS. Pure $MnSiO_3$ has m. p. 1305°, pure MnS 1615°, and pure Fe_2SiO_4 1130°. The solubility of MnS in MnO is 7·5%, in $MnSiO_3$ about 1·5%, and in Fe_2SiO_4 about 2%. The solubility in MnS of MnO is 16%, of $MnSiO_3$ about 1%, and of Fe_2SiO_4 about 2·5%. As MnS is soluble in FeO, Fe_2SiO_4, and $MnSiO_3$ the S prints obtained from Fe and steel would appear to indicate not only the distribution of S, but also the distribution of slag inclusions, the S merely serving as a means of bringing about the detection of slag. A. R. POWELL.

System cobalt chloride–zinc chloride. H. BASSETT and W. L. BEDWELL (J.C.S., 1931, 2479—2492; cf. A., 1930, 1251).—The f. p. of $CoCl_2$ and $ZnCl_2$ are 735±7° and 313°, respectively; discordant vals. of earlier workers are explained. On cooling fused mixtures, solid solutions are formed up to 7% $CoCl_2$, thereafter $CoCl_2$ separates; the eutectic point (7% $CoCl_2$) is at 312±1°. All mixtures have the blue colour of anhyd. $CoCl_2$, corresponding with the absence of compound formation. C. W. DAVIES.

Oxide hydrates and active oxides. XLVI. System bismuth oxide–water. G. F. HÜTTIG, T. TSUJI, and B. STEINER (Z. anorg. Chem., 1931, 200, 74—81; cf. this vol., 799).—Hydrated Bi_2O_3 dried over 40% H_2SO_4 has the composition $Bi_2O_3,2·5H_2O$. Isobaric dehydration and *X*-ray examination of hydrates containing up to 3·24 mols. H_2O point to the existence of a compound $Bi_2O_3,3H_2O$. Throughout the whole dehydration range the products consist of a mixture of two phases, one of which has the lattice of the trihydrate, the other that of Bi_2O_3. During isobaric dehydration the first mol. of H_2O is given off continuously, the second sharply at 310°, and the third continuously at higher temp. O. J. WALKER.

Polyhalides. II. Physical properties. H. W. CREMER and D. R. DUNCAN (J.C.S., 1931, 2243—2254).—All polyhalides dissociate to leave the metal combined with one atom of the most electronegative halogen present. The dissociation pressures of $KIBr_2$, KIBrCl, and $KICl_2$ have been measured using a glass spring manometer. The relative stabilities of many alkali polyhalides and alkylammonium dibromoiodides have also been determined by distribution experiments with CCl_4. For cations the order of increasing stability is Na, K, NH_4, Rb, Cs, irrespective of the anion. With the substituted NH_4 compounds there is alternation, those with an even number of alkyl groups being the most stable. In the anion stability is favoured by symmetry, and by the presence of one, but not more than one, I atom. The m. p. are discussed and the effects of prolonged drying described. Data are given for the solubilities of the dibromoiodides in H_2O, for that of I in CCl_4 and for the v. p. of Br at 25°. Evidence is adduced that the *compound* CsIBrF exists. $KIBr_2$ crystallises from H_2O as a *monohydrate*, m. p. 58°. C. W. DAVIES.

System lithium sulphate–aluminium sulphate–water. J. P. SANDERS and J. T. DOBBINS (J. Physical Chem., 1931, 35, 3086—3089).—Between 0° and 50°, Li_2SO_4,H_2O and $Al_2(SO_4)_3,18H_2O$ are the only stable phases in contact with aq. solutions; no alum exists as a stable solid between these temp. The solubility of each salt is depressed by the other. Change of temp. has little effect on the solubility of Li_2SO_4 in the presence of $Al_2(SO_4)_3$, but a fall in temp. decreases that of $Al_2(SO_4)_3$ in the presence of Li_2SO_4. L. S. THEOBALD.

System silver–copper–oxygen; quasi-binary section, silver–cuprous oxide. J. A. A. LEROUX and K. W. FRÖHLICH (Z. Metallk., 1931, 23, 250—254).—The quasi-binary system Ag–Cu_2O has been investigated by thermal analysis and by micrographic examination. In the liquid state there is a miscibility gap above 1134° extending from about 5 to 82% Ag. The Cu_2O–Ag eutectic contains 2·1—2·3% Cu_2O and melts at 941°; the solid solubility of Cu_2O in Ag is about 0·3% and that of Ag in Cu_2O about 2—3% according to the temp. No evidence of the formation of CuO in any of the alloys could be found but in Cu_2O-rich alloys the presence of Cu as Ag–Cu eutectic was observed. This is attributed to the reaction $Cu_2O \rightleftharpoons Cu+CuO$ taking place from left to right at high temp. with absorption of the CuO by the refractories used in the melting. A. R. POWELL.

Action of sulphur on the molten equilibrium $Fe+NiSiO_3 \rightleftharpoons Ni+FeSiO_3$. H. ZUR STRASSEN (Z. anorg. Chem., 1931, 200, 46—56; cf. A., 1930, 1375).—The above equilibrium is only slightly displaced by the addition of S, which simply dilutes the metallic phase, and it still follows the mass action law. In concentrations greater than 0·5 mol. S to 1·0 mol. metal the S has a strong reducing action on the metallic oxide of the silicate phase. The metal sulphide melt dissolves NiO appreciably, FeO less, and this brings about secondary reactions which cause apparent deviations from the mass action law. In the melt $NiSiO_3$ is appreciably dissociated into NiO and SiO_2. O. J. WALKER.

Equilibrium diagram of the system magnesium hydroxide–potassium chloride–water at 25°. A. P. PALKIN (Bull. Univ. Asie centr., 1929, no. 18, 73—75).—The solubilities of $Mg(OH)_2$ and KCl are independent. CHEMICAL ABSTRACTS.

Measurement of heat effects. H. Ramstetter and G. Hantke (Z. physikal. Chem., Bodenstein Festband, 1931, 662—668).—A method of calculating the heat effect of a reaction between a liquid and a gas is illustrated by reference to the manufacture of KOCl, the dissolution of NH_3 and of SO_2, and the neutralisation of aq. NaOH with SO_2. H. F. Gillbe.

Differential heats of dilution and the electrothermal effect. G. Jung (Z. physikal. Chem., Bodenstein Festband, 1931, 298—302).—Theoretical. Part of the differential heat of dilution must be regarded as an electrothermal effect. H. F. Gillbe.

Heats of dissociation of chlorine monoxide and chlorine dioxide. (Miss) J. I. Wallace and C. F. Goodeve (Trans. Faraday Soc., 1931, **27**, 648—654).—The heats of dissociation of Cl_2O and ClO_2 have been found by direct measurement of the heats of explosion to be 560 and 26,585±390 g.-cal. respectively. R. Cuthill.

Heat of formation of water and heats of combustion of methane and carbon monoxide. A correction. F. D. Rossini (Bur. Stand. J. Res., 1931, **7**, 329—330).—The data previously recorded (this vol., 170, 433) were reduced to a const. pressure of 1 atm. This is incorrect. The corrected values for H_2O are 285,850±50, for CH_4 889,720±230, and for CO 282,938±110 abs. joules. W. R. Angus.

Heat of formation of titanium dioxide. W. A. Roth and G. Becker (Z. physikal. Chem., Bodenstein Festband, 1931, 55—60).—Combustion of Ti in O_2 at 38—40 atm. yields anatase, d^{21} 3·862. The heat of formation is 218·1±0·3 kg.-cal. per mol. H. F. Gillbe.

Hydrates of pentaphenylchromium hydroxide. F. Hein and W. Retter (Z. physikal. Chem., 1931, **156**, 81—85; cf. A., 1922, i, 77).—It is calc. from the dehydration isotherms that the heat of formation of the tetrahydrate from the dihydrate and H_2O vapour is 13·4 kg.-cal. per mol. and that of the dihydrate from the anhyd. base 23·4 kg.-cal. at about 30°. R. Cuthill.

Free energy, heat and entropy of formation of *l*-malic acid. H. Borsook and H. F. Schott (J. Biol. Chem., 1931, **92**, 559—567).—Using a potentiometric method (cf. this vol., 1189) the equilibrium ionic ratio, *l*-malate''/fumarate'', at 25° is approx. 3·1. The free energy of formation of solid *l*-malic acid at 25° is −210,450 ±500 g.-cal. whilst the free energy of the *l*-malate ion at 1-molar activity is −201,940 ±150 and the heat content −258,100 g.-cal. The entropy of solid *l*-malic acid at 25° is 49 units. F. O. Howitt.

Transport numbers and transport potentials in metallic solutions. H. Schwarz (Z. physikal. Chem., 1931, **156**, 227—231; cf. this vol., 685).—The transport nos. of Zn, Tl, Sn, and Bi in amalgams of different concentrations at 25° and 35° have been calc. from e.m.f. determinations. No measurable values of the e.m.f. were obtained in Au and Pb amalgams. M. S. Burr.

Electro-endosmosis and electrolytic water transport. II. H. C. Hepburn (Proc. Physical Soc., 1931, **43**, 524—537; cf. A., 1927, 422).—Measurements of liquid transport with 0·0005—1*N*-$CuSO_4$ solutions and a paper parchment diaphragm indicate a const. electrolytic water transport per faraday, modified by a sp. action of the diaphragm. A. B. D. Cassie.

Mobility of ions in solvents which can yield a similar ion. P. Walden (Z. physikal. Chem., Bodenstein Festband, 1931, 19—29).—Solubility measurements have been made with various salts in MeOH, EtOH, $MeNO_2$, NH_2Et, PhOH, and $CH_2Cl{\cdot}CO_2H$, in order to determine whether the abnormally high mobility of the OH and H ions in aq. solutions is a general phenomenon. The results show, however, that salts having an ion in common with the solvent possess normal conductivities over a considerable concentration range. The observed mobilities of the H, OH, OEt, and OMe ions correspond with those of other ions, and may be explained in terms of solvation; the H ion, *e.g.*, in MeOH and EtOH is associated with 0·5—1·2 mols. of the solvent and in $MeNO_2$ with 2 mols. H. F. Gillbe.

Ionic mobility in highly conducting solid electrolytes. C. Tubandt and H. Reinhold (Z. physikal. Chem., Bodenstein Festband, 1931, 874—880).—α-Ag_2S differs from other solid electrolytes in its extremely high conductivity, negative temp. coeff., the inapplicability of the Einstein law, and the reversible depression of the conductivity produced by treatment with S vapour. Electrolytic conduction in α-Ag_2S must involve a mechanism different from that of the diffusion process. H. F. Gillbe.

Internal structure of solid inorganic compounds at high temperatures. IV. Diffusion in and conductivity of certain halides. W. Jander (Z. anorg. Chem., 1931, **199**, 306—320).—Measurement of the extent of inter-diffusion in the systems K_2SrCl_4–K_2BaBr_4 (450—520°), Na_2CdCl_4–Na_2ZnBr_4 (230—260°), K_2SnCl_4–K_2PbBr_4 (190—250°) show that the halogen ions are much more mobile than those of Sr, Ba, Cd, Sn, Zn, or Pb. This result, together with conductivity measurements, indicates that these double salts possess simple ionic lattices. In K_2PtCl_4 and K_2PdBr_4, on the other hand, both the halogen and the Pt and Pd ions are immobile at temp. up to 380°, and the salts therefore possess complex ionic lattices. H. F. Gillbe.

Physico-chemical properties of solutions in liquefied gases. Conductivity of alkali nitrates in liquid ammonia. A. M. Monosson and W. A. Pleskov (Z. physikal. Chem., 1931, **156**, 176—194).—The conductivity of solutions of Li, Na, K, Rb, and Cs nitrates in liquid NH_3 at −40°, at dilutions varying from 10 to 100,000 litres, has been measured. By the Kohlrausch extrapolation method the values of μ_∞ at −40° are 290, 300, 338, 344, and 345, respectively. The same calculation applied to Franklin and Bray's results at −33·5° gives 299, 315, and 354 for the Li, Na, and K salts, respectively. For concentrations below 0·0003—0·0002*M* the results agree qualitatively with the theory of Debye and Onsager, but the experimental val. of α in the equation $\mu=\mu_\infty-a\sqrt{c}$ is 2·5 to 4 times the theoretical val. calc. from Onsager's formula. The mobilities of the five cations at

—40° are 121, 131, 169, 174, and 175, respectively, and of the first three at —33·5°, 122, 138, and 177, respectively. M. S. Burr.

Resistance of an electrolytic conductor at various frequencies. D. E. Richardson (Physical Rev., 1930, [ii], 35, 297).—The equation connecting the resistance of a conductor with the frequency of current has been verified for 30% H_2SO_4 for wavelengths up to 37 m. L. S. Theobald.

Zinc electrode. F. H. Getman (J. Physical Chem., 1931, 35, 2749—2757).—The e.m.f. of the cell $Zn|ZnCl_2$ (0·002—1·0M)$|Hg_2Cl_2,Hg$ has been measured at 25° with single crystals or cryst. aggregates of Zn. The former resemble single crystals of Cu and Cd (this vol., 569) in showing a tendency to give larger differences of potential than do the cryst. aggregates. The normal electrode potential of Zn, computed from e.m.f. measurements by three different methods, has the average val. of 0·7613 volt. L. S. Theobald.

Potential of the calomel electrode. L. E. Sabinina (Bull. inst. res. biol. Perm, 1931, 7, 333—336).—When H_2 is passed through a calomel electrode a potential change at 25° of 0·8—1·9 mv. is observed. In presence of O_2 a rise of the potential is explained by a shift to the right in the equilibrium $Hg_2Cl_2 \rightleftharpoons Hg+HgCl_2$; in presence of H_2 the equilibrium $H_2+Hg_2Cl_2 \rightleftharpoons 2HCl+2Hg$ is shifted to the left. Chemical Abstracts.

Galvanic potential and concentration changes of the relevant ion. M. Andauer and E. Lange (Z. physikal. Chem., Bodenstein Festband, 1931, 247—256).—The problem of determining the conditions under which it is legitimate to calculate the changes of ionic concentration in two-phase systems from the accompanying changes of the galvanic potential has been examined. If the variations of concentration occur in only one phase, these may be calc., but if in both phases the change in one phase must be known for calculation of that in the other. The case of the system $Ag|AgNO_3, NaNO_3$ is treated in detail. The equations derived are in general applicable to systems in which complexes are formed, such as $Ag|AgCN,KCN$, without regard to the chemical condition of the ions which determine the potential. H. F. Gillbe.

Property of the glass electrode. G. Buchböck and (Frl.) M. Reise (Z. physikal. Chem., 1931, 156, 232—236).—Zirkler's observation (this vol., 914) that an e.m.f. may be set up between the inside and outside of the bulb of a glass electrode, although the metal electrodes and the inner and outer solutions are identical, has been confirmed. The phenomenon is attributed to the different states of tension of the two glass surfaces. A method for measuring the e.m.f. of the glass electrode is described. M. S. Burr.

Electrode potentials and adsorbed ionic films. H. V. Tartar and H. K. McClain (J. Amer. Chem. Soc., 1931, 53, 3201—3212; cf. A., 1930, 998).—When the distance between two accurately parallel polished Pt electrodes in 0·056M-Na_2HPO_3, 0·01M-KH_2PO_3, -$CuSO_4$, -$Pb(NO_3)_2$, -$Al_2(SO_4)_3$, or -$NiCl_2$, or 0·2M-H_3BO_3 containing 0·01M-KCl is diminished in the presence of air or O_2, the potential varies for distances less than 0·5—0·05 mm., the limiting distance depending on the solution. Similar effects are observed if one Pt electrode is replaced by Au; the potential is also affected by the proximity of quartz or bakelite. These and other observations support the theory that the potential is due partly to an adsorbed ionic film extending from the electrode to a measurable distance in the solution. J. G. A. Griffiths.

Indefinite metal–solution potentials and their utilisation for the electrochemical separation of radio-elements. O. Erbacher (Z. physikal. Chem., 1931, 156, 135—141).—The potentials of certain metals have been followed for a period of 2 hr. after immersion in 0·1N-HCl at 20° and at 79°. The data afford a means of investigating the possibility of utilising these metals for displacing radioactive elements from their solutions. R. Cuthill.

Electrochemical method [of separating radio-elements from solution]. O. Erbacher (Z. physikal. Chem., 1931, 156, 142—149).—Ra-E, Po, and Th-C may be displaced from solution by means of Pt charged with H, and by subsequent treatment of the Pt with acid solutions of the active compound free from inactive salts are obtained. R. Cuthill.

Titration of hydroxy-organic acids in presence of ferric and cupric salts. C. V. Smythe (J. Biol. Chem., 1931, 92, 233—244).—Glass electrode titration curves of lactic, glycollic, oxalic, malic, tartaric, and citric acids mixed with $CuCl_2$ and $FeCl_3$ respectively show that the mixtures are more acidic than the acids alone. The additional amount of alkali is the same as that required for the precipitation of the hydroxides from the pure salt solutions. This is explained by the formation of complexes between the Cu or Fe and the hydroxylic H atoms leading to enhanced acidity of the latter. A. Cohen.

Existence of e.m.f. in closed metallic electric circuits at the same temperature. O. Scarpa (Z. physikal. Chem., 1931, 156, 225—226).—A claim for priority (B., 1929, 823) against Schwarz (this vol., 685). M. S. Burr.

E.m.f. developed between silicon and other elements in aqueous hydrofluoric or sulphuric acids, or sodium hydroxide. C. Bedel (Compt. rend., 1931, 193, 527—528).—The e.m.f. of cells consisting of Si (containing 0·1% Fe) and other elements in 13·7% HF, N-H_2SO_4, and N-NaOH has been measured. Although actual figures for different samples of Si show large variations, and the order of magnitude in the different solutions varies, it is found that Pt, Ag, and C (graphite) are always electropositive, Pb, Sn, and Zn electronegative; Cu, Ni, and Fe are negative in H_2SO_4 and positive in NaOH, whereas Cu and Ni are positive and Fe is negative in HF. Variation of concentration of HF has little effect. C. A. Silberrad.

E.m.f. relationships of formic acid. E. Müller and J. Görne (Z. physikal. Chem., Bodenstein Festband, 1931, 44—54).—The reduction potential of HCO_2H varies with the roughness of the electrode

surface, and approaches the reversible H potential only when the surface is extremely rough. It is suggested that the H atoms of the acid, prior to the decomp., are adsorbed on the electrode, and that on account of the configuration of the mol. such adsorption takes place with difficulty on a plane surface, but readily on a roughened surface. This view explains the fact that only highly dispersed metals are capable of catalytically decomposing HCO_2H at room temp.
H. F. Gillbe.

Deposition potential of nickel. F. Foerster and K. Georgi (Z. physikal. Chem., Bodenstein Festband, 1931, 453—467).—The current density–voltage curves obtained during the electrodeposition of Ni from solutions of $NiCl_2$, $NiSO_4$, and $Ni(ClO_4)_2$ show that Glasstone's conclusion, viz., that deposition commences at a definite potential which differs considerably from the equilibrium potential and proceeds thereafter without retardation, is incorrect. Glasstone's result is attributed to the shortness of the period of observation; thus whereas under specified conditions and with a current density of $0{\cdot}56\times10^{-4}$ amp. per sq. cm. no deposition is apparent during the first 30 min., by prolongation of the experiment for 24 hr. the amount of Ni deposited is sufficient to permit the calculation of the current yield.
H. F. Gillbe.

Polarographic studies with the dropping mercury cathode. XXI. Limiting currents for electrodeposition of metals and hydrogen. I. Šlendyk (Coll. Czech. Chem. Comm., 1931, **3**, 385—395).—The limiting currents due to the electrodeposition of metals at the dropping Hg cathode, *e.g.*, Cu, Cd, or Mn from solutions of the chloride, follow Eucken's theory, decreasing to half val. when an excess of indifferent salt (KCl or $BaCl_2$) is added. The limiting current associated with H_2 deposition decreases with addition of indifferent salts to a greater extent than that indicated by Eucken's formula. The current is smaller the higher is the valency of the added cation. The phenomenon is discussed with reference to Heyrovský's theory of H overvoltage (A., 1925, ii, 675; 1927, 1145).
M. S. Burr.

Polarographic studies with the dropping mercury cathode. XXII. Hydrolysis of cobaltous chloride. R. Brdička (Coll. Czech. Chem. Comm., 1931, **3**, 396—405; cf. A., 1930, 1254).—The current–voltage curves registered polarographically, when aq. solutions of $CoCl_2$ are electrolysed using the dropping Hg cathode, show an increase in current at approx. $-1{\cdot}05$ volt, about $0{\cdot}2$ volt below the increase due to the deposition potential of Co. This gives a "wave" in the curve which becomes more pronounced when the solution is warmed, or when a small amount of alkali hydroxide is added to the solution. The wave disappears entirely after acidification to p_H 4. The first increase in current is probably due to the deposition of Co from the ion $[Co(H_2O)_5OH]^{\cdot}$, the hydrated form of the ion $CoOH^{\cdot}$. At the second increase $[Co(H_2O)_6]^{\cdot\cdot}$ ions are deposited. This is possible if the equilibrium $[Co(H_2O)_6]^{\cdot\cdot}+H_2O \rightleftharpoons H^{\cdot}+[Co(H_2O)_5OH]^{\cdot}$ is only slowly established, so that each kind of ion has its own deposition potential at which the complex ion is torn into the simple ions by the action of the strong electric field at the surface of a polarised electrode.
M. S. Burr.

Polarographic studies with the dropping mercury cathode. XXIV. Disappearance of adsorption currents at the electrocapillary zero potential. J. Heyrovský and E. Vascautzanu (Coll. Czech. Chem. Comm., 1931, **3**, 418—429).—The characteristic reproducible max., which appear at cathodic reduction potentials on current–voltage curves in electrolysis with the dropping Hg cathode, disappear if the reduction potential coincides with the potential at which the interfacial tension of polarised Hg is a max. Cd deposits at this electrocapillary zero potential ($=0{\cdot}56$ volt when the calomel electrode is zero) and a simple diffusion "wave" only is indicated on the polarogram, but this can be changed into a max. if reagents are added which either change the deposition potential of Cd, *e.g.*, cyanide or aq. NH_3, or which change the position of the electrocapillary zero, *e.g.*, iodide or thiocyanate. Similarly positive max. can be changed to negative, disappearing at the zero point. Similar results are obtained with Pb and Cr, which deposit near $-0{\cdot}56$ volt, and in the electro-reduction of undissociated mols., *e.g.*, maleic acid, when the reduction potential coincides with the electrocapillary zero. Adsorption at an electrode therefore vanishes at the electrocapillary zero (cf. A., 1930, 1527).
M. S. Burr.

Hydrogen and oxygen overvoltages on nickel-iron alloys. M. de K. Thompson and A. L. Kaye (Trans. Amer. Electrochem. Soc., 1931, **60**, 9—14).—H and O overvoltages for alloys ranging from pure Fe to pure Ni have been determined at various current densities in *N*-KOH (cf. this vol., 570). H overvoltages increase almost linearly from 0% to about 50% Fe, but with higher Fe content remain approx. const. or fall slightly. At high current densities curves for O overvoltage against % Fe show a max. followed by a min. but at low current densities only a min. For an alloy of given composition the H overvoltage is approx. given by $\eta=a+b\log d$, where d is the current density and a and b are consts., but for O overvoltage vals. of a and b change when the current density exceeds a certain val.
H. J. T. Ellingham.

Nature of the passive film produced anodically on iron in solutions containing sulphate. W. J. Müller and W. Machu (Z. physikal. Chem., Bodenstein Festband, 1931, 687—703).—The natural oxide film of Fe renders the metal passive towards Na_2SO_4 solutions, but is removed by very dil. acids. In H_2SO_4 solutions of concentration greater than $0{\cdot}5N$ a film of $FeSO_4.7H_2O$ is formed after removal of the oxide film. Chemical passivity is produced at potentials greater than 2 volts, and is due to a second type of oxide film, which is extremely sensitive towards conc. solutions of electrolytes, but is very stable in dil. solutions. By prolonged activation in dil. sulphate solutions a porous film of a basic salt is formed.
H. F. Gillbe.

Current-yielding process in the Leclanché element. C. Drucker (Z. physikal. Chem., Bodenstein Festband, 1931, 912—918).—The assumption that the essential reaction in the Leclanché cell yields

Mn_2O_3 and $Zn(NH_3)_2Cl_2$ is incorrect, since calculation from thermochemical data in conjunction with an initial temp. coeff. of the e.m.f. of about 0·6 mv. per degree yields 1·46 for the e.m.f. of the cell. It is probable that not MnO_2, but the free O adsorbed on natural, and more especially on artificial, MnO_2 is primarily involved in the production of the current, since the oxidation of Zn by O would yield an e.m.f. of about 1·8 volts and that of a new cell is often more than 1·7 volts. The recovery of a cell after a period on closed circuit is due to replacement of the adsorbed O by atm. O_2. H. F. GILLBE.

Electrical [etc.] phenomena in crystallisation [of sodium acetate]. A. TSCHERMAK (Z. Krist., 1931, **79**, 465—494).—The rise in temp. on crystallisation of a supersaturated solution of NaOAc decreases parabolically from about 42° at 0°, to nil at 56°; the velocity of crystallisation increases with concentration and with nearness to (above or below) 15°. The existence of a di- (tables) and mono- (long prisms) hydrate, and of only one form of the anhyd. salt is inferred (cf. A., 1887, 323; 1913, i, 1300). If a supersaturated solution of $NaOAc,3H_2O$ is inoculated at a point A, and electrodes (of Au or Pt) placed at B and C, A, B, and C being approx. in a line, a current passes when the crystallisation front reaches B, and a reverse one when it reaches C, due to the crystallisation front carrying a positive charge. Other possible causes are shown to be inadequate, the current being due to energy evolved on crystallisation. Its strength varies with concentration, and is of the order of 10^{-7} amp. C. A. SILBERRAD.

Reaction velocity in relation to the concentration and activity of the reacting components. H. M. DAWSON (Proc. Leeds Phil. Soc., 1931, **2**, 230—234).—The view that the velocities of certain reactions are determined by the activities of the reactants, and not by their respective concentrations, is reversed by a consideration of data for the hydrolysis of $MeCO_2Et$ and the transformation of *N*-chloro- into *p*-chloroacetanilide. N. M. BLIGH.

Empirical rule in the chemical kinetics of bimolecular reactions. W. A. HOLZSCHMIDT (Z. anorg. Chem., 1931, **200**, 82—86).—A survey of the data available for bimol. reactions in solution shows that the energy of activation, *A*, and the factor, *B*, in the Arrhenius equation are related by the expression $B=Ke^{A/C}$, where *C* is a const. and *K* is a quantity which depends on the nature of the solvent. This expression can be deduced from the similar one which holds for unimol. reactions (cf. this vol., 1014). O. J. WALKER.

Effect of pressure on rate of polymerisation. G. TAMMANN and A. PAPE (Z. anorg. Chem., 1931, **200**, 113—132).—The polymerisation of liquid styrene, isoprene, vinyl acetate, dimethylbutadiene, and indene follows the unimol. law, suggesting that the mols. undergo some change before union, the rate of this reaction determining the speed of the process as a whole. The velocity increases with increase in pressure much more rapidly than in other reactions occurring in liquids, but the form of the relation between the velocity coeff. and the pressure varies from one reactant to another. Increase in pressure also results in a fall in the temp. at which polymerisation starts. The physical properties of the products of polymerisation have been examined. R. CUTHILL.

Kinetics of a thermal *cis-trans* isomerisation. G. B. KISTIAKOVSKY and M. NELLES (Z. physikal. Chem., Bodenstein Festband, 1931, 369—378).—The isomerisation of Et dimethylmaleate into Et dimethylfumarate in the neighbourhood of 300° is a purely homogeneous, quasi-unimol. reaction. The activation energy of the reaction is 26·5 kg.-cal., and its rate is slower than that of any other known unimol. reaction. The abnormally low rate of activation, which is only about 10^{-3} that calc. on the assumption that only two degrees of freedom are involved, is discussed in relation to the mechanism of the intermol. movement and to the possibility of the reaction taking place through the formation of an enolic compound. H. F. GILLBE.

Discontinuity in the velocity coefficient of a chemical reaction at the critical temperature. H. S. SUTHERLAND and O MAASS (Canad. J. Res., 1931, **5**, 48—63).—A technique for investigating reaction mixtures at high pressures and relatively high temp. is described. The velocity of the reaction between propylene and HCl increases with rise of temp. in the liquid state, but above the crit. temp. becomes almost zero. This supports the view that regional orientation occurs in a binary liquid mixture and that this furthers the reaction. Decrease in the regional orientation with rise in temp. is more than compensated by increased activity of the mols. until the crit. temp. is reached, when the regional orientation and the temp. coeff. both fall rapidly. J. W. SMITH.

Kinetics of the combination of hydrogen atoms in triple impact. W. STEINER and F. W. WICKE (Z. physikal. Chem., Bodenstein Festband, 1931, 817—830).—The combination of H atoms in the pressure interval 0·3—0·7 mm. and at at. concentrations of 15—80% has been investigated. The surface reaction is negligible. The velocity coeff. *k* at 0·7 mm., calc. on the assumption that atoms and mols. are equally active in a triple impact, is $7·6\times10^{15}$, whilst if it is assumed that the H mols. alone are active the coeff. k' becomes $9·6\times10^{15}$; *k*, but not k', increases with increase of the mol. concentration. The results indicate, in contradiction to previous work, that a mol. as third partner in a triple impact is more active than an atom. H. F. GILLBE.

Spectrographic identification of the intermediate oxide of nitrogen in the reaction between nitrogen pentoxide and ozone. G. SPRENGER (Z. Elektrochem., 1931, **37**, 674—678).—Examination of the absorption spectrum and kinetic considerations indicate the intermediate formation of NO_3. E. S. HEDGES.

Reaction of hydrogen sulphide with oxygen. L. FARKAS (Z. Elektrochem., 1931, **37**, 670—673).—The reaction between H_2S and O_2 is a chain reaction, starting at the wall of the vessel at 220—320°. The steady reaction becomes explosive when the production of heat is sufficient to raise the temp. above 340°. E. S. HEDGES.

Oxidation of hydrogen sulphide. H. A. Taylor and E. M. Livingston (J. Physical Chem., 1931, 35, 2676—2683).—The rates of pressure change for given mixtures of H_2S and O_2, saturated at 21° with H_2O vapour, show that the slow reaction near 300° is mainly homogeneous and partly heterogeneous. The crit. explosion pressures for different mixtures agree with Semenoff's theory. Oxidation proceeds by a mechanism involving both straight and branched chains. H_2S, O_2, H_2O, SO_2, SO_3, and S are present after explosion. The dryness of the initial gases affects the rate of reaction. L. S. Theobald.

Combustion limits of mixtures of air with gas or vapour at low pressures. II. E. Berl and K. Barth (Z. physikal. Chem., Bodenstein Festband, 1931, 211—229).—The influence of low pressure on the limits of combustion of mixtures of air with Et_2O, C_2N_2, CS_2, C_2H_2, and EtOH, and of CS_2 with NO_2 and NO has been studied with the aid of the gas interferometer. In all cases the limits approach with decrease of pressure, until the crit. ignition pressure is attained, below which the reaction does not proceed. These crit. pressures are for most substances in the same order as the ignition temp. During the combustion of C_2N_2–air mixtures, even in presence of an excess of O_2, CO_2 is produced in addition to CO only if H_2O is present. In the neighbourhood of the crit. ignition pressure pre-combustion takes place, and even in presence of H_2O CO alone is formed during this process; it is probable therefore that CO is always formed as an intermediate product of the combustion of C_2N_2. H. F. Gillbe.

Low-temperature explosion of mixtures of ozone and hydrogen bromide. B. Lewis and W. Feitknecht (J. Amer. Chem. Soc., 1931, 53, 3565—3566; cf. this vol., 1130).—HBr reacts with pure O_3 almost instantaneously at room temp., and above a definite limiting pressure explosion occurs. The limiting pressure (20—30 mm. for an equimol. mixture) is only a little greater at −104°. The difference between the induction periods in different vessels, the effect of coating the walls with the products (Br and ice, at −104°) and of packing the vessel indicate that the reaction proceeds by way of chains initiated at a surface. Glass is less active than a Br–ice surface. At −104°, the slow reaction is completed in 20—240 sec., in accordance with the equation $2HBr+O_3=H_2O+Br_2+O_2$. With excess of O_3, the slow reaction ceases when all the HBr has disappeared, but in an explosion the excess of O_3 is decomposed. J. G. A. Griffiths.

Oxidation of ethane. H. A. Taylor and E. W. Riblett (J. Physical Chem., 1931, 35, 2667—2675).—The rate of pressure change for mixtures of C_2H_6 and O_2 at 450—470° under different conditions has been determined. The induction period (up to 5 min.), the effects of pressure, temp., composition, surface, and diluents show that the oxidation is a homogeneous chain reaction. The crit. explosion pressures agree with Semenoff's theory, but are best explained as chain explosions preceded by thermal accelerations. L. S. Theobald.

Velocity coefficients for the thermal dissociation of ethane and propane. L. F. Marek and W. B. McCluer (Ind. Eng. Chem., 1931, 23, 878—881).—The decomp. of C_2H_6 and C_3H_8 has been studied by passing them through a Cu reaction vessel heated at the required temp. With rapid rates of flow below 700° C_2H_6 gives C_2H_4 and H_2 as the chief products of decomp. C_3H_8 suffers dehydrogenation and loss of CH_4, the two reactions taking place at about the same rates. The pyrolysis of both these hydrocarbons follows a unimol. law. The velocity coeffs. and their temp. coeffs. have been determined. F. J. Wilkins.

Thermal decomposition of propylamine. H. A. Taylor and H. E. Achilles (J. Physical Chem., 1931, 35, 2658—2666).—The decomp. of NH_2Pr^a at 520—580° is a homogeneous reaction, and above 200 mm. pressure the primary reaction is apparently unimol. Below 200 mm., the times for a given fractional decomp. increase with a fall in pressure. At lower pressures the addition of H_2, N_2, or He has little or no effect for the first 75% of decomp. The energy of activation, 44,400 g.-cal., is similar to that previously found for NH_2Et (43,400 g.-cal.), and may indicate a similar primary rupture of the mol. in the two cases. L. S. Theobald.

Application of the method of stationary velocities to the reaction $MeOH+H_2O \longrightarrow 3H_2+CO_2$. J. A. Christiansen (Z. physikal. Chem., Bodenstein Festband, 1931, 69—77).—An expression is developed for the reciprocal velocities of a stationary reaction sequence, and application to experimental results for the reaction $MeOH+H_2O \longrightarrow 3H_2+CO_2$ yields for the sequence involved: $H_2O+CHO \rightleftharpoons CO_2H+H_2$; $CO_2H \rightleftharpoons CO_2+H$; $H+MeOH \longrightarrow 2H_2+CHO$. In absence of H_2O the sequence becomes, by analogy: $CHO+MeOH \rightleftharpoons CO_2Me+H_2$; $CO_2Me \longrightarrow CO+CHO+H_2$; $CO_2Me+MeOH \longrightarrow HCO_2Me+CHO+H_2$. H. F. Gillbe.

"After-burning" during gaseous explosions: its ability to cause ignition. O. C. de C. Ellis and R. V. Wheeler (J.C.S., 1931, 2467—2472).—Two types of "after-burning" are described, a "central" type, which is primarily a continued and uninterrupted equilibrium change caused by rise in pressure, and a "prolonged combustion," originating at the wall of the explosion vessel, which is primarily a resumed equilibrium change caused by fall in temp. The central type of "after-burning" projected into mixtures of either CH_4 or CO with air can cause their ignition. E. S. Hedges.

Ignition of gases. VI. Ignition by a heated surface. Mixtures of methane with oxygen and nitrogen, argon, or helium. C. A. Naylor and R. V. Wheeler (J.C.S., 1931, 2456—2467).—When mixtures of CH_4 and O_2 (mixed with an inert gas) are admitted to a reaction vessel of quartz, the reactions resulting in the production of flame are thermal reactions catalysed by the products of an initial slow and flameless combustion. The total amount of heat acquired by the reacting gases depends on the thermal properties of the inert gas, which absorbs part of the heat developed by the oxidation. When the N_2 in CH_4–air mixture is replaced by A, having both a lower sp. heat and a lower thermal conductivity, the "ignition temps." are lowered, whilst replacement by

He, of high thermal conductivity, raises them. CH_2O and CO are produced during the period of "lag" on ignition. Addition of small amounts (0·02%) of CH_2O or CO to any CH_4–air mixture lowers its ignition temp. and shortens the lag on ignition, CH_2O being the more effective. Traces of I, EtI, EtBr, CCl_4, or $PbEt_4$ raise the ignition temp. of CH_4–air mixtures and decrease the speed of reactions occurring below the ignition temp. The inhibiting action of these substances appears to take place on the surface of the reaction vessel. E. S. HEDGES.

Explosions in closed cylinders. V. Effect of restrictions. W. A. KIRKBY and R. V. WHEELER (J.C.S., 1931, 2303—2306).—Synchronised records of the movement of flame and the development of pressure have been obtained during explosions of CH_4 and air and of CO and air in a cylinder containing restricting rings equally spaced apart. The restrictions greatly increase the speed of an explosion. The sudden expansion caused by the almost simultaneous combustion of the gas in each of the compartments formed by the restrictions, as a tongue of flame shoots through them, produces a shock wave yielding vibrations of large amplitude. E. S. HEDGES.

Velocity of decomposition of hydrogen peroxide by ferric salts as an index of their degree of hydrolysis. I. S. TELETOV and V. M. SIMONOVA (Ukrain. Chem. J., 1931, 6, [Sci.], 75—92).—The activity at equimol. concentration of Fe salts is in the order: $Fe(OH)_3$ sol$<Fe_2(SO_4)_3<FeCl_3<Fe(NO_3)_3$. The reaction is in all cases unimol. The velocity is a function of the degree of hydrolysis of the given salt, and at a given concentration of Fe salt this val. diminishes as the reaction proceeds, to attain a const. val. at the equilibrium point. The velocity coeff. increases with increasing Fe salt concentration, eventually to attain a limiting val. Decomp. of H_2O_2 is due solely to colloidal $Fe(OH)_3$ produced by hydrolysis; mol. or ionic Fe is inactive.
R. TRUSZKOWSKI.

Equilibria and reaction rates for the reaction sodium arsenite–sodium tellurate. P. T. STROUP and V. W. MELOCHE (J. Amer. Chem. Soc., 1931, **53**, 3331—3338).—The velocity of the reaction $Na_3AsO_3+Na_2TeO_4=Na_3AsO_4+Na_2TeO_3$ has been determined in both directions at temp. between 89·6° and 120°. The equilibrium const. $K_{89\cdot6}=[AsO_4][TeO_3]/[AsO_3][TeO_4]$ is 2400 from the concentrations at equilibrium and 2320 from the bimol. velocity coeff. The crit. increment calc. by means of the Arrhenius equation is 14,380. The relatively slow rate of reaction may be related to the transfer of an O atom as well as an electron. The reaction in acid solution is extremely slow, but is accelerated by the addition of NaOH and the previously negligible reaction between arsenite and tellurite becomes prominent; the latter affords a purple solution of polytelluride. J. G. A. GRIFFITHS.

Decomposition of sodium hypochlorite—an ion reaction. W. F. UNDERWOOD and E. MACK, jun. (J. Physical Chem., 1931, **35**, 2650—2657).—Data for the decomp. of aq. solutions of NaOCl at 45° in the presence of NaCl, $CaCl_2$, Na_2SO_4, and Na_2HPO_4 show that the rate of reaction increases with an increase in salt concentration, and that the slope of the curve obtained by plotting log k against (ionic strength)$^{0\cdot5}$ is $+1$, as is predicted from Brönsted's theory on the assumption that the reaction is $2ClO' \longrightarrow 2Cl'+O_2$. The reaction is bimol. in conc. salt solutions. L. S. THEOBALD.

Effect of solvent on the rate of acetylation of ethyl alcohol by acetic anhydride. F. G. SOPER and E. WILLIAMS (J.C.S., 1931, 2297—2303).—The rate of acetylation of EtOH by Ac_2O in hexane, heptane, CCl_4, PhCl, C_6H_6, PhOMe, $CHCl_3$, and $PhNO_2$ shows that the accelerating influence of the solvent is in the inverse order of the usual one, where solvents of high polarity accelerate the reaction. The increased rate of reaction in solvents of low polarity cannot be explained by assuming the formation of reactive associated mols. of EtOH, masking the more usual influence of the solvent. A study of the catalysis of the acetylation by acids and bases in CCl_4, $COMe_2$, and EtOH indicates that the uncatalysed reaction appears to predominate over a considerable range of concentration of the acid or base. The results are discussed in relation to the effect of the solvent on the resolution of the intermediate crit. complex (A., 1929, 1244). E. S. HEDGES.

Studies of stereokinetics. I. Saponification of chloroacetanilides. G. SEMERANO (Gazzetta, 1931, 61, 501—519).—The rates of saponification of acetanilide and of some of its chloro-derivatives in aq.-alcoholic NaOH have been measured. The velocity coeffs. are in the order 2 : 4 : 5>2 : 5>2 : 4>3 : 5>2>3>4, the numbers denoting the positions of the Cl atoms in the derivatives. The various theories on the effect of substitution in aromatic compounds on activity are reviewed, and the results shown to be in accord with the theory of Lapworth and Robinson. O. J. WALKER.

Relation between molecular structure and reaction velocity in the combination of triethylamine and ethyl iodide in different solvents. H. G. GRIMM, H. RUF, and H. WOLFF (Z. physikal. Chem., 1931, B, 13, 301—315).—The velocity in hexane, *cyclo*hexane, PhMe, and C_6H_6 is low, as would be expected from their high electrical symmetry, and increases in the order given. In PhF, PhCl, PhBr, and PhI it is greater and increases in the order given, *i.e.*, with increasing size and deformability of the solvent mols. In *o*-, *m*-, and *p*-$C_6H_4Cl_2$ it decreases in the order given, *i.e.*, with decreasing dipole moment (cf. A., 1929, 404). The velocity in $NHPh_2$ is much greater than in Ph_2O and CH_2Ph_2 (which have nearly equal effects), but its dipole moment is only a little greater than theirs. Electrical asymmetry at one place in the mol. (*e.g.* the :NH group) may therefore have more influence than that of the mol. as a whole. Experiments with PhCN, $PhNO_2$, *p*-$C_6H_4Me{\cdot}NO_2$, *p*-$C_6H_4(OMe){\cdot}NO_2$, and *o*-$C_6H_4Cl{\cdot}NO_2$ also show that a direct relation between dipole moment and velocity is to be sought only in a range of *o*-, *m*-, and *p*-isomerides. In most of the cases studied the energy of activation is 12·0±0·5 kg.-cal. Addition of *cyclo*hexane to the other solvents retards the reaction, but their effects remain in the same order.
N. H. HARTSHORNE.

Mechanism of, and constitutional factors controlling, the hydrolysis of carboxylic esters. IV. Hydrolytic stability maxima of some dihydroxypropyl esters of aliphatic acids. C. K. Ingold, A. Jackson, and (Mrs.) M. I. Kelly (J.C.S., 1931, 2035—2042).—Further esters of the series $R{\cdot}CO_2R'$ (cf. A., 1930, 869) are studied, where R′ is now dihydroxypropyl and R is Me, Et, Pr^{α}, Pr^{β}, Bu^{α}, and Bu^{β}; the methods are substantially those of the earlier paper. The propionate has the highest k_{H} at three temp. studied; but p_{H}^{*} (the p_{H} for min. velocity of hydrolysis), and also the consts. A and B in the equation $\log k_{\text{H}}=A-B/T$ and hence the crit. energy increment, vary regularly in the homologous series.
C. W. Davies.

Mechanism of, and constitutional factors controlling, the hydrolysis of carboxylic esters. V. Effect of alkyl groups on hydrolytic stability maxima. C. M. Groocock, C. K. Ingold, and (Mrs.) M. I. Kelly (J.C.S., 1931, 2043—2046).—Regularities are shown on intercomparing the hydrolysis data already reported for the three series $C_2H_3(OH)_2{\cdot}CO_2R$, $R{\cdot}CO_2C_3H_5(OH)_2$, and $MeCO_2R$; these afford support for the conclusion that the displacement of p_{H}^{*} caused by a substituent group is a direct function of the polar effect of the group, and is determined by the product of two numerical factors separately dependent on its nature and its position. Similar regularities on comparing these p_{H}^{*} vals. with the speeds of aromatic chlorination for corresponding compounds of the series $RO{\cdot}C_6H_4{\cdot}CO_2H$ and $RO{\cdot}C_6H_4Cl$ adumbrate a wider generalisation and show that the same quant. measure of polarity may be derived from different reactions.
C. W. Davies.

Mechanism of, and constitutional factors controlling, the hydrolysis of carboxylic esters. VI. Kinetics of the hydrolysis of some paraffin-αω-dicarboxylic esters in very dilute aqueous solution, and the derivation, with corrections for solvent electrostriction, of their molecular dimensions. Spatial form of polymethylene derivatives in dilute solution. C. K. Ingold (J.C.S., 1931, 2170—2179).—New measurements are reported of k_1 and k_2 for Me and Et esters of the series succinic to azelaic acids. A calculation of k_1 is given which eliminates interference from second-stage hydrolysis. The new vals. of r (cf. this vol., 1126) support the mol. model advanced; since they do not in this case relate to the bivalent anion they confirm the conclusion that the rigidity is conferred by an intrinsic property of the CH_2 group and not by ionic repulsion.
C. W. Davies.

Inversion of sucrose by tartaric acid. D. Singh, K. Lal, and C. Anand (Proc. XV Indian Sci. Cong., 1928, 174).—The inversion of sucrose at different concentrations by a const. quantity of acid is linear, but for a given concentration of sugar with different quantities of acid the rates of inversion do not show a simple relation.
Chemical Abstracts.

Dependence of reaction velocity on surface and agitation. I. Theoretical. A. W. Hixson and J. H. Crowell (Ind. Eng. Chem., 1931, 23, 923—931).—The relation between the time t during which a crystal has been dissolving and the wt. w remaining undissolved is of the form $t=f\,.\,w^{\frac{1}{3}}$.
F. J. Wilkins.

Dependence of reaction velocity on surface and agitation. II. Experimental procedure in study of surface. A. W. Hixson and J. H. Crowell (Ind. Eng. Chem., 1931, 23, 1002—1009).—The cube root law for the dissolution of solids in liquids has been verified experimentally for the case of $C_{10}H_8$ in various solvents under different conditions of agitation, and also for a solid–gas system ($C_{10}H_8$–air). When a solid dissolves in a liquid, forming a ppt. through chemical reaction (*e.g.*, alum in aq. NH_3), the action is normal provided the agitation is sufficiently intense to remove the coating as fast as it is formed; otherwise, the ppt. has a protective effect.
E. S. Hedges.

Velocity of decomposition of marble in acids. I. W. Jacek (Bull. Acad. Polonaise, 1931, A, 117—142).—The velocities of decomp. of marble in dil. AcOH and dil. HCl have been studied.
W. R. Angus.

Theory of dissolution of metals. III. M. Straumanis (Z. physikal. Chem., 1931, 156, 150—158; cf. this vol., 436).—The differences in the rates of dissolution of the various faces of a metal crystal cannot be explained by differences in equilibrium potential, for no such differences are possible. The suggested explanation is that the rate of dissolution at any face is determined by the conditions of local action at that face, and that since the inclusions of impurities in the crystal have a definite orientation, these conditions will differ from one face to another.
R. Cuthill.

Displacement of arsenic from solutions of its salts by hydrogen under pressure. V. V. Ipatiev, jun., M. N. Platonova, and V. S. Malinovski (Ber., 1931, 64, [*B*], 1959—1964; cf. A., 1930, 306; this vol., 52).—With pressure up to 150 atm. and small alterations of concentration (up to 50%) the quantity of As precipitated from solutions of $AsCl_3$ in HCl is proportional to the pressure. Between 15 and 250 atm. and with solutions not exceeding N, the displacement of As by H is a reaction of the first order. Between 125° and 175°, $\log K$ is a linear function of $1/T$. Assuming the reaction to proceed uniformly as a change of the first order, within the limitations of the first sentence the approx. expression $K'=(1/tp)\,.\log[a/(a-x)]$ is derived, from which the amount of As separated under given conditions can be calc. to within about 5—8%. The activating energy of the replacement of As by H is calc. to be 28,000±2000 g.-cal. It is calc. that the displacement of 1% of As from N-$AsCl_3$ solution at room temp. and 100 atm. pressure of H_2 requires 1140 years. Increase in the concentration of HCl accelerates the change, which is inhibited by NaCl or HCl.
H. Wren.

Displacement of antimony from solutions of its salts by hydrogen under pressure. V. V. Ipatiev, jun., and V. I. Tichomirov (Ber., 1931, 64, [*B*], 1951—1959).—Under low pressures (up to 150 atm.) and with small variations in concentration (up to 50%), the amount of Sb displaced from solutions of $SbCl_3$ by H_2 under pressure is proportional to the pressure. Within the limits of pressure, 15—150 atm., and with concentrations not exceeding N the reaction is of the first order. Between 100° and 150°, log K is a linear function of $1/T$. If it is assumed that the change proceeds uniformly as a reaction of the first order, and account is taken of the first sentence (see above) the approx. expression, $K'=(1/tp)\log[a/(a-x)]$ is obtained which, for any val. of pressure, time, and temp., permits the calculation of the amount of precipitated Sb to within 5—8%. The activation energy for the displacement of Sb by H, calc. from the Arrhenius expression, amounts to 26,000±1000 g.-cal. It is calc. that at room temp. 160 years are necessary for the separation of 1% of Sb from N-$SbCl_3$ solution under 100 atm. of H_2. The reaction is retarded by increase in the acidity of the solution. H. Wren.

Displacement of bismuth from solutions of its salts by hydrogen under pressure. V. V. Ipatiev, jun., I. R. Molkentin, and V. P. Theodorovitsch (Ber., 1931, 64, [*B*], 1964—1970).—Under pressure up to 150 atm. and within slight changes of concentration (up to 50%) the amount of Bi displaced from solutions of its salts by H_2 is proportional to the pressure. Between 15 and 250 atm. and with approx. N-solutions the displacement is a reaction of the first order. Between 100° and 150° log K is a rectilinear function of $1/T$. The activating energy of the replacement of Bi by H_2 is calc. to be 25,400±600 g.-cal. It is calc. that about 37 years are necessary for the displacement of 1% of Bi from N-$BiCl_3$ by H_2 under 100 atm. and at room temp. Increase in the concentration of HCl retards the reaction. Displacement of Bi from solution in AcOH occurs more rapidly and more completely than from solution in HCl.

H. Wren.

Behaviour of purest aluminium towards acids and bases. M. Centnerszwer (Z. Elektrochem., 1931, **37**, 598—603).—99·95% Al is practically unattacked by HNO_3 or H_2SO_4. Reaction with HCl becomes observable at 25° and a concentration of $2N$, the rate of dissolution increasing at an extraordinary rate with increasing concentration and rising temp. The increase of rate of dissolution with concentration of acid is given by $dv/dt=K_nC^n$, where K_n and n are consts. The temp. coeff. between 25° and 35° is 7·0, although it lies between 1·73 and 2·39 for 99% Al. In alkali, 99·95% Al behaves in a similar manner to 99% Al, previously investigated. The pure Al also dissolves in NH_3 aq., the velocity of the process varying with the [OH′] according to the formula $dv/dt=KC^{\frac{1}{2}}$. E. S. Hedges.

Velocity of dissolution of thallium in acids. M. Centnerszwer [with S. Levi] (Z. Elektrochem., 1931, **37**, 603—610).—Tl dissolves readily in HNO_3 solutions, after passing through an induction period, the velocity increasing with increasing concentration up to $0{\cdot}25N$, where it attains a max., falling at higher concentrations. The temp. coeff. of the reaction increases with rise of temp., eventually reaching the val. 4·4. The rate of dissolution is increased by stirring. In H_2SO_4 and HCl the rate of dissolution of Tl is relatively very slow, the ratio for $2N$-acids being $HNO_3 : H_2SO_4 : HCl = 428 : 1{\cdot}78 : 1$. The velocity is almost independent of the concentration of H_2SO_4 or HCl and is approx. equal to the rate of dissolution in H_2O. E. S. Hedges.

Dissolution of aluminium in alkaline solutions. G. Schikorr (Z. Elektrochem., 1931, **37**, 610—613).—In solutions containing up to $0{\cdot}95N$-NaOH the rate of dissolution of Al rises to a max., falls to a min. (zero velocity in the case of dil. solutions), and then rises to another max., at which it remains practically const. The amount of H_2 evolved during the first reactive period corresponds with the equation $Al+NaOH+2H_2O=Al(OH)_2ONa+1{\cdot}5H_2$; the subsequent, second period of reaction is produced by the NaOH being freed once more through the reaction $Al(OH)_2ONa+H_2O=Al(OH)_3+NaOH$. The reaction is similar in $0{\cdot}1N$-KOH, $Ba(OH)_2$, or Na_2CO_3. The presence of H_2SiO_3 increases the interval between the two periods of reaction by hindering the formation of nuclei of cryst. $Al(OH)_3$. The rate of dissolution is influenced very little by impurities in the Al.

E. S. Hedges.

Effect of temperature on corrosion of zinc. G. L. Cox.—See B., 1931, 928.

Cathodic passivity phenomena. E. Liebreich (Z. physikal. Chem., 1931, **156**, 51—76).—The current–polarisation voltage curve of Zn in $0{\cdot}1N$-H_2SO_4 exhibits irregularities soon after the commencement of polarisation; with increase of polarisation the curve does not progress directly to the point at which H_2 evolution begins, but moves to a position parallel to the original position of the curve, and it is at this stage that visible evolution of H_2 begins. With decreasing polarisation the curve at first follows this second portion and then falls suddenly to the normal position. The effect is attributed to mechanical passivity. In contrast to those on other metals, the passive film on Zn becomes loosened with decreasing polarisation, and the activity of the metal is then maintained until the current falls to zero.

H. F. Gillbe.

Reactivity of powdered metals. Haid, Goetze, Selle, Koenen, Schmidt, and Becker (Jahresber. Chem.-tech. Reichsanst., 1930, **8**, 136—141; Chem. Zentr., 1931, i, 2717).—The reactivity increases greatly with increase in fineness. The ignition temp. is const. only for a particular surface; for Al it varies between 250° and 1000°, and depends also on the oxide content, Al free from O igniting more readily. The velocity of interaction with H_2O also increases with fineness. A. A. Eldridge.

Kinetics of decomposition of hydrogen peroxide by ferric hydroxide sol. I. S. Teletov and E. A. Alexeeva (Ukrain. Chem. J., 1931, **6**, [Sci.], 61—74).—The decomp. of H_2O_2 by $Fe(OH)_3$ sol is a unimol. reaction. The velocity coeff. is proportional to the active surface, and can thus serve for the determination of the degree of dispersion of the colloid. This diminishes during the reaction, with eventual consequent coagulation of the sol.

R. Truszkowski.

Kinetic analysis of the formation of calcium cyanamide. H. H. Franck, F. Hochwald, and G. Hoffmann (Z. physikal. Chem., Bodenstein Festband, 1931, 895—906).—The reaction between CaC_2 and N_2 at 1050—1150° commences after an induction period which is reduced by addition of $CaCN_2$ or $CaCl_2$; addition of CaF_2 tends to increase the period. The velocity attains its max. val. within 1—3 min. and the reaction is then approx. unimol.; this stage may be prolonged by increasing the active surface, but when the surface is largely converted into $CaCN_2$ the rate of diffusion through the surface determines the reaction velocity. The presence of CaF_2, especially at 1065°, favours the diffusion and leads to a greater final yield. $CaCl_2$ tends to lower the yield.

H. F. Gillbe.

Kinetics of the evolution of nitrogen from ammonium nitrite. E. Abel, H. Schmid, and J. Schafranik (Z. physikal. Chem., Bodenstein Festband, 1931, 510—522).—The velocity of decomp. of NH_4NO_2 at a given ionic concentration is proportional to the $NH_4^{\cdot}$, NO_2', and HNO_2 concentrations, and diminishes with increase of the ionic concentration, but is independent of the NO pressure. The reaction takes place in two stages, viz., the formation and decomp. of an intermediate compound, probably of the diazo-type, produced from HNO_2, $NH_4^{\cdot}$, and NO_2'; the HNO_2 necessary is formed by hydrolysis.

H. F. Gillbe.

Action of cyanogen on zinc. H. Braune [with W. Schulze] (Z. physikal. Chem., Bodenstein Festband, 1931, 415—422).—The velocity of the reaction between Zn and C_2N_2 at 115°, at const. vol., rises in the early stages and then becomes proportional to the gas pressure; after a time it falls and the reaction finally ceases before all the C_2N_2 has disappeared. If the initial pressure is re-established by addition of more C_2N_2 the same phenomena occur, but the steady velocity is much smaller and the final pressure is higher. The gradual divergence from the unimol. law is less marked at room temp., and is due not to the impermeability of the $Zn(CN)_2$ formed but, probably, to the formation of a paracyanogen film. The velocity coeff. rises from $2{\cdot}34\times10^{-8}$ at 0° to $1{\cdot}16\times10^{-5}$ at 115°, and the heat of activation is 13·4 kg.-cal. Readily adsorbed compounds such as CO_2 and C_6H_6 vapour do not influence the reaction, but O_2 greatly reduces its velocity, and at sufficiently high concentration inhibits it completely.

H. F. Gillbe.

Formation of water vapour in the dissociation of a salt hydrate. B. Topley and M. L. Smith (Nature, 1931, 128, 302).—The reaction $MnC_2O_4.2H_2O \longrightarrow MnC_2O_4+H_2O$ (in a vac. at 76°) is sensitive to small concentrations of H_2O vapour. The curve obtained by plotting the ratio, rate vac./rate at p_{H_2O} against p_{H_2O} falls rapidly to a min., then rises more slowly to a max. of the same order as the rate in a vac., and finally falls gradually to 0 at the dissociation pressure. An explanation is outlined.

L. S. Theobald.

Reactions in the solid state at high temperatures. VIII. Determination of the velocity of reactions which involve the evolution of gas. W. Jander and E. Hoffmann (Z. anorg. Chem., 1931, 200, 245—256).—A simple form of apparatus is described. Measurements of the velocity of the reaction between $BaCO_3$ and SiO_2 at 970—840° agree well with the calc. vals. Measurements with $BaCO_3$ and Nb_2O_5 at 624—748° show that the reaction velocity increases 22-fold over this temp. interval. The velocities of the reactions in the systems $BaCO_3$–SiO_2 and $CaCO_3$–MoO_3 are independent of the external pressure between 73 mm. and 754 mm., and are therefore not influenced by the diffusion of CO_2 through the powder.

H. F. Gillbe.

Reactivity in the solid state and its dependence on disjunctive factors. J. A. Hedvall (Z. angew. Chem., 1931, 44, 781—788).—Principally an account of work published at intervals during the last 20 years, with a discussion of the various factors which may reduce the stability of a crystal lattice and thus permit reaction between solids.

H. F. Gillbe.

Influence of the halogens on the union of hydrogen and oxygen. C. N. Hinshelwood and W. L. Garstang (Z. physikal. Chem., Bodenstein Festband, 1931, 656—661).—I catalyses the oxidation of MeOH at 452° and of C_6H_6 at 540—550°. Cl_2 and Br retard the homogeneous reaction between O_2 and H_2 at about 500°, but when present in greater proportion they accelerate the surface reaction. Br resembles I in that it inhibits the explosion at low pressures more readily than does Cl_2. Possible explanations of the results are discussed. Removal of the intermediate reducing substance by free halogen is probably of greater importance than the decomp. of the oxidising substances (OH, H_2O_2) by the halide.

H. F. Gillbe.

Decomposition of ozone, sensitised by bromine. B. Lewis and W. Feitknecht (Z. physikal. Chem., Bodenstein Festband, 1931, 113—125).—The decomp. of O_3 in presence of Br is characterised by two temp. intervals. In the lower the reaction takes place on a solid intermediate oxide, of which the rate of decomp. determines the rate of reaction; no decomp. takes place in the gas phase. At higher temp. the sphere of reaction extends to the gas phase, in which the decomp. then chiefly takes place. The decomp. velocity is proportional to the Br concentration up to a certain limit, above which the velocity increases at an increased rate; it is independent of the O_3 concentration provided that this exceeds a definite limit, below which it increases with decrease of the O_3 pressure. It appears that Br accelerates the decomp. of the intermediate oxide. On the assumption that only the surface mols. of the latter take part in the reaction, the velocity of decomp. of this compound, calc. from the temp. coeff., is $1{\cdot}2\times10^{-3}$, in satisfactory agreement with the val. obtained by Lewis and Schumacher.

H. F. Gillbe.

Bromine-sensitised oxidation of unsaturated hydrocarbons. G. R. Schultze (J. Amer. Chem. Soc., 1931, 53, 3561—3562).—A contraction greater than that corresponding with the unsaturated hydrocarbon present occurs when C_2H_4, C_3H_6, or C_4H_8, in the presence of pure O_2, is absorbed by Br water. A Br-sensitised oxidation of the hydrocarbon to CO_2 and H_2O is indicated.

J. G. A. Griffiths.

Chemical kinetics and ionic reactions. III. Neutral salt action and catalysis in ionic reactions. A. Kiss (Magyar Chem. Fol., 1931, 37, 17—23; Chem. Zentr., 1931, i, 2718).

Reduction of peroxysulphate by vanadyl ion with silver ion as catalyst. D. M. Yost and W. H. Claussen (J. Amer. Chem. Soc., 1931, **53**, 3349—3354; cf. A., 1926, 251, 365).—$VO^{\cdot\cdot}$ does not react with S_2O_8'' at room temp., but in the presence of $Ag^{\cdot}$ the velocity of the net reaction $S_2O_8''+2VO^{\cdot\cdot}+4H_2O=2SO_4''+2HVO_3+6H^{\cdot}$ is directly proportional to $[S_2O_8'']$ and $[Ag^{\cdot}]$, but independent of $[VO^{\cdot\cdot}]$. The sp. reaction rate is the same as that when $Cr^{\cdot\cdot\cdot}$ is the reducing agent, thus showing the absence of sp. effects due to $Cr^{\cdot\cdot\cdot}$ or $VO^{\cdot\cdot}$. The facts indicate the mechanism $S_2O_8''+Ag^{\cdot}=2SO_4''+Ag^{\cdot\cdot\cdot}$ (slow) followed by $Ag^{\cdot\cdot\cdot}+2VO^{\cdot\cdot}+4H_2O=Ag^{\cdot}+2HVO_3+6H^{\cdot}$ (rapid). The sp. effects of other reducing agents may be ascribed to the different reactivity of a Ag ion–reducing agent complex. The variation of velocity with change of ionic strength is qualitatively in accord with Brönsted's theory.

J. G. A. Griffiths.

Influence of strong electrolytes on the catalytic inversion of sucrose by hydrochloric acid at 30°. W. W. Floyd (J. Physical Chem., 1931, **35**, 2968—2984).—The velocity coeff. of the inversion of sucrose by $0{\cdot}1M$-HCl in the presence of N- and $2N$-NaCl, $BaCl_2$, K_2SO_4, and $MgSO_4$ have been determined at 30°. The chlorides increase the velocity of inversion at a rate which increases rapidly with concentration, and produce positive primary salt effects which in dil. ranges are linear, and in the complete range are exponential, functions of salt concentration. Sulphates decrease the velocity, producing negative salt effects. It appears that the more highly hydrated are the ions of the added salt the larger are the positive primary salt effects in the $H^{\cdot}$ catalysis of the sucrose inversion. The equation, $k=k_0\times10^{rM}$, (A., 1927, 21), does not represent the negative salt effects of the sulphates, but for concentrations $>0{\cdot}5M$ it describes the positive effects of the chlorides. The vals. of k_{30}/k_{25} for HCl solutions containing NaCl or $BaCl_2$ are practically the same as that (2·057) for HCl alone. The val. for $MgSO_4$ is lower. Calc. vals. of the heats of activation for HCl or HCl+chloride approximate to the classical val. of 26,000 g.-cal. per mol.

L. S. Theobald.

Acids and their catalytic action in water–alcohol mixtures. Oxidation of ethyl alcohol by chromic acid in presence of acids. M. Bobtelsky and C. Radovensky-Cholatnikov (Z. anorg. Chem., 1931, **199**, 241—261).—The oxidation of EtOH by H_2CrO_4 in dil. aq. solution is bimol., but at room temp. the velocity is zero in absence of a catalyst. Strong acids act as catalysts, although the reaction is not very sensitive to the p_H of the solution. The influence of $HClO_4$ is the same as that of HNO_3, and the velocity is proportional to the square root of the acid concentration, but with H_2SO_4 the relation is linear. HCl is anomalous, since its influence is small and independent of concentration above about N; this effect may be due to the formation of a labile compound between HCl and H_2CrO_4. With increase of the EtOH concentration from 30 to 60% the reaction velocity falls, but at higher concentrations the velocity increases at a rapidly increasing rate. It is suggested that in presence of an excess of H_2O_2 the oxidation is concerned principally with the oxidation of H_2O–EtOH complexes or of EtOH mols. surrounded by an aq. envelope, and that if an excess of EtOH is present the reaction consists of the oxidation of anhyd. EtOH mols.

H. F. Gillbe.

Basic catalysis in the decomposition of diacetone alcohol. J. G. Miller and M. Kilpatrick, jun. (J. Amer. Chem. Soc., 1931, **53**, 3217—3224; cf. A., 1930, 42).—The effect of NH_3, NH_2Me, $NHMe_2$, and NH_2Et on the velocity of decomp. of diacetone alcohol at 25° has been determined in buffer solutions of the type NH_3–NH_4Cl diluted with NaCl solution. In each case, the mol. base catalyses the reaction and catalytic consts. have been evaluated. The dissociation consts. of the bases have been calc.: NH_3 0·175, NH_2Me 6·32, $NHMe_2$ 6·7, and NH_2Et $3{\cdot}4\times10^{-4}$. When allowance is made for catalysis by the mol. base, Åkerlöf's data (A., 1928, 485) afford dissociation consts. in better agreement with recorded vals. (this vol., 308). J. G. A. Griffiths.

Inhibitory action of anthracene in the autoxidation of benzaldehyde. H. L. J. Bäckström and H. A. Beatty (J. Physical Chem., 1931, **35**, 2530—2567).—Experiments on the induced oxidation of anthracene show that its inhibitory action in the autoxidation of PhCHO is connected with an induced oxidation of the inhibitor. The primary oxidation product is anthranol which is autoxidisable and reacts with O_2 to form a peroxide. This slowly decomposes, forming anthraquinone. With increasing concentration of anthracene the relative amounts of the oxidation products formed approach 1 mol. of BzOH per mol. of anthraquinone. The induced oxidation of the anthracene is the result of a reaction with a peroxide of PhCHO, and the assumption of the existence of an unstable primary peroxide, possibly $Ph{\cdot}CH{<}^{O}_{O}{>}O$, is a necessary link in the reaction chain. The results can be explained by a chain mechanism (this vol., 572). In the photochemical reaction, there occurs a side reaction (20%) in which anthraquinol is an intermediate product and reacts with O_2 to give equimol. amounts of anthraquinone and H_2O_2. A second side reaction, favoured by a rise in temp. and common to both photochemical and thermal reactions, yields complex, coloured products. In the thermal reaction, the relative ratios of autoxidation reaction and induced oxidation depend only on the composition and temp. of the solution. The photochemical reaction is complicated by a screening effect of the anthracene. The solubility of anthraquinone in PhCHO at 0° and 25° is 0·0081 and 0·0210 mol. per litre, respectively. L. S. Theobald.

Oxidation of linseed oil emulsions in the presence of hæmatin and potassium cyanide. G. P. Wright and M. Van Alstyne (J. Biol. Chem., 1931, **93**, 71—82).—The acceleration of the autoxidation of linseed oil emulsions by hæmin and the failure of KCN to inhibit the reaction are confirmed (cf. A., 1924, ii, 320). Hæmatin–KCN accelerates the oxidation as effectively as hæmatin–pyridine, wide variations in the KCN concentrations having little influence on the rate of reaction. The acceleration of oxidation by animal charcoal is inhibited by KCN. Hæmatin–pyridine has no influence on the rate of oxidation of cystine, whilst addition of small quantities of KCN induces a rapid oxidation, an effect also produced by addition of hæmatin–KCN in the absence of pyridine. F. O. Howitt.

Spontaneous oxidation of cysteine. II. Autoxidation of cysteine free from iron. E. G. Gerwe (J. Biol. Chem., 1931, 92, 399—411; cf. this vol., 718).—The acceleration by a trace of Fe of the slow spontaneous oxidation of pure cysteine is proportional to the amount of added Fe. The oxidation rate of Fe-free cysteine is too high to be due to the minute trace of Fe calc. on the sensitivity of the colour reaction used for Fe. Pure cysteine is therefore autoxidisable. A. Cohen.

Spontaneous oxidation of cysteine. III. Action of cyanides and cystine on cysteine oxidation. E. G. Gerwe (J. Biol. Chem., 1931, 92, 525—533).—Autoxidation of Fe-free cysteine is not inhibited by CN′. The acceleration due to presence of Fe, however, is inhibited, due to conversion of the $Fe^{\cdot\cdot}$ or $Fe^{\cdot\cdot\cdot}$ into the corresponding Fe–KCN compound. Addition of Fe as $K_4Fe(CN)_6$ or $K_3Fe(CN)_6$ does not accelerate the reaction. Cystine does not influence the oxidation of cysteine (cf. A., 1923, i, 416). F. O. Howitt.

Effect of iron and cyanides on the spontaneous oxidation of dialuric acid. E. S. Hill (J. Biol. Chem., 1931, 92, 471—481).—The spontaneous oxidation of dialuric acid is greatly accelerated by addition of Fe except at the normal optimum range of p_H 7·0—7·4 due, perhaps, to the inability of O_2 to enter the solution at a rate greater than normal. Autoxidation of the acid is not inhibited by KCN, whilst the acceleration due to presence of Fe is inhibited. Comparison is made with cysteine and glutathione in cell oxidation. F. O. Howitt.

Active centres in hydrogenation catalysis. G. M. Schwab [with L. Rudolph] (Z. Elektrochem., 1931, 37, 666—669).—Theoretical. E. S. Hedges.

Action of active charcoal on lead sulphide. F. Püschel (Arch. exp. Path. Pharm., 1931, 161, 455—466).—Freshly prepared suspensions of PbS are oxidised in presence of animal charcoal so that the Pb becomes sol. in HCl and NH_4OAc. The action of the charcoal is independent of the Fe content, but is closely correlated with its adsorptive power and apparently depends essentially on the absorption of O on its surface. PbO and not $PbSO_4$ is the chief primary product from PbS in presence of charcoal. W. O. Kermack.

Catalytic oxidation of nitric oxide. II. L. Szegö and L. Guacci (Gazzetta, 1931, 61, 333—358; cf. A., 1930, 713).—The catalysis of the reaction $2NO+O_2=2NO_2$ by SiO_2 and Al_2O_3 gels has been studied between 13° and 110°. From 30° to 80° the reaction obeys Arrhenius' law, but at higher temp. reaction in the gaseous phase begins to prevail. Below 30° the catalytic effect is slower owing to a decrease of the free surface caused by adsorption of NO_2. The decrease of the apparent heat of activation and the variation of the integration const. with different types of gels are explained by variations in the sp. gr. and porosity of the gels. Measurement of the adsorption isotherms for two samples of SiO_2 gel indicate the existence of catalytically active centres. The high val. calc. for the heat of adsorption of NO is accounted for by the solubility of this gas in the adsorbed NO_2. This furnishes a possible mechanism of the catalytic reaction. The velocity coeff. of this reaction is inversely proportional to the diameter of the catalyst granules, and this relationship should hold theoretically for diameters having mol. dimensions. O. J. Walker.

Kinetics of the reaction $2SO_2+O_2 \rightleftharpoons 2SO_3$ on platinum. G. B. Taylor and S. Lenher (Z. physikal. Chem., Bodenstein Festband, 1931, 30—43).—Study of the reaction at 525—700° from both sides of the equilibrium point shows that the rate of formation of SO_3 varies directly with the distance from equilibrium and with $1/[SO_3]^{\frac{1}{2}}$; the rate of the reverse reaction varies directly only with the distance from equilibrium. No single expression could be obtained by consideration of the process in terms of simultaneous reactions. The apparent heat of activation of the formation of SO_3 is 16 kg.-cal., and that of the dissociation on a Pt surface 40 kg.-cal. The mechanism of the reaction probably involves the combination of SO_2 mols. on striking O_2 mols. adsorbed at an active point on the catalyst; the SO_3 mols. formed do not evaporate immediately, and therefore prevent access of other mols. to the active centres. H. F. Gillbe.

Influence of heat on the preparation of nickel catalyst on infusorial earth. H. I. Waterman and M. J. van Tussenbroek (J.S.C.I., 1931, 50, 227—228T).—The catalyst obtained by reducing Ni oxide precipitated on kieselguhr as a support at different temp. was heated with dil. HCl, which reacts with Ni with the evolution of H_2. The Ni oxide on the support was reduced successively at 400°, 500°, and 600°. At 400°, after passing H_2 over it during several hr., only a small quantity of Ni yielding H_2 with HCl was formed. The H_2O formed during the reduction apparently originates for the greater part from the moisture which was driven out. At 500° the expulsion of O_2 from the Ni oxide is much stronger; but reduction to Ni is not complete, the H_2 evolved scarcely exceeding half the theoretical quantity. At 600° reduction increased greatly, the percentage of Ni calc. from the evolution of H_2 approaching the theoretical. Also the products from which O_2 had not been completely removed have a good catalytic effect on the hardening of soya-bean oil. This applies to the products prepared at 400° and at 500°; those reduced at 600° had only a very low activity, except in a single experiment.

Reduction of sodium cyanate. J. Drucker and F. A. Henglein (Z. physikal. Chem., Bodenstein Festband, 1931, 437—442).—The rate of decomp. of NaCNO at 700° is fairly small (about 1% per hr.), but in presence of Fe the decomp. is greatly accelerated. Reduction to NaCN by CO is complete at 700°, but at higher temp. decomp. with evolution of N_2 takes place. The composition of the gas phase at 500—700° has been determined. The heat effect of the reaction is −8·5 kg.-cal., that calc. from the heats of formation being −10·5 kg.-cal.

H. F. GILLBE.

Binary mixed catalysts containing molybdenum for the synthesis of ammonia. A. MITTASCH and K. KEUNECKE (Z. physikal. Chem., Bodenstein Festband, 1931, 574—582).—The activities of binary catalysts containing Mo and Co, Fe, Cu, Cr, W, and Mn have been compared. An increase of activity occurs only when compounds are formed between the components; thus the activity of a Mo–Cu catalyst is purely additive. If mixed crystals, but no compounds, are formed, as in the Mo–W and Mo–Cr systems, the activity diminishes. Compound formation alone, however, does not necessarily cause an increase of activity, and in certain cases poisoning occurs. Sp. chemical factors, which vary considerably from one element to another, are of importance. The activation heat of the NH_3 synthesis varies from about 24 to 38 kg.-cal., according to the constituents and percentage composition of the catalyst.

H. F. GILLBE.

Intermediate compound formation in the catalytic synthesis of ammonia. Formation of a nitride film on tungsten. G. MESSNER and W. FRANKENBURGER (Z. physikal. Chem., Bodenstein Festband, 1931, 593—607).—Whereas NH_3 and H_2 are adsorbed normally on W with formation of a unimol. layer, the absorption of N_2 increases with rise of temp., and is irreversible, and is shown from kinetic considerations to be due to compound formation. In the temp. interval 20—200° the quantity of H_2 adsorbed rapidly by the nitride film is less than that adsorbed by the pure metal, but slow adsorption of H_2 persists for several hr.; with rise of temp. further absorption takes place. Hydrogenation therefore occurs in the nitride film. H. F. GILLBE.

Catalytic decomposition of ammonia by iron. E. WINTER (Z. physikal. Chem., 1931, B, 13, 401—424).—By using a streaming method it has been shown that the decomp. of NH_3 on Fe at 492—670° follows the equation $-dp_{NH_3}/dt=Kp_{NH_3}^{0\cdot9}/p_{H_2}^{1\cdot5}$. The heat of activation is 54 kg.-cal. at 500° and 51 kg.-cal. at 700°. The relation between the amount of FeN produced and the NH_3 and H_2 concentrations has also been investigated. The catalysis is explained by supposing that a chemical equilibrium is set up in the adsorption film. J. W. SMITH.

Determination of the increased activity at the interface between zinc carbonate and zinc oxide. G. F. HÜTTIG [with E. ROSENKRANZ] (Z. physikal. Chem., Bodenstein Festband, 1931, 591—592).—Whereas $AgNO_3$ is decomposed only very slowly by basic $ZnCO_3$ and by ZnO, the activity of mixtures prepared by heating basic $ZnCO_3$ is a max. when about 50% of the $ZnCO_3$ has decomposed, *i.e.*, when the interface between the $ZnCO_3$ and the ZnO is a max. H. F. GILLBE.

Surface reactions of atoms and radicals. G. I. LAVIN and W. F. JACKSON (J. Amer. Chem. Soc., 1931, 53, 3189; cf. this vol., 321).—The oxidation of CO is used as a test for OH, and from the yield of CO_2 it is shown that whilst a dehydration catalyst is efficient, a dehydrogenation catalyst is inefficient in causing the H+OH combination. A method of separating H and OH is indicated.

J. G. A. GRIFFITHS.

Catalytic hydrogenation of carbon suboxide. K. A. KOBE and L. H. REYERSON (J. Physical Chem., 1931, **35**, 3025—3035).—C_3O_2, catalytically hydrogenated by passage with H_2 over Ni- or Pd-coated SiO_2 gels, yields CO_2 and propylene as the two chief products. The principal reactions which occur are $C_3O_2+5H_2\longrightarrow C_3H_6+2H_2O$; $C_3O_2+2H_2O\longrightarrow CH_2(CO_2H)_2$; $CH_2(CO_2H)_2\longrightarrow AcOH+CO_2$ and $CH_2(CO_2H)_2+nC_3O_2\longrightarrow$ polymeride. The Ni catalyst favours the formation of the polymeride, whilst the Pd catalyst gives practically no polymeride but more AcOH. Only small amounts of saturated hydrocarbons are formed. C_3O_2 is an active poison for the hydrogenation of C_2H_4. An improved apparatus (A., 1922, ii, 641) gives 60—73% yields of C_3O_2 from diacetyltartaric anhydride. L. S. THEOBALD.

Catalytic action of an aluminium oxide catalyst. W. D. BANCROFT and A. B. GEORGE (J. Physical Chem., 1931, **35**, 2943—2949).—Previous theories concerning the catalytic activity of Al_2O_3 have been investigated by studying the decomp. of AcOEt at 450° by Al_2O_3 catalysts prepared in different ways. The increase in the amount of C_2H_4 obtained by sintering the catalyst is less than the difference which exists in this respect between the dehydrating and decarboxylating catalysts. Washed pumice alone gives large amounts of C_2H_4 and little CO_2, whilst catalysts prepared by heating $Al(NO_3)_3,9H_2O$ favour the formation of C_2H_4 when compared with those obtained by precipitation with aq. NH_3. The increase in C_2H_4 resulting from sintering is small compared with the effect, positive or negative, of adsorbed substances. Taylor's theory of sp. catalytic activities of the adsorbed ions explains the results better than does Adkins' theory of mol. porosity.

L. S. THEOBALD.

Rectifying action and heterogeneous catalysis with copper–cuprous oxide systems. WO. OSTWALD and H. ERBRING (Kolloid-Z., 1931, 57, 7—14).—The relation between rectifying action, photo-electric effect, and catalysis previously suggested (this vol., 35) is confirmed by quant. investigations in which the rectifying action of $Cu–Cu_2O$ plates has been compared with their catalytic effect on the oxidation of *p*-phenylenediamine. Plates which form good " detectors " give the best yields of aniline-black and quinhydrone. Oxidation and reduction of the plates produces a parallel effect on both the rectifying action and the catalytic power. E. S. HEDGES.

Catalysts for synthesis of methyl alcohol. V. N. IPATIEV and B. N. DOLGOV.—See B., 1931, 962.

Activity of mixed catalysts. E. PIETSCH and F. SEUFERLING (Z. Elektrochem., 1931, 37, 655—665).—The activity of catalysts has been determined by measuring the amount of heat received by the catalyst from the reaction. Examination of the systems Pb–Tl and Pb–KCl as catalysts for the recombination of at. H has been directed at the mol. relations of the components. The activity of mixtures of Pb and Tl is consistently below that in accordance with an additive law, there being a sharp min. at about 33%

Pb. In the Pb–KCl system a considerable increase of activity is caused by the addition of the first 10% of Pb and a considerable decrease by the first 10% of KCl. The relation is additive only between 45 and 70 at.-%. E. S. Hedges.

Determination of the activity of mixed catalysts. E. Pietsch and F. Seuferling (Z. physikal. Chem., Bodenstein Festband, 1931, 523—532).—By thermo-electric measurement of the heat developed in the catalyst the activity of the latter may be determined. Details are given of the method and of apparatus suitable for use with various types of catalyst. H. F. Gillbe.

Decomposition of ethyl and *iso*propyl alcohols at surfaces of manganous compounds. A. T. Williamson and H. S. Taylor (J. Amer. Chem. Soc., 1931, 53, 3270—3275).—The reactions of EtOH and $Pr^{\beta}OH$ at 1 atm. at the surfaces of MnO, $MnSO_4$, $Mn_3(PO_4)_2$, and $Mn_2P_2O_7$ between 330° and 425° are mainly dehydrations and dehydrogenations. Under similar conditions, the rate of decomp. of $Pr^{\beta}OH$ is much greater than that of EtOH. Dehydration decreases more than dehydrogenation with increasing age of the catalyst, and with EtOH and MnO, the percentage of dehydrogenation decreases with rise of temp. The apparent energy of activation is therefore higher for the dehydration process. In accordance with the theory that dehydrogenation occurs at the positive ions of the surface and dehydration at the negative ions, the dehydrogenation/dehydration ratio decreases with increasing valency of the anion. J. G. A. Griffiths.

Thermal decomposition of gaseous propaldehyde on the surface of platinum. E. W. R. Steacie and R. Morton (Canad. J. Res., 1931, 4, 582—590).—The reaction at 820—935° follows the unimol. law and occurs catalytically on the Pt surface, the main products being, however, different from those of the homogeneous reaction. Since the heat of activation is 96,500 g.-cal., it seems that only adsorbed mols. react. R. Cuthill.

Autoxidation of benzaldehyde. II. Action of catalysts. E. Raymond (J. Chim. phys., 1931, 28, 421—441).—Since salts of Mn, Co, Ni, Fe, Ag, and Cu activate the autoxidation of PhCHO in the dark at rates which decrease in the order named, but are dependent on the nature of the anion, the activities of solutions of the respective benzoates, prepared both by double decomp. and from the metal oxide, were compared by determinations of the vol. of O_2 absorbed. Benzoates of Mg, Zn, Al, Pb, and Bi were inactive, those of Ag and Cu slightly active, whilst Mn, Co, Ni, and Fe gave highly active salts. Cu and Ag gave different rate of oxidation–time curves, especially during the period of induction. Primary oxidation of the aldehyde to BzO_2H probably occurs, followed by oxidation of the catalyst to an unstable per-salt which itself oxidises the aldehyde more rapidly than the per-acid. Since the rate of oxidation is proportional to (mass of catalyst)$^{\frac{1}{2}}$, it is probable that the primary oxidation is due to the formation of ions in solution, a conclusion confirmed by conductometric measurements. Since the rate of oxidation in light with a catalyst is never the sum of the rates observed in the dark with, and in light without, a catalyst, there is evidence that the cations concerned may also exercise an antioxygenic effect. J. Grant.

Thermal dissociation of benzoic acid vapour. W. Moser (Helv. Chim. Acta, 1931, 14, 971—997).—BzOH, when heated in glass vessels at 400—500°, is decomposed almost completely into C_6H_6 and CO_2 at a rate which increases with rise of temp. and with the surface area of the glass. Small amounts of PhOH and CO are also formed. Excess of CO_2 slightly retards the action. The main reaction is accelerated by Al slightly, by Zn or Fe greatly, and all three catalysts promote side reactions giving rise to Ph_2 and H_2. Cu or Cd accelerates the main reaction and suppresses side reactions. Cd increases the speed 200 times. The reverse change is not analytically detectable. F. L. Usher.

Preparation of fluorine by electrolysis. L. M. Dennis, J. M. Veeder, and E. G. Rochow (J. Amer. Chem. Soc., 1931, 53, 3263—3269).—A V-shaped cell of heavy Cu tubing in which foaming is avoided and no diaphragm is required is described. Difficulties encountered by other workers are eliminated by using pure graphite electrodes and specially pure electrolyte (KF,HF) dried at 130°. F_2 is evolved immediately on passing the electrolysing current; the cell may be used intermittently and has an efficiency of about 76% at 9·3 amp. J. G. A. Griffiths.

Preparation of hydrogen peroxide and ammonium persulphate with streaming electrolytes. E. H. Riesenfeld and A. Solovian (Z. physikal. Chem., Bodenstein Festband, 1931, 405—414).—Since during the electrolytic prep. of both H_2O_2 and $(NH_4)_2S_2O_8$ the products undergo partial decomp. at the electrodes, the use of a streaming electrolyte considerably increases the yield. Under suitable conditions a concentration of 0·58 millimol. H_2O_2 per litre and a yield of 18% have been obtained. With $(NH_4)_2S_2O_8$ the yield at first rises with increase of the streaming velocity, but later falls; the max. yield obtained is 71%. If the cathode is placed above the anode, so that the O_2 liberated at the latter comes into contact with the former, and if the electrolyte passes first over the cathode and then over the anode, H_2O_2 and $(NH_4)_2S_2O_8$ may be simultaneously prepared. H. F. Gillbe.

Boron hydrides. XV. Electrolysis of solutions of boron trihydride in ammonia. A. Stock, E. Wiberg, H. Martini, and A. Nicklas (Z. physikal. Chem., Bodenstein Festband, 1931, 93—100).—Two principal reactions occur during the electrolysis of a solution of B_2H_6 in anhyd. NH_3 at −75°. In the first the salt $B_2H_4,2NH_4$, which is formed in the solution and is responsible for the conductivity, decompose into $B_2H_4(NH_2)_2$ and H_2, and the conductivity simultaneously diminishes; this reaction proceeds to completion. In the second reaction the B_2H_4 and NH_4 resulting from the electrolysis of the intermediate compound yield H_2 and amino-substituted B_2H_6, *e.g.* $B_2H_5NH_2$. This compound is still feebly acidic, and its NH_4 salt undergoes further electrolysis and slow and incomplete ammination, with the partial re-formation of $B_2H_4(NH_2)_2$; alternatively, the B_2H_4

group reacts with NH_3 to yield B_2H_6 and N_2. Ammination of B_2H_6 to the extent of 2·3 NH_2 groups per mol. has been observed. H. F. GILLBE.

Beryllium. I. Electrolysis in non-aqueous solvents. II. Electrolysis of beryllium compounds in organic nitrogen derivatives. H. S. BOOTH and G. G. TORREY (J. Physical Chem., 1931, 35, 2465—2477, 2492—2497).—I. Starting with the purified basic acetate, methods for the prep. of the oxide, hydroxide, anhyd. chloride and nitrate, and acetylacetonate are described. The double K chloride or sulphate could not be obtained. Solutions of Be salts in EtOH, C_5H_{11}·OH, EtBr, glacial AcOH, acetylacetone, Me_2O–BF_3, $COCl_2$, PCl_3, liquid SO_2. and $SeOCl_2$ are mainly poor conductors of electricity and none is a satisfactory source of Be.

II. Solutions of different Be salts in the org. derivatives of NH_3 are either non-conducting or are poor conductors which yield Be only in small amounts (especially piperidine and pyrrole). In general, the solutions form gelatinous colloidal substances which make the practical separation of Be problematical. L. S. THEOBALD.

Electrodeposition of silver from sulphate, nitrate, fluoborate, and fluoride solutions. E. B. SANIGAR.—See B., 1931, 930.

Silver plating solutions. B. EGEBERG and N. PROMISEL.—See B., 1931, 930.

Electro-deposition of copper in the presence of gelatin. R. TAFT and H. E. MESSMORE (J. Physical Chem., 1931, 35, 2585—2618; cf. Trans. Kan. Acad. Sci., 1929, 32, 42).—The variations in form of the cathodic deposit from cells of the type Cu|$CuSO_4$, gelatin|Cu with the concentration and type of gelatin are recorded. Cathodes of Au, Pt, Ag, and brass have only an initial effect. The increase in wt. of the Cu deposit, determined for different concentrations of gelatin and $CuSO_4$, different current densities, times, and temp., is best explained by the assumption that the deposited Cu adsorbs gelatin on its surface. Measurements of cathodic polarisation indicate that complex ions are formed between $Cu^{\cdot\cdot}$ and gelatin, but that the electrochemical process occurring at the cathode is primarily a discharge of $Cu^{\cdot\cdot}$. L. S. THEOBALD.

Characteristics of working of the lead accumulator. E. DENINA and A. FRATES.—See B., 1931, 981.

Electrolytic manufacture of aluminium, and aluminium plating. V. O. PLOTNIKOV, M. M. GRACJANSKI, and M. S. FORTUNATOV.—See B., 1931, 979.

Changes produced on electrodes by electric sparks. L. BELLADEN (Gazzetta, 1931, 61, 537—543).—The changes which occur at the surface of electrodes by passing a spark obtained by means of an induction coil and condensers have been studied using electrodes of Cu, Zn, brass, Cd, Sb, Bi, Tl, Mg, Pb and Al, and with turpentine, liquid vaseline, paraffin, abs. EtOH, and air as dielectrics. With the liquid dielectrics the size and no. of the craters formed on the electrode surface do not vary with the nature of the electrode or of the dielectric. In air, however, the changes produced depend largely on the nature of the metallic surface and on the properties of the oxide film. O. J. WALKER.

Definition and determination of "free cyanide" in electroplating solutions. W. BLUM.—See B., 1931, 930.

Electrodeposition of chromium and influence of the cathode metal. J. W. CUTHBERTSON.—See B., 1931, 929.

Electrodeposition of tungsten from aqueous solutions. C. G. FINK and F. L. JONES.—See B., 1931, 930.

Preparation of pure electrolytic nickel. III. C. G. FINK and F. A. ROHRMAN.—See B., 1931, 930.

Gaseous combustion in electric discharges. VIII. The cathodic combustion of hydrogen–oxygen mixtures. G. I. FINCH and E. A. J. MAHLER (Proc. Roy. Soc., 1931, A, 133, 173—178; cf. this vol., 44).—The study of the cathodic combustion of electrolytic gas has been extended to that occurring at electrodes of Au, Ag, Ta, and W, and to the effect of such diluents as O_2, H_2, and H_2O. Dilution with H_2, even up to 99·5% of H_2, results in a rapid increase of combustion at a non-sputtering cathode, the effect being much less pronounced at a freely sputtering cathode. The formation of H_2O_2 during the combustion is favoured by increase of pressure, absence of sputtered metal particles, and dilution with H_2 (for a non-sputtering cathode). The presence of steam results in an increase in the rate of combustion at a non-sputtering cathode, but has no effect at a freely sputtering cathode. Electrolytic gas burns much more rapidly at a W than at a Ta cathode. L. L. BIRCUMSHAW.

Condensation of hydrocarbons by electrical discharge. VIII. Condensation as a function of time and pressure. S. C. LIND and G. R. SCHULTZE (J. Amer. Chem. Soc., 1931, 53, 3355—3366; cf. this vol., 60).—With const. duration of discharge (1 hr.), the fraction of CH_4 which reacts and the % of H_2 produced increase rapidly with decrease of initial pressure. Appreciable quantities of C_2H_4 are found only at about 200 mm. With const. initial pressure of CH_4, a steady state of synthesis and decomp. of hydrocarbons is established in 20 min., and further action of the discharge increases the yield of liquid and H_2. In the case of CH_4 and C_2H_4, the ratio of hydrocarbon disappearing to H_2 produced is independent of duration of reaction between 20 and 60 min., and the formulæ of the liquid products are unchanged. Unlike the product from C_2H_2, those from CH_4 and C_2H_4 are slowly decomposed by further action of the discharge. H_2 is produced during the polymerisation of C_2H_2 and some hydrogenation occurs. J. G. A. GRIFFITHS.

Formation and decomposition of ammonia in high-frequency glow discharge. R. RINKEL (Ann. Physik, 1931, [v], 10, 129—142).—The velocity of decomp. of NH_3 in a high-frequency glow discharge has been determined. With an initial pressure of 3—4 mm. the equilibrium lies at about 98% N_2 and 2% H_2. The formation of NH_3 from mixtures of N_2 and H_2 of varying composition was studied. The most favourable ratio is $N_2 : H_2 = 1 : 1$. The influence of different electrode materials and of electrically neutral metal sheets and gauzes introduced between the electrodes was also studied. No alteration in reaction velocity with wave-length in the range 400—1700 m. was found. W. GOOD.

Reaction of previously illuminated chlorine with hydrogen. W. JOST and H. SCHWEITZER (Z. physikal. Chem., 1931, **B**, **13**, 373—378).—Reaction still occurs 10^{-1} sec. after illumination has ceased, but this is approx. the limit. The concentration of Cl atoms decreases more rapidly than calculation predicts owing to turbulence in the apparatus increasing the number of collisions with the walls. N. H. HARTSHORNE.

Photosensitised decomposition of ozone by bromine. J. W. T. SPINKS (Nature, 1931, **128**, 548).—The $Br–O_3$ photo-reaction has a high quantum efficiency. In general, there is no after-effect, and no appreciable change in transmission of 365 or 546 mμ takes place on insolation, indicating the absence of absorption of an intermediate compound on surface walls. The quantum efficiencies at 546 and 365 mμ are practically equal and the same efficiency is obtained for mixtures of 0·3—3·3% Br and 0·5—4% O_3. The rate of reaction is directly proportional to the intensity. An oxide of Br is considered to be the " carrier " in both the thermal and photo-reactions. L. S. THEOBALD.

Photochemical conversion of carbonic acid. G. KÖGEL (Z. wiss. Phot., 1931, **30**, 196—201).—Theoretical. The synthesis of CH_2O is represented as a keto–enol change, activated by chlorophyll as light absorbent (cf. B., 1919, 738A). J. LEWKOWITSCH.

Kinetics and photochemistry of carbonyl bromide. H. J. SCHUMACHER and P. BERGMANN (Z. physikal. Chem., 1931, **B**, **13**, 269—284; cf. A., 1928, 1200).—K_c for the reaction $COBr_2 \rightleftharpoons CO+Br_2$ is $1{\cdot}77\times10^{-4}$ at 20°, $1{\cdot}50\times10^{-4}$ at 50°, and $1{\cdot}21\times10^{-4}$ at 100°, whence the heat of formation at const. vol. of $COBr_2$ is 1035±100 g.-cal. per mol. within this temp. range. In visible and long-wave ultra-violet light atoms and activated mols. of Br take no measurable part in the reaction between 10° and 73°, nor do they affect the formation of CO_2 when O_2 is present between 20° and 250°. The absorption of light by $COBr_2$ begins at 3200 Å., increases rapidly, and then remains const. to 2100 Å. In this range the photochemical decomp. of $COBr_2$ requires 1 quantum per mol. Gaseous impurities which do not absorb the light have no influence on the velocity of the decomp., the temp. coeff. of which is 1·0 per 10° between 10° and 40°. Alternative mechanisms suggested are (i) $COBr_2+E=COBr+Br'$, then $COBr=CO+Br$; (ii) $COBr_2+E=CO+Br+Br'$. N. H. HARTSHORNE.

Formation of hydrazine during electrical and photochemical decomposition of ammonia. A. KOENIG and T. BRINGS (Z. physikal. Chem., Bodenstein Festband, 1931, 541—552).—Since N_2H_4 is formed during the decomp. of NH_3 both photochemically and under the influence of the glow discharge, it is probable that NH_2 and/or NH are formed as intermediate products. At about −80° the formation of N_2H_4 preponderates over that of N_2, although the yield, referred to the electrical energy used, is less than with the streaming gas at room temp. H. F. GILLBE.

Photochemical reduction of ferric iron in tri-iodide solution. S. F. RAVITZ and R. G. DICKINSON (J. Amer. Chem. Soc., 1931, **53**, 3381—3384; cf. this vol., 308).—I and $Fe^{\cdot\cdot}$ in approx. equiv. proportions are at first formed more rapidly in light of $\lambda>5000$ Å. than in the dark in fresh solutions at 0° containing appropriate concentrations of I, I′, and $Fe^{\cdot\cdot\cdot}$. The light accelerates the reduction of $Fe^{\cdot\cdot\cdot}$ by I′. J. G. A. GRIFFITHS.

Desensitisation of photolysis of uranyl formate. C. OUELLET (Helv. Chim. Acta, 1931, **14**, 936—966).—Photolysis of HCO_2H in the presence of $UO_2^{\cdot\cdot}$ is markedly retarded by Cl′, I′, $Fe^{\cdot\cdot}$, $K_2Cr_2O_7$, $AgNO_3$, $NaNO_2$, KCN, $HgSO_4$, or quinol. The effect is relatively greatest at low concentrations of the desensitising substance or of the photolyte. The velocity (v) of the reaction in the presence of a desensitiser (D) is related to that (v_0) in its absence as expressed by the formula $v=v_0/(\alpha+\beta[D])$. Baur's formula (A., 1929, 892) for the relation between a stationary state and intensity of illumination is confirmed by a study of the reversible photolysis of KI in the presence of UO_2SO_4. F. L. USHER.

Highly disperse [photographic] emulsions. LÜPPO-CRAMER (Z. wiss. Phot., 1931, **30**, 201—207; cf. Phot. Korr., 1931, **67**, 1).—The sensitising properties of Na_2SO_3, $NaHSO_3$, $NaNO_2$, erythrosin, and pinachrome on an unripened " grainless " AgBr emulsion are compared. The changes on ripening, with and without the addition of 3% AgI, are studied. J. LEWKOWITSCH.

Photodichroism and photoanisotropy. X. Photographic experiments with polarised light. II. F. WEIGERT and F. STIEBEL (Z. wiss. Phot., 1931, **30**, 177—195; cf. following abstract).—Primary Ag is proved experimentally to act as sensitiser for the production of photodichroism; the proportion of primary Ag so available is estimated. CrO_3 treatment reverses the sign of the photodichroism. $Fe_2(C_2O_4)_3$ only develops extra-micellar Ag; developer containing Na_2SO_3 (*e.g.*, *p*-phenylenediamine) lays bare and develops intramicellar Ag as well, allowing its properties to be differentiated. Polarised light can even induce weak dichroism within the micelle. J. LEWKOWITSCH.

Photodichroism and photoanisotropy. VIII. F. WEIGERT and F. STIEBEL (Z. physikal. Chem., 1931, **B**, **13**, 285—298).—The anomalous additive dichroism produced by the simultaneous action of two beams of polarised light of different colours has been more completely studied (cf. A., 1930, 1238). The anomalies are especially marked when red light is one of the components. Experiments in which the one beam is polarised and the other is not show that red and blue polarised light are mainly concerned with the anisotropic " form factor " and with the " activation factor " of the latent image respectively. N. H. HARTSHORNE.

Intensifying action of hydrogen peroxide and organic peroxides on the latent photographic

image. C. E. BARNES, W. R. WHITEHORNE, and W. A. LAWRANCE (J. Physical Chem., 1931, 35, 2637—2649).—Time-gamma curves indicate that latent image intensification by H_2O_2 depends largely on the developer used. H_2O_2 produces an increase in speed with all developers except "glycine"; pyrogallol and metol show the highest degree of intensification, but the time-gamma curves reveal a wide difference in their action. *m*-Chlorobenzoyl peroxide is the only one of the org. peroxides investigated which shows true intensification. The effect of treatment with H_2O before development is discussed. L. S. THEOBALD.

Instability of silver halides, and photographic processes in the silver halide plate; light-sensitivity and development. K. FREDENHAGEN and (FRAU) M. WELLMANN (Z. physikal. Chem., Bodenstein Festband, 1931, 135—144).—The partial pressure of Ag over solid AgCl, AgBr, and AgI at room temp., calc. from existing v.-p. measurements, is considerably greater than the saturation v. p. of Ag. The gas phase in contact with a photographic plate is therefore supersaturated with respect to Ag, and many aspects of the behaviour of a plate on exposure and development are explained as due to removal of this supersaturation. H. F. GILLBE.

Elimination of ammonia from amino-acids and other substances by the light of the quartz lamp. F. LIEBEN and F. URBAN (Biochem. Z., 1931, 239, 250—256; cf. this vol., 607).—The elimination of NH_3 from the α-NH_2-group of NH_2-acids ($NH_2\cdot CH_2\cdot CO_2H$, alanine, aspartic acid, cystine, arginine, lysine, tyrosine, tryptophan, histidine, anthranilic acid) and from guanine, guanidine, and benzidine by light from the quartz–Hg lamp has been measured. The acids exhibit great differences in regard to the amount of NH_3 lost; histidine, then cystine, loses most. No relation exists between the amount of NH_3 eliminated and the accompanying total decomp. (measured colorimetrically) of histidine, tyrosine, and tryptophan. The action proceeds more rapidly in acid than in neutral or alkaline medium. No NH_3 is eliminated from guanidine, but the NH_2-groups in guanine, anthranilic acid, and benzidine are affected by the light to much the same extent as is that of a straight chain. The ϵ-NH_2-group in lysine is probably also attacked. W. MCCARTNEY.

Photochemical decomposition of amines and the photochemical interaction of amines and ethylene. H. J. EMELÉUS and H. S. TAYLOR (J. Amer. Chem. Soc., 1931, 53, 3370—3377; cf. this vol., 442).—NH_2Me and NH_2Et at 125—260° in the full radiation of the quartz–Hg vapour lamp slowly decompose into H_2, CH_4, C_2H_6, N_2, and a non-volatile liquid containing N. In the presence of O_2, a relatively rapid reaction occurs. The photo-decomp. of the amines induces the polymerisation of C_2H_4, especially at the higher temp. The velocity of reaction is independent of the pressure of C_2H_4 between 2 and 25 cm. and of the pressure of the amines when the absorption of light is complete. Preliminary experiments indicate that C_2H_6 probably inhibits the photo-decomp. of NH_3 and amines, but some polymerisation of C_2H_6 occurs. J. G. A. GRIFFITHS.

Photo-reaction between bromine and *cyclo*hexane. W. JOST (Z. physikal. Chem., Bodenstein Festband, 1931, 291—297).—Contrary to Rideal's report, no appreciable reaction takes place between Br and *cyclo*hexane in the dark. Both the band and continuous regions of the Br absorption spectrum are photocatalytically active, and produce the same type of reaction. The velocity coeff., $(d \log [Br_2])/dt$, is approx. proportional to the square root of the *cyclo*hexane concentration. In presence of H_2 the velocity is unchanged; O_2 produces a marked decrease, and the gradual increase of the coeff. during the reaction indicates that O_2 disappears as the reaction proceeds. The quantum yield at 73—100° is of the order of 12 to 40. The temp. coeff. of the reaction is about 2 per 30°, and the quantum yield at room temp. is thus about 2. The mechanism is discussed. H. F. GILLBE.

Quantum yield of 0·5 in photochemical reactions. F. WEIGERT and F. PRUCKNER (Z. physikal. Chem., Bodenstein Festband, 1931, 775—784).—The yield of the photochemical conversion of *o*-nitrobenzaldehyde, at concentrations of 0·02—8% in $COMe_2$, into *o*-nitrosobenzoic acid is 0·5 and is independent of wave-length between 3130 and 4360 Å. even when, as at 3130 Å., the solvent absorbs the greater part of the radiation. In presence of more than one absorbing substance, therefore, a photochemical Beer's law cannot be said to exist. This apparent anomaly is explicable on the assumption that the $COMe_2$ acts as a sensitiser in the same manner as does Cl at high concentrations on the decomp. of O_3. At concentrations below 0·5% the yield at 3130 and 3660 Å. falls, the min. val. being about 0·35, owing to a breakdown of Beer's law. H. F. GILLBE.

Effect of sea-water irradiated with ultraviolet light on the velocity of alcoholic fermentation of dextrose solutions. L. SANZO and F. PIRRONE.—See this vol., 1333.

Photochemical synthesis of carbohydrates. G. EMSCHWILLER (Bull. Soc. chim., 1931, [iv], 49, 1167—1187).—A lecture.

Action of light on catalytic oxidation by complex metallic salts. Y. SHIBATA and S. GODA (Bull. Chem. Soc. Japan, 1931, 6. 217—220).—The rate of oxidation of *d*-catechin in presence of racemic $[Co\ en_2NH_3Cl]Br_2$ is smaller in green light than in red or white light. The absorption spectrum of the complex salt exhibits bands at 5000 and 3640 Å., but both these wave-lengths are transmitted by the green screen used. It thus appears that excited H_2O mols. are more effective than excited mols. of the complex salt; this view is confirmed by the low reaction velocity in light which has passed through an aq. $CuSO_4$ screen. It is suggested that ordinary H_2O mols. are activated, possibly by dissociation, by the complex salt. H. F. GILLBE.

Decomposition of benzophenone diazide under the influence of *X*-rays. G. CRONHEIM, S. GÖTZKY, and P. GÜNTHER (Z. physikal. Chem., Bodenstein Festband, 1931, 785—791).—*X*-Rays of wave-length 0·60—1·54 Å. cause rapid decomp. of benzophenone diazide, and evolution of N_2; the compound at first fluoresces and finally becomes red. In this wave-length region the quantity of energy transferred to the secondary electrons per mol. of N_2 evolved is 25 kg.-cal., and is independent of the wave-length. The results confirm Glockler's theory (A., 1928, 970) of the chemical activity of *X*-rays. H. F. GILLBE.

Temperature coefficient of the synthesis of hydrogen bromide by α-particles. S. C. LIND and E. F. OGG (Z. physikal. Chem., Bodenstein Festband, 1931, 801—806).—The combination of H_2 and Br under the influence of α-particles is not a chain reaction at temp. up to 300°. The reaction velocity appears to be a function of the square root of the radiation intensity, and propagation of the reaction is therefore probably due to Br atoms; since, however, the photochemical reaction does not proceed at room temp., the atoms produced by the action of α-particles are more reactive than are those produced photochemically. At 40° the thermal rate is negligible, and the rate under α-particle bombardment, *i.e.*, the ratio of the no. of mols. of HBr formed to the no. of ion-pairs produced, is 0·54. The thermal rate is appreciable at 100° and is about 1/6 of the total rate. The α-particle rate rises to a max. val. of 1·51 at 192° and approaches zero at 265°; at higher temp. negative vals. may be obtained. The rate of HBr (liquid) decomp. under bombardment at room temp. is about 2·8, and this effect preponderates at higher temp.; the inhibitive influence of HBr is then negligibly small. For the interval 40—192° the temp. coeff. of the total reaction is about 1·1 per 10°, and at higher temp. it approaches that of the thermal reaction, viz., 2—2·3. H. F. GILLBE.

Photographic action of α-rays. J. EGGERT and F. LUFT (Z. physikal. Chem., Bodenstein Festband, 1931, 745—754).—The blackening of a photographic plate by α-rays is directly proportional to the concentration of the emulsion. The range of action within the emulsion is about 25—30μ. Each nucleus with which a particle collides becomes capable of development. The sensitivity of the plate towards α-rays does not vary appreciably with temp. H. F. GILLBE.

Photographic action of cathode rays. A. BECKER and E. KIPPHAN (Ann. Physik, 1931, [v], **10**, 15—51).—The effect has been investigated on 3 different AgBr emulsions for electron velocities 15—100 kv. The validity of the reciprocal law is confirmed. Almost to the appearance of solarisation the relationship between the blackening, *S*, and the electron quantity, *Q*, can be represented by $S=C\log(aQ+1)$ where *a* and *C* are consts. The initial photographic sensitivity of all the films used is proportional, between 15 and 100 kv., to the electron energy falling on them. Vals. of the photochemical yield are given. W. GOOD.

Action of radon on unsaturated hydrocarbons. G. B. HEISIG (J. Amer. Chem. Soc., 1931, **53**, 3245—3263).—Under the action of α-rays from radon, the number of mols. of hydrocarbon reacting per ion pair (*M/N* ratio) is for allene 10·0, allylene 8·3, CMe⋮CMe 5·8, β-butene 3·8, and isoprene 12·7, decreasing to 10 during the reaction. Liquid products together with H_2 and CH_4 are obtained, but in the case of the first two, the liquids are transformed into solids. The results indicate that the *M/N* ratios are additive and constitutive. The *M/N* ratio varies inversely as the ratio $\Delta(H_2+CH_4)/\text{-}\Delta$(hydrocarbon). J. G. A. GRIFFITHS.

Action of atomic on molecular hydrogen. K. H. GEIB and P. HARTECK (Z. physikal. Chem., Bodenstein Festband, 1931, 849—862).—The reaction between H atoms and para-H_2 has been studied, by means of a special apparatus, at 0·5 mm. and 10—100°. The reaction mechanism is the same as that found by Farkas (this vol., 174) for the thermal reaction, viz., para-H_2+H=H+ortho-H_2. The heat of activation is 7250±250 g.-cal. The extent of decomp. of para-H_2 may be employed to detect H atoms at low concentrations, such as are produced, *e.g.*, in NH_3, HBr, or H_2O by irradiation with the Zn arc. In addition, the mean life of the H atoms may be estimated. Thus in NH_3 the mean life is 7×10^{-4} sec., and recombination by triple impact is therefore improbable. H. F. GILLBE.

Atomic hydrogen occluded in iron nitride. S. SATOH (Nature, 1931, **128**, 457).—At. H has been observed in Fe nitride prepared by heating Fe in gaseous NH_3 (cf. this vol., 53). L. S. THEOBALD.

Reaction between sodium vapour and oxygen. III. Autoxidation. F. HABER and H. SACHSSE (Z. physikal. Chem., Bodenstein Festband, 1931, 831—848).—The reaction between dil. Na vapour and O_2 at relatively high partial pressure, in presence of an inert gas, takes place in the gas phase, and consists primarily in the addition of O_2 mols. to Na atoms; subsequently further Na atoms react with the NaO_2 formed. H. F. GILLBE.

Complex potassium, ammonium, and sodium silver thiosulphates. I. Ammonium silver thiosulphate. G. SPACU and I. G. MURGULESCU (Z. anorg. Chem., 1931, **199**, 273—282).—Potentiometric measurements with 0·01—6*M* solutions show that when $Ag_2S_2O_3$ and $(NH_4)_2S_2O_3$ react 4 complexes are obtained, viz., $(NH_4)_2[Ag_4(S_2O_3)_3],H_2O$, $(NH_4)[Ag(S_2O_3)]$, $(NH_4)_4[Ag_2(S_2O_3)_3],H_2O$, and $(NH_4)_5Ag(S_2O_3)_3$. Details are given of the prep. of these compounds. H. F. GILLBE.

Formation of copper peroxides in non-aqueous media. I. S. TELETOV and A. D. VELESCHINIETZ (Ukrain. Chem. J., 1931, **6**, [Sci.], 53—60).—A ppt. containing CuO_2 and CuO in various proportions is obtained by the addition of an Et_2O extract of H_2O_2 to a MeOH solution of $Cu(NO_3)_2$. The proportion of CuO_2 in the ppt. increases with the relative H_2O_2 concentration of the solution. H_2O_2 is decomposed by the ppt., which also decomposes on consequent diminution in H_2O_2 concentration, and Cu again passes into solution. The stability of the ppt. is not affected by the presence of H_2O. Cu compounds catalysing the decomp. of H_2O_2 form CuO_2 as an intermediate product. R. TRUSZKOWSKI.

Chemical reactions in crystals. II. Cupric sulphate. V. KOHLSCHÜTTER and H. NITSCHMANN (Z. physikal. Chem., Bodenstein Festband, 1931, 494—509).—*X*-Ray, microscopic, and chemical study of the decomp. of $CuSO_4,5H_2O$ shows the process to be extremely complex. The hydrates with 5, 4, and 3 H_2O, and the anhyd. salt, possess very different lattice structures. The monohydrate, when prepared in vac. at 20—40°, is completely amorphous, but it becomes crystalline on warming. The product of dehydration of the pentahydrate to approx. $2H_2O$ in vac. at 20° consists of amorphous monohydrate and pentahydrate, and only on heating at 100° is the trihydrate formed. At 50°, in air, the decomp. of $CuSO_4,5H_2O$ commences at minute white points and greenish-blue surface streaks; the former consist of monohydrate and the latter of trihydrate. The streaks are parallel with the *c* axes of the crystals, *i.e.*, with the direction of the smallest lattice const. Similarly, crystals of $[Cu(NH_3)_4][SO_4(H_2O)]$, after being heated at 90—93°, become divided into a series of plates by fissures perpendicular to the longest axis. The significance of these and other observations is discussed in detail. H. F. GILLBE.

Silver ferrites. II. Structure of yellow hydroxide obtained by hydrolysis of a hot ferric chloride solution. A. KRAUSE and W. BUCZKOVSKI (Z. anorg. Chem., 1931, **200**, 144—152; cf. this vol., 695).—The yellow hydroxide obtained by hydrolysis of aq. $FeCl_3$ at 120—160° is ferrous acid (γ-FeOOH), for the H which it contains is replaceable by Ag. Owing to the position of its isoelectric point, it may contain basic chloride. At 160° the hydrolysis also yields α-Fe_2O_3. R. CUTHILL.

Behaviour of gold and its alloys with silver and copper towards nitric and sulphuric acids. G. TAMMANN and E. BRAUNS (Z. anorg. Chem., 1931, **200**, 209—231).—Au is practically unattacked by H_2SO_4 at temp. up to 200°; at 300° the quantity of Au dissolved is appreciable unless the acid has previously been boiled. Whereas HNO_3 of *d* 1·3 is inert at 20—100°, HNO_3 of *d* 1·5 dissolves appreciable quantities of Au at 20°, but the acid rapidly loses its activity. Au–Ag alloys containing 0·75 and 0·55 mol. Au are scarcely attacked by boiled H_2SO_4 at 100°. H_2SO_4 at 150° and HNO_3 (*d* 1·3) at 100° do not attack Au–Ag alloys containing more than 0·50 mol. Au, but with a lower Au content, even 0·49 mol., the action is marked; the same obtains with HNO_3 at 90° for Au–Cu alloys. After removal of the surface Ag, further atoms move from the interior of the alloy to the surface and are then dissolved; the quantity of metal dissolved is proportional to the quantity of Ag in the alloy. H. F. GILLBE.

Preparation of phosphorescent substances. IV. CaS, SrS, and BaS. N. F. ZHIROV (J. Appl. Chem., Russia, 1930, 3, 1007—1021).—SrS is best for investigating secondary solvents, the theory of which is developed. If tungstates are used the ignition temp. is lowered to 900—1000°. $CaWO_4$ shifts the spectrum to the violet and $SrWO_4$ to the red. MgO is the only satisfactory secondary solvent. CdS gives highly coloured luminophores of poor quality. CHEMICAL ABSTRACTS.

Stability of barium sulphate at high temperatures. E. G. MAHIN and B. KILIAN (Proc. Indiana Acad. Sci., 1929, **36**, 155—156).—$BaSO_4$ is stable at temp. obtainable with ordinary laboratory burners; small losses occur at higher temp. CHEMICAL ABSTRACTS.

Aluminium oxide as basis of luminescent systems: Al_2O_3–Pt and Al_2O_3–Mn phosphors. E. TIEDE and R. PIWONKA (Ber., 1931, **64**, [*B*], 2252—2258).—Al_2O_3 prepared at 900° is hygroscopic and incapable of yielding luminescent preps., for which only the α-form is suitable. Pure NH_4 alum is heated at 900°, then pressed into rods, and heated in SiO_2 boats at 1200—1300° until the corundum lattice is well developed. Portions which have been in contact with the boats are rejected. Before ignition the alum is mixed with the sulphates, nitrates, chlorides, etc. of Fe, Pd, Os, Rh, Ru, Ir, Au, Co, Ni, Ag, Bi, Cu, Cd, Ti, Cr, Mn, W, Pt, U. Only those preps. activated with Pt or Mn are true phosphors in Lenard's sense. Al_2O_3 containing Ti, Rh, or Cr must be classified separately. The luminescent behaviour of the phosphors is described in detail. Rh can be present in much higher concentration than Pt. It appears that in the true phosphors, Al_2O_3–Pt and Al_2O_3–Mn, the active metal or metallic oxide is to be regarded as attached to the corundum lattice as a lattice-foreign component with consequent distortion of both components. It appears essential that the smallest at. distances of the active elements, *e.g.*, Pt (2·76 Å.) or Mn (2·58 Å.), must be smaller than the smallest at. distances of the metal in the basic material, *e.g.*, Al (2·86 Å.). H. WREN.

Reaction between thallic chloride and potassium thiocyanate. I. K. TAIMNI (J.C.S., 1931, 2433—2435).—The reaction of $TlCl_3$ with KCNS in aq. solution can be represented by the equation $3TlCl_3 + 4KCNS + 4H_2O = 3TlCNS + 4KCl + HCN + 5HCl + H_2SO_4$. Evidently, $Tl(CNS)_3$ is unstable, and H_2SO_4 is formed through the oxidising power of $Tl^{\cdots}$ ions. E. S. HEDGES.

Residual silica from the attack of leucite with acids. G. A. BLANC (Atti R. Accad. Lincei, 1931, [vi], **13**, 327—330).—If a warm aq. solution of a mineral acid is circulated through a granular layer of leucite crystals the liquid at first becomes turbid and then clear. The resulting layer of SiO_2 hydrogel is able to remove SiO_2 from certain colloidal suspensions passed through it. It loses this property after washing with distilled H_2O, but its activity can be restored by addition of electrolytes. The phenomenon is not purely one of flocculation of the dispersed SiO_2, since addition of electrolyte alone to the stable colloidal SiO_2 suspension does not bring about coagulation. The granules of the SiO_2 hydrogel are able to adsorb an amount of electrolyte sufficient to discharge the ultramicrons of the disperse phase which are brought in contact with the solid phase. O. J. WALKER.

Preparation of pure cerium. M. BILLY and F. TROMBE (Compt. rend., 1931, **193**, 421—423).—A 70% yield of Ce is obtained by electrolysis for 1½ hr. at 850° of 25 g. of $CeCl_3$, 16 g. of KCl, and 25 g. of CaF_2 at 10 amp. and 12 volts in a small quartz crucible at the bottom of a larger C crucible (anode), with a revolving axial Mo cathode, the top of which is protected in a quartz tube. The only impurity

was 0·08% Si; Brinell hardness 42·5 (250 kg.), *d* (in CCl_4) 6·75, m. p. (at 0·005 mm. pressure) 815±5°.
J. GRANT.

Lead halogenocarbonates. D. TSCHAVDAROV (Z. anorg. Chem., 1931, 200, 200—208; cf. A., 1930, 164).—The substance formed by interaction of aq. Na_2CO_3 with aq. $PbBr_2$ or aq. $PbCl_2$ is not a pure compound, but a mixture in varying proportions of $PbCO_3$, $Pb_2(OH)_2CO_3$, Pb(OH)Br or Pb(OH)Cl, and $Pb_2Br_2CO_3$ or $Pb_2Cl_2CO_3$. Pure $Pb_2Br_2CO_3$ has been prepared.
R. CUTHILL.

Action of oxidising agents on hydrazine sulphate. A. PURGOTTI (Ann. ist. super. agrar. Portici, 1929, [iii], 3, 47—54).—In alkaline solution: $3N_2H_4+4KMnO_4=4MnO_2+4KOH+4H_2O+3N_2$; in acid solution NH_3 is also formed. With $Fe^{\cdots}$ salts: $5N_2H_4+4Fe_2O_3=8FeO+4NH_3+3N_2+4H_2O$; with PbO_2 in acid or alkaline solution: $2PbO_2+N_2H_4=2H_2O+N_2+2PbO$. With $AgNO_3$ in alkaline solution: $2Ag_2O+N_2H_4=4Ag+N_2+2H_2O$. $K_4Fe(CN)_6$ in alkaline solution affords N_2 and H_2O but not NH_3. Cr may be determined by oxidation with Na_2O_2 to chromate, which is decomposed by N_2H_4 in presence of H_2SO_4, the vol. of N_2 liberated being measured.
CHEMICAL ABSTRACTS.

Action of nitric acid on phosphorous acid. B. BLASER and I. MATEI (Ber., 1931, 64, [*B*], 2286—2289).—HNO_3 free from oxides of N has no action on H_3PO_3. In 55% acid containing oxides of N, H_3PO_3 is completely oxidised in 15 min. at 100°; under similar conditions with 44%, 31%, and 17% HNO_3 4%, 93%, and 100% of the H_3PO_3 is unchanged. The existence of two forms of H_3PO_3 is suggested.
H. WREN.

Trithiazyl trichloride, $(NSCl)_3$. A. MEUWSEN (Ber., 1931, 64, [*B*], 2311—2315).—Analyses and determination of mol. wt. in freezing C_6H_6 show that the product obtained by the action of Cl_2 on N_4S_4 in $CHCl_3$ or CCl_4 is *trithiazyl trichloride* for which the constitution $\mathrm{N}{<}\begin{smallmatrix}\mathrm{SCl{:}N}\\ \mathrm{SCl{\cdot}N}\end{smallmatrix}{>}\mathrm{SCl}$ is suggested; by analogy the compound $N_4S_4Br_4$ is considered to be $(NSBr)_3$. It is violently decomposed by alkali, more quietly by dil. acids. When dry it remains unchanged for a few days but is best preserved under CCl_4.
H. WREN.

[Tetrathioltetrazole,] $(HSN)_4$. A. MEUWSEN [in part with H. HOLCH] (Ber., 1931, 64, [*B*,] 2301—2311; cf. A., 1929, 1252).—The compound $\mathrm{N}{<}\begin{smallmatrix}\mathrm{SH{:}N{\cdot}SH}\\ \mathrm{SH{\cdot}N{:}SH}\end{smallmatrix}{>}\mathrm{N}$ (*loc. cit.*) is reduced by Na and EtOH to Na_2S and $(NH_4)_2S$; NH_2SH is not isolable as an intermediate product. It is hydrolysed by alkali hydroxide to NH_3 and $Na_2S_2O_3$ with small amounts of Na_2SO_3 and Na_2S. With $AgNO_3$ in MeCN and $COMe_2$ it affords the *compound* $(HSN)_4,2AgNO_3$, decomposing in the course of a few hr., immediately on contact with moisture. With NH_2K in liquid NH_3 it affords the *substance* KSN,NH_2K, immediately decomposed by moist air; it is freely sol. in liq. NH_3 if an excess of $(HSN)_4$ is present but so much NH_2K is invariably present in equilibrium that addition of PbI_2 ppts. a mixture of $Pb(SN)_2,NH_3$ with PbNH and PbN,PbI,NH_3. Direct action of solutions of PbI_2 or $Pb(OAc)_2$ on $(HSN)_4$ in liquid NH_3 never yields the compound $Pb(SN)_2,NH_3$ of Ruff and Geisel (A., 1904, ii, 396) whilst under the conditions used by the authors the action of PbI_2 on N_4S_4 in liquid NH_3 leads to the *substance*, $PbN_2S,N_4S_4,3NH_3$. When treated with MgEtBr in $Et_2O–C_6H_6$, N_4S_4 yields the *compound* $\mathrm{SEt}{<}\begin{smallmatrix}\mathrm{N}\\ \mathrm{N}\end{smallmatrix}{>}\mathrm{SH}$, b. p. 39—41°/0·2 mm. Repetition of the work of Lengfeld and Stieglitz on the action of NH_2Et on S_2Cl_2 confirms the isolation of the substance $(EtNS)_4$; since it evolves N_2 quantitatively as NH_2Et when hydrolysed with alcoholic alkali the constitution $\mathrm{NEt}{<}\begin{smallmatrix}\mathrm{S{\cdot}NEt{\cdot}S}\\ \mathrm{S{\cdot}NEt{\cdot}S}\end{smallmatrix}{>}\mathrm{NEt}$ is assigned to it.
H. WREN.

Oxalatoarsenious acid and its salts. I. T. P. BARAT (Z. anorg. Chem., 1931, 200, 232—234).—Study of the system $As_2O_3–H_2C_2O_4–H_2O$ at 30° and of solutions of the two acids in a variety of solvents failed to indicate the existence of a solid complex acid. In aq. solution, however, the solubility of each acid is depressed by the presence of the other.
H. F. GILLBE.

Effect of some ions on the transformation of orange antimony trisulphide to the black form. L. LEHRMAN (J. Physical Chem., 1931, 35, 2763—2765).—Ions accelerate the change in the order $S''>H_2O>NO_3'>Cl'>SO_4''>AcO'$ and $H^{\cdot}>H_2O>Na^{\cdot}>NH_4^{\cdot}$. The change to the black form is gradual, a series of colours being displayed. A rise in temp. also accelerates the transformation.
L. S. THEOBALD.

Internally complex salts of bismuth and of ter- and quinque-valent antimony and arsenic. A. ROSENHEIM [with I. BARUTTSCHISKY, W. BULGRIN, W. PLATO, and G. EBERT] (Z. anorg. Chem., 1931, 200, 173—199).—Salts of bismuth have been prepared as follows. *Tartrates*: $[Bi(C_4H_4O_6)]OH,H_2O$, $NH_4[Bi(C_4H_2O_6)]$, $C_9H_8N[Bi(C_4H_2O_6)]$, $C_5H_6N[Bi(C_4H_2O_6)],7H_2O$. *Saccharate*: $K[Bi_2(C_6H_{19}O_{16})]$. *Citrates*: $Na[BiOH(C_6H_5O_7)],3H_2O$, $K[BiOH(C_6H_5O_7)]$. *Glycollates*: $[Bi_2(C_2H_3O_3)_3(OH)_2]NO_3,2H_2O$, $[Bi(C_2H_3O_3)_2]OH,H_2O$, $[Bi(C_2H_3O_3)_2]_2SO_4$. 3-*Nitropyrocatecholoxides*: $NH_4[Bi(C_6H_3O_2NO_2)_2]$, $K[Bi(C_6H_3O_2NO_2)_2]$. The following salts of Sb^{III} have been obtained. *Glycollates*: $K[Sb(CH_2O\cdot CO_2)_2]$, $Na[Sb(CH_2O\cdot CO_2)_2]$, $NH_4[Sb(CH_2O\cdot CO_2)_2],H_2O$, $C_5H_6N[Sb(CH_2O\cdot CO_2)_2],0\cdot 5H_2O$. *Pyrocatecholoxides*: $NH_4[Sb(C_6H_4O_2)_2]$, $K[Sb(C_6H_4O_2)_2],1\cdot 5H_2O$, $C_5H_6N[Sb(C_6H_4O_2)_2]$, $C_5H_6N[Sb(C_6H_4O_2)_2],C_6H_4(OH)_2$. *Homocatecholoxide*: $NH_4[Sb(Me\cdot C_6H_3O_2)_2],0\cdot 5H_2O$. *Dipyrocatecholphenylstibinic acid*, $H_2[SbOPh(C_6H_4O_2)_2],4H_2O$, and its pyridine *salt*, $(C_5H_6N)_2[SbOPh(C_6H_4O_2)_2]$, are described. The following salts of As^{III} have been prepared. *Pyrocatecholoxides*: $C_6H_4O_2{:}As\cdot OH$, $NH_4[As(C_6H_4O_2)_2]$, $K[As(C_6H_4O_2)_2]$, $K[As(C_6H_4O_2)_2],C_6H_4(OH)_2,4H_2O$, $Na[As(C_6H_4O_2)_2],C_6H_4(OH)_2,6H_2O$, $Ba[As(C_6H_4O_2)_2]_2,5H_2O$, and corresponding pyridinium, quinolinium, and anilinium *salts*, all without H_2O of crystallisation. *Homocatecholoxides*: $K[As(C_6H_3O_2Me)_2]$, $NH_4[As(C_6H_3O_2Me)_2]$. *Pyrogalloloxide*: $OH\cdot As(C_6H_3O_2\cdot OH)$.
R. CUTHILL.

Distribution [and isolation] of protoactinium in the industrial treatment of the mineral from the Belgian Congo. F. Reymond (J. Chim. phys., 1931, 28, 409—410).—Pitchblende containing 75% U_3O_8 was digested with H_2SO_4, and the residual SiO_2 heated 3 hr. with warm HF (1 : 3) containing a little Ta_2O_5. The dry extract was fused with $BaSO_4$, $KHSO_4$, and $HTaO_3$, the sol. sulphates were removed by hydrolysis, the $BaSO_4$ (and Ra) by dil. HF, and Po by calcination. Comparative activity measurements of the resulting Ta_2O_5 showed that 4—6% of the proto-Ac was present in the residues, 85% being removed with the U in the preliminary digestion with H_2SO_4. This was recovered by adsorption on a gel of $HTaO_3$. Failure to confirm the results of Hahn and Meitner (A., 1921, ii, 150) is attributed to differences in the initial treatment of the mineral. J. Grant.

Sulphurous acid and its salts. IX. Action of sulphurous acid on sulphides of iron, zinc, and manganese. F. Foerster and J. Janitzki (Z. anorg. Chem., 1931, 200, 23—45; cf. A., 1929, 159).—When SO_2 is passed into aq. suspensions of MnS, FeS, or ZnS the action of the H_2SO_3 on the sulphide varies with the solubility of the latter in H_2O, since this determines the concentration ratios of the ions SH', SO_3H', and $H^{\cdot}$. The most sol. sulphide, MnS, gives almost entirely thiosulphate and free S, whereas the most insol. sulphide, ZnS, gives mainly pentathionate and tetrathionate. With FeS at first thiosulphate, S, and trithionate are formed, but on further action the thiosulphate formation decreases and higher polythionates are formed. At first the primary intermediate product SO reacts as follows: $SO+2HSO_3' \longrightarrow H_2O+S_3O_6''$, but this gives place to $SO+2HS_2O_3' \longrightarrow H_2O+S_5O_6''$. The higher is $[H^{\cdot}]$ the smaller is the concentration of thiosulphate necessary for the commencement of pentathionate formation.

O. J. Walker.

Alleged selenium trioxide of Worsley and Baker. G. B. L. Smith and C. L. Mehltretter (J. Amer. Chem. Soc., 1931, 53, 3562—3563; cf. A., 1930, 48).—SeO_2 contaminated with chlorides and H_2O is precipitated by the action of O_3 on solutions of Se in $SeOCl_2$. J. G. A. Griffiths.

Molybdenum octacyanides. G. A. Barbieri (Atti R. Accad. Lincei, 1931, [vi], 13, 375—377).—The brick-red molybdenum cyanide obtained by the action of warm HNO_3 on $K_4Mo(CN)_8,2H_2O$ (cf. A., 1928, 160) is not $H[MoO_2(CN)_2,2H_2O]$, but contains the ion $[Mo(CN)_8]''''$ and consists of 3 mols. of molybdic acid and 1 mol. of $H_4Mo(CN)_8$. It can also be obtained by treating $K_4Mo(CN)_8,2H_2O$ with a molybdate in acid solution. O. J. Walker.

Volatilisation of polonium and of a deposit of thorium in a current of gas. M. Lecoin (J. Chim. phys., 1931, 28, 411—420).—An electrolytic deposit of Po on Ni was heated in a quartz tube (0·2 cm. diameter) at 750—1000° for 30 sec. in a current of gas, which was then scrubbed with *N*-HCl. The phosphorescence of the tube was photographed, and the Po in solution and dissolved from the walls of the tube (in HCl containing 0·01% HF) was determined from the ionisation activity of a drop of known wt. Volatile Po compounds are produced in A (especially if impure) and in $CO+CO_2$, but not in N_2 or in H_2. A high yield of Th-*C''* is obtained in O_2 (but none in O_2-free N_2) from a mixture of Th-*B*, Th-*C*, and Th-*C''*; complete separation of this mixture, although difficult, appears to be possible. J. Grant.

Rhenium tetrachloride and the rhenichlorides. H. V. A. Briscoe, P. L. Robinson, and E. M. Stoddart (J.C.S., 1931, 2263—2268).—$ReCl_4$ is the primary product of heating Re in Cl_2. No evidence has been obtained of the existence of the reported $ReCl_6$ and $ReCl_7$. K_2ReCl_6 can be made by synthesis; it gives ppts. with solutions containing the ions $Ag^{\cdot}$, $Hg^{\cdot}$, $Tl^{\cdot}$, but not with solutions containing the ions $Pb^{\cdot\cdot}$, $Cu^{\cdot\cdot}$, $Ba^{\cdot\cdot}$, $Co^{\cdot\cdot}$, $Ni^{\cdot\cdot}$, $Mn^{\cdot\cdot}$, $Mg^{\cdot\cdot}$, $Fe^{\cdot\cdot}$, $Fe^{\cdot\cdot\cdot}$, $Zn^{\cdot\cdot}$, $Li^{\cdot}$, and $Hg^{\cdot\cdot}$. E. S. Hedges.

Monothioper-rhenic acid. W. Feit (Z. anorg. Chem., 1931, 199, 262—270).—By passing H_2S into a conc. solution of a per-rhenate, the monothioperrhenate is produced quantitatively; the end-point may be estimated approx. by titration with aq. $TlNO_3$. The solution is not very stable, but if polythioper-rhenates are removed by addition of $TlNO_3$ a greenish-yellow solution of the pure compound is obtained. With $AgNO_3$ Ag_2S is precipitated; Pb yields a red ppt. which rapidly turns black and Hg a ppt. which is at first yellow and finally white. The free acid decomposes slowly after liberation in dil. solution yielding Re_2S_7. The *K* salt is very sol. in H_2O and EtOH; the *Rb* and *Cs* salts are less sol., and the pure *Na* salt has been prepared only in solution. The NH_4 and Tl salts are described. The stability of $HReO_4$ is considerably reduced by introduction of 1 atom of S, and the solubility relationships of the salts, all of which are anhyd., are markedly altered.

H. F. Gillbe.

Crystalline ferric oxide tetrahydrate. P. A. Thiessen and R. Köppen (Z. anorg. Chem., 1931, 200, 18—22; cf. A., 1930, 559).—The conditions for obtaining well-defined cryst. hydrates of Fe_2O_3 are discussed. By slow hydrolysis of a boiling dil. solution of $Fe(OEt)_3$ in abs. EtOH cryst. $Fe_2O_3,4H_2O$ has been obtained. The lattice is probably cubic, *d* 3·0—3·1. O. J. Walker.

Metallic carbonyls. IX. Reactions of iron tetracarbonyl. W. Hieber and H. Vetter (Ber., 1931, 64, [*B*], 2340—2346; cf. A., 1930, 1008).—$Fe(CO)_4$ is converted by EtOH into $Fe(CO)_5$ and the *substance* $2Fe(CO)_3,EtOH$, which appears to be dissociated in freezing H_2O into $Fe(CO)_3$ (or its hydrate) and $Fe(CO)_3,EtOH$. Higher alcohols, glycol, etc. appear to yield similar products, but their isolation is complicated by their instability towards heat and the difficult volatility of the reactant. Steam condensed on $Fe(CO)_4$ causes volatilisation of $Fe(CO)_5$ and formation of a red solution probably containing small amounts of $Fe(CO)_3$ hydrate. MeCN and $Fe(CO)_4$ afford $Fe(CO)_5$ and $2Fe(CO)_3,MeCN$, but the change is not accompanied by marked evolution of CO. Decomp. of the tricarbonyl derivatives by acids occurs essentially according to the schemes, $2Fe(CO)_3+2H^++Fe^{++}+2CO+H_2+Fe(CO)_4$ (polymerised) and $4Fe(CO)_3+2H^+=Fe^{++}+[Fe(CO)_4]_3+H_2$, which are seldom ideally fulfilled. Reactions depend greatly on the nature, temp., and concentration of acid and are complicated by disproportionations, $3Fe(CO)_3 = Fe(CO)_5 + 2Fe(CO)_2$ or $2Fe(CO)_3 + 2H^+ = Fe^{++} + Fe(CO)_5 + CO + H_2$. H. WREN.

Complex ruthenium compounds. R. CHARONNAT (Ann. Chim., 1931, [x], 16, 5—121).—The solution obtained by the action of HCl on RuO_4 contains principally $RuCl_4$, but after boiling with EtOH the *compound* $RuCl_3,HCl,2H_2O$, which exists in two isomeric forms, one red and the other green, separates, both forms yielding $RuCl_3$ when heated. By interaction of the red compound with NH_2Me,HCl the *compound* $[Ru(H_2O)_2Cl_4](H{\cdot}NH_2Me)$ (red) may be obtained. *Pyridinium chlororuthenite*, $(C_5H_5NH)_3RuCl_3,H_2O$ (red), has been prepared in the same way as the NH_4 salt (cf. A., 1925, ii, 586). The only satisfactory method of preparing K_2RuCl_5 is to heat $K_2Ru(H_2O)Cl_5$ or K_2RuCl_6. This compound takes up Cl_2, with formation of K_2RuCl_6, whereas with Br progressive substitution of Cl and finally destruction of the mol. occur. The following complex *compounds* of Ru chlorides with ethylenediamine and pyridine have been prepared: $[Ru(H_2O)Cl_7]H_4,en_2$ (red), $[Ru(OH)Cl_7]H_4,en_2$ (brown), $[RuC_5H_5NCl_5]H_2,(C_5H_5N)_2$ (brown), $[Ru(C_5H_5N)_2Cl_4]$, and $[Ru(C_5H_5N)_2Cl_4]H(C_5H_5N)$ (yellow), and also the *compound* $[Ru(NO)Cl_5]H_2,en$ (red). R. CUTHILL.

Reaction between alkali phosphates and chloroplatinic acid in ammoniacal solution. B. E. DIXON (J.C.S., 1931, 2306—2313).—By reaction of Na_2HPO_4 with $(NH_4)_2PtCl_6$ in presence of excess of aq. NH_3, using very dil. reagents at room temp., the *compound* $H_2PO_4[Pt(NH_3)_4Cl(NH_2)]OH$ is obtained in a pure state. The action of H_3PO_4 gives the *compound* $[Pt(NH_3)_4Cl(NH_2)](H_2PO_4)_2$, evidence of the basicities of the two salts and of the nature of the phosphate radicals being obtained by titrations, using methyl-orange and phenolphthalein in presence of $CaCl_2$. The former compound furnishes a concrete example of the type of intermediate basic salt assumed in the formation and hydrolysis of the chloroamidotetrammine series. The behaviour of Pt dissolved from Pt apparatus during the course of silicate analyses is discussed with special reference to its co-precipitation with $MgNH_4PO_4$. In the accurate analysis of high Fe- and Cr-bearing silicate rocks and minerals it is advisable to separate the Pt at an early stage. E. S. HEDGES.

Sensitivity of chemical precipitation reactions. I. M. KOLTHOFF (Z. anal. Chem., 1931, 86, 34—40).—A discussion of the relations between solubility, particle size, turbidity, and the sensitivity of nephelometric tests. E. S. HEDGES.

Nephelometric titrations. IV. Effect of shaking and cooling the analytical systems. C. R. JOHNSON (J. Physical Chem., 1931, 35, 2581—2584; cf. this vol., 1141).—The effect of shaking and cooling on typical systems used in at. wt. determinations is to leave an excess of chloride in the supernatant liquid, yielding a low val. for the calc. at. wt. L. S. THEOBALD.

Determinations with the centrifuge and factors affecting them. H. S. GREENE (J. Amer. Chem. Soc., 1931, 53, 3275—3284; cf. A., 1922, ii, 309).—Under const. conditions of rate and duration of centrifuging, temp. and rate of precipitation, concentration of solutions, time of keeping before centrifuging, and nature of precipitant, the relation between wt. and vol. of $BaSO_4$ is reproducible to within 1% for appropriate quantities. A similar degree of accuracy is approached in determining S in steel, CaC_2O_4, $Al(OH)_3$, Ni dimethylglyoxime, and nitron nitrate, provided the bore of the capillary is varied between 1·1 mm. for dense crystalline ppts. and 10 mm. for gelatinous ppts. J. G. A. GRIFFITHS.

Systematic analysis of the anions. A. B. DUSCHAK and M. C. SNEED (J. Chem. Educ., 1931, 8, 1177—1186). CHEMICAL ABSTRACTS.

Absorption and separation of hydrogen by means of silver permanganate solutions. F. HEIN and W. DANIEL (Chem. Fabr., 1931, 381—383).—The absorbent consists of 300 c.c. of saturated $KMnO_4$ solution to which are added 40·6 g. of $AgNO_3$ and 20 g. of silvered SiO_2 gel. Absorption of H_2 is complete within 6—10 min., but CH_4 and C_2H_6 are not appreciably absorbed in 90 min. Excellent results are obtained for the analysis of coal gas if CO and unsaturated hydrocarbons are removed before determination of the H_2. A special type of pipette and a mechanical shaking device are described. H. F. GILLBE.

Micro-acidimetric studies. III. Micro-titration of strong acids. J. MIKA (Z. anal. Chem., 1931, 86, 54—61).—The errors involved are discussed and a procedure is recommended. E. S. HEDGES.

Oxidation–reduction indicators of the triarylmethane group. J. KNOP (Z. anal. Chem., 1931, 85, 253—275).—The following 12 indicators of this group give satisfactory reversible colour changes in oxidation–reduction titrations and may be used for $KMnO_4$ titrations without making allowance for the quantity of indicator used: acronol brilliant-blue, cyanin B, cyanol fast-green 2G, erioglaucin A, erio-green B, patent-blue A, setocyanin O, setoglaucin O, setopalin conc., xylene-blue AS, xylene-blue VS and xylene-cyanol FF. For the titration of Fe with $KMnO_4$ after reduction with $SnCl_2$ in HCl setoglaucin is recommended; $MnSO_4$ should be added and Ni and Co do not interfere. The colour change with all the above indicators takes place within the oxidation–reduction potential range of +0·71 to 0·81 volt, *i.e.*, very close to the equivalence point of the $Fe^{\cdot\cdot}$–$KMnO_4$ titration, the potential of which is 0·73 volt. A. R. POWELL.

Determination of water content by distillation with liquids less volatile than water. I. Tetrachloroethane. H. LUNDIN (Chem.-Ztg., 1931, 55, 762—763).—An apparatus and procedure for the determination of small or large amounts of H_2O in various materials by distilling with $C_2H_2Cl_4$ are described. Experiments with yeast gave results which were independent of the distillation time, provided this exceeded 25 min. E. S. HEDGES.

Conductometric studies. I. Influence of small amounts of carbonic acid on the conductometric titration of acids and alkalis and its elimination. W. POETHKE (Z. anal. Chem., 1931, 86, 45—54).—In the conductometric titration of strong acids with a strong base a small amount of carbonate in the base may generally be neglected, but when a strong base is titrated with a strong acid in an open vessel the CO_2 taken up from the air produces a measurable error. The smallest amount of CO_2 affects the titration of a strong base with a weak acid or a weak base with a strong acid. A procedure for determining the true end-point by taking a large no. of readings in its neighbourhood and extrapolating is described; this is more convenient than attempting the complete exclusion of CO_2. E. S. Hedges.

Volumetric determination of water. J. Lindner (Z. anal. Chem., 1931, **86**, 141—153).—Improvements in apparatus and manipulation for the determination of H_2O by decomp. of $C_{10}H_7{\cdot}POCl_2$ (A., 1925, ii, 901) are described. The modified procedure, applied to the determination of H in an org. substance, gives a mean error of only 0·05% on a 1 mg. sample. E. S. Hedges.

Halogen determinations by Gasparini's method. IV. K. Heller [with E. Franke and G. Peucker] (Z. anal. Chem., 1931, **86**, 25—29; cf. A., 1929, 528, 1158).—Gasparini's method (A., 1907, ii, 650) is not recommended for org. halogen compounds which sublime or are decomposed with difficulty by electrolysis. After electrolytic oxidation of the org. substance in H_2SO_4–HNO_3 mixture, Cl can be determined gravimetrically. Illari's method (A., 1930, 101) is inaccurate. E. S. Hedges.

Determination of chlorides with the highest accuracy. A. B. Keys (J.C.S., 1931, 2440—2447).—The method recommended is essentially a small-vol. Volhard titration, using only 1—2% excess of $AgNO_3$, all operations being carried out in a single vessel. Only 1—2 c.c. of solution are required and the abs. sensitivity is of the order of 0·001 mg. Cl. A scheme for routine chloride determinations is given. E. S. Hedges.

Determination of traces of chloride in bromides. I. E. Orlov.—See B., 1931, 971.

Determination of traces of bromide in concentrated chloride solutions by a single titration. M. Bobtelsky and R. Rosovskaja-Rossienskaja (Z. anorg. Chem., 1931, **199**, 283—288).—The method is based on oxidation of the mixture by H_2CrO_4–H_2SO_4 at room temp. and under specified conditions, whereby Br alone is evolved. $MgCl_2$ behaves anomalously and if it is present the total halogen evolved is determined and the amount of Cl, which is proportional to the $MgCl_2$ concentration, is subtracted; Mn should be absent. HCl and $FeCl_3$ are not decomposed at concentrations below $4N$. In presence of Ca an excess of K_2SO_4 must be added. H. F. Gillbe.

Determination of small amounts of bromide in chloride. B. S. Evans.—See B., 1931, 1009.

Separation and detection of halogen ions involving the use of chloramine-*T*. E. M. Gerstenzang (J. Chem. Educ., 1931, 8, 1187—1189). Chemical Abstracts.

Determination of fluorine as calcium fluoride by the method of Berzelius. M. Karasiński (Bull. Acad. Polonaise, 1931, **A**, 143—147).—Berzelius' method has been modified by discontinuing the use of AcOH in the analysis since CaF_2 is fairly soluble in AcOH. CaF_2 is precipitated alone with $CaCO_3$ and residues in the filtrate are worked up. The gelatinous ppt. of CaF_2 is changed by roasting into a cryst. form which facilitates filtration. The cryst. CaF_2 is less sol. in H_2O. The modified method is more accurate than the old method. W. R. Angus.

Determination of oxygen by the polarographic method. J. Heyrovský (Arh. Hemiju, 1931, **5**, 162—173).—The content of electro-reducible substances in solutions can be determined from the current–voltage curves obtained in electrolysis with a dropping Hg cathode and a large Hg anode. When solutions exposed to air are examined, the curves exhibit two summits, corresponding with reduction of O_2 first to H_2O_2 and then to H_2O. The method is applicable to the determination of peroxides and atm. O_2, in the absence of ions of noble metals, which should previously be removed by alkali hydroxides. R. Truszkowski.

Determination of oxidising agents by the aid of the residual current. G. Tammann and H. Thiele (Pflüger's Archiv, 1931, **226**, 694—696; Chem. Zentr., 1931, i, 2785).—O_2 can be detected, and H_2O_2 determined approx., by measurement of the residual current, using a Pt wire anode and platinised Pt foil cathode, and stirring in a closed glass vessel. Blood shaken with O_2 gives a max. residual current of 0·002 milliamp.; in venous blood it is less than 0·0001 milliamp. A. A. Eldridge.

Determination of thiocyanate using the step-photometer. C. Urbach (Biochem. Z., 1931, **237**, 189—198).—$FeCl_3$–HNO_3 reagent is added to the suitably-diluted fluid, and the extinction coeff. is determined and compared with standard extinction coeff.–concentration curves. F. O. Howitt.

Determination of nitrogen. W. Shimidzu (J. Imp. Fisheries Inst. Japan, 1931, **26**, 35—39).—NH_3 is distilled over with steam and the residual liquid removed by passing steam in the reverse direction. Chemical Abstracts.

Determination of nitrates by the brucine method. A. Byčichyn (Chem. Listy, 1931, **25**, 302—303).—1 c.c. of 2% brucine in $CHCl_3$ and 21 c.c. of conc. H_2SO_4 are added to 10 c.c. of the H_2O, and HNO_3 is determined by comparison of the coloration produced with a standard. R. Truszkowski.

Determination of nitrates by Grandval and Lajoux' method. B. A. Skopintzev (Z. anal. Chem., 1931, **85**, 244—252; cf. A., 1885, 1093).—The colorimetric determination of NO_3' with phenoldisulphonic acid gives good results only when the solution contains less than the equiv. of 0·5 c.c. of $0{\cdot}1N$-free alkali or alkali carbonate. NH_4 salts should be destroyed by adding the equiv. NaOH prior to evaporation. Contamination with SO_2 from the burner gases leads to loss of NO_3' during evaporation. The amount of K_2SO_4 in each test should not exceed 80 mg. A. R. Powell.

Determination of nitrate by electrolytic reduction. L. Szebellédy and B. M. Schall (Z.

anal. Chem., 1931, 86, 127—134).—NO_3' can be determined by electrolytic reduction at a Cu or Ni cathode in presence of H_3BO_3, followed by direct titration of the NH_3. Some improvements in manipulation are described. The fact that Ni cathodes in addition to Cu cause quant. reduction to NH_3 indicates that the process is not a catalytic effect of the $Cu^{\cdot}$ ion.

E. S. Hedges.

Reduction of phosphomolybdic acid by methyl-*p*-aminophenol and its use in the determination of phosphorus. S. L. Lieboff (J. Lab. Clin. Med., 1931, 16, 495—499).—The reducing agent is satisfactory, and is stable in presence of Na_2SO_3.

Chemical Abstracts.

Determination of phosphoric acid by the filtration method. H. T. Bucherer and F. W. Meier (Z. anal. Chem., 1931, 85, 331—344).—Precipitation of H_3PO_4 as $Pb_3(PO_4)_2$ or as $(NH_4)_3PO_4,12MoO_3$ is untrustworthy for its gravimetric determination. A hydroxyquinoline molybdate method which is capable of very high accuracy is described. This method is also applicable to the determination of citric acid or citrate-sol. P_2O_5 in fertilisers. J. W. Smith.

Determination of small quantities of phosphate. S. G. Clarke.—See B., 1931, 928.

Micro-analytical determination of phosphoric acid by the molybdate method. H. Thurnwald and A. A. Benedetti-Pichler (Z. anal. Chem., 1931, 86, 41—45).—The phosphomolybdate ppt. is dissolved in aq. NH_3, $MgCl_2$ is added to the boiling solution, and the ppt. is weighed as $MgNH_4PO_4,6H_2O$. The greatest deviation from the theoretical val. was 0·07%. E. S. Hedges.

Use of iodide catalyst in the titration of arsenious acid and permanganate. R. Lang (Z. anal. Chem., 1931, 85, 176—180).—For a smooth functioning of the KI catalyst in titrations of As_2O_3 with $KMnO_4$ the solution should be at least 0·5*N* with respect to $H^{\cdot}$ and at least 0·1*N* with respect to Cl'. Increase of either concentration separately has no effect, but increase of both simultaneously above the equiv. of 1·3*N*-HCl retards the reaction. HCN and $HgCl_2$ act as catalyst poisons and the presence of F', PO_3', and WO_3'' which form complexes with $Mn^{\cdot\cdot\cdot}$ interferes with the reaction by retarding the rate of reduction of $Mn^{\cdot\cdot\cdot}$. A. R. Powell.

Determination of silicon in ferrosilicon. W. Hartmann.—See B., 1931, 976.

Decomposition flask for the determination of carbon by the wet method. H. Engel (Z. anal. Chem., 1931, 85, 242—243).—The flask has a wide neck through which is passed a H_2O-cooled condenser extending just below the bottom of the neck; the condenser carries a removable glass apparatus through which air is passed into the flask through a tube passing down the centre of the condenser and reaching to the bottom of the flask. The air is freed from CO_2 by passage through 50% KOH solution contained in the inner tube of the apparatus above the condenser. All joints are ground glass. A. R. Powell.

Determination of carbon monoxide. H. A. J. Pieters (Z. anal. Chem., 1931, 85, 50—60).—In admixture with air CO may be determined by measuring the decrease in vol. when the gases are bubbled through a 10% suspension of I_2O_5 in oleum (25% SO_3). If CH_4 or H_2 is present the oleum should contain only 10% SO_3 and 15—20 min. are necessary for removal of CO. Traces of CO in air may be determined colorimetrically by a method based on the green colour produced in the above reaction using oleum with 25% SO_3. In gases free from O_2 CO may be determined by adding an excess of H_2 and passing the mixture at 250° over asbestos impregnated with reduced Ni, whereby CO is reduced to CH_4 with a reduction in vol. equal to 3 times the vol. of the CO; the method is applicable to the determination of CO in water-gas and in coal gas after the CO_2, O_2, and unsaturated hydrocarbons have been removed in the usual way. A modification of Nicloux' blood method is also described.

A. R. Powell.

Determination of carbon monoxide in admixture with air. H. A. J. Pieters (Z. anal. Chem., 1931, 85, 113—117).—CO is completely oxidised to CO_2 at room temp. by Ag_2O saturated with CO_2 and by MnO_2 prepared by reducing a solution of NH_4MnO_4 with MeOH and drying the ppt. at 120°. The MnO_2 can also be prepared by reducing $HMnO_4$ with $H_2C_2O_4$ or $MnSO_4$. CO is also quantitatively oxidised to CO_2 at 150° by CuO deposited on quartz.

A. R. Powell.

Helium. X. Determination of traces of radium. F. Paneth and W. Koeck (Z. physikal. Chem., Bodenstein Festband, 1931, 145—161).—The method described permits the determination of quantities of Ra-Em of the order of 10^{-13} Curie with an error of about 20%; it is applicable to a few g. of mineral or ferrous meteorite, and in combination with the method described previously for the determination of the He content of the latter may be employed to calculate the age of the meteorite. The basis of the determination is the differential measurement of the charge in two ionisation chambers, one of which contains the emanation.

H. F. Gillbe.

Determination of potassium together with sodium and magnesium. V. K. Fedorenko (Ukrain. Chem. J., 1931, 6, [Sci.], 105—116).—The material is ignited to remove NH_4 salts, if present; the residue is dissolved in 25% H_2SO_4 at 100° (5 c.c. per g. of substance), and digested 1·5—2 hr., in order to expel HCl, when excess of 4% $Ba(OH)_2$ is added (100 c.c. per 5 c.c. of acid+5 c.c. per 0·1 g. of substance). The solution is boiled for 15 min., CO_2 is passed for 5—10 min., and the filtrate and washings are evaporated to a small vol. The solution is titrated on the water-bath with 0·1*N*-H_2SO_4 with Me-red indicator, acid being added as the red coloration fades, until a dry, red residue remains. This is extracted with H_2O, and the solution is filtered, the residue being washed free from SO_4''. The filtrate, containing K, Na, and Mg sulphates, is evaporated to dryness, and the residue is dried to const. wt. and dissolved in 300 c.c. of H_2O. SO_4'' is determined in one 100-c.c. portion and Mg as pyrophosphate in another. The wt. of residue less the calc. val. gives the sum of K and Na sulphates, from the SO_3 content of which the proportion of K to Na is calc. An accuracy of 3% is obtained. R. Truszkowski.

Determination of potassium and nitrite in very dilute solution. R. A. Herzner (Biochem. Z., 1931, 237, 129—132).—The coloration produced by sulphanilic acid and α-naphthylamine in AcOH solution in presence of nitrite is applied to the determination of nitrite directly and to that of K following precipitation as K Na cobaltinitrite.

F. O. Howitt.

Colorimetric micro-determination of potassium. J. Fischer (Biochem. Z., 1931, 238, 148—161).—The K in 1 c.c. of neutral or slightly acid solution is precipitated with 1 c.c. of freshly prepared 10% solution of purified stable $Na_3Co(NO_2)_6$. After keeping for 5 hr. in the cold the ppt. is washed free from nitrite with 96% EtOH and dissolved in hot H_2O. The nitrite content (and hence also the K content) of the solution is then determined colorimetrically with the help of Riegler's reagent (A., 1897, ii, 464). From 0·001 to 1·0 mg. of K can thus be determined (error ±3%). Salts of NH_4, Rb, Cs, Ba, Ag, Pb, and Hg^I and also large amounts of H_3PO_4 interfere with the precipitation. If NH_4 salts are present the solution is boiled with dil. NaOH and then neutralised with dil. H_2SO_4.

W. McCartney.

Volumetric method of determining sodium. J. T. Dobbins and R. M. Byrd (J. Amer. Chem. Soc., 1931, 53, 3288—3291).—20—25 mg. of Na in 2—3 c.c. of H_2O are precipitated as Na Zn uranyl acetate by adding 20—30 c.c. of reagent (85 g. of uranyl acetate in 50 c.c. of AcOH+400 c.c. H_2O mixed with 200 g. of $Zn(OAc)_2$ in 25 c.c. of AcOH+250 c.c. of H_2O). The liquid is kept in ice for 1 hr. and the ppt. is then dissolved in 100 c.c. of H_2O and titrated with NaOH, the end-point being determined at the b. p. by means of phenolphthalein. The results agree with the equation $NaZn(UO_2)_3(OAc)_9+10NaOH=9NaOAc+Na_2U_2O_7+ZnUO_4+5H_2O$.

J. G. A. Griffiths.

Determination of cæsium and rubidium, especially in mineral waters. L. Fresenius (Z. anal. Chem., 1931, 86, 182—190).—Details are given of a spectral method and a gravimetric method for determining small quantities of Cs and Rb in presence of complex mixtures of other salts. E. S. Hedges.

Accurate titration. II. W. Ponndorf (Z. anal. Chem., 1931, 85, 1—44; cf. this vol., 1022).—Details are given of methods for the standardisation, with an error of 0·01—0·02%, of $AgNO_3$ solutions with NaCl, of KI solutions with $AgNO_3$, and of $Na_2S_2O_3$ solutions with KI, I, or $K_2Cr_2O_7$; possible sources of error and methods for avoiding these are also discussed. 0·1*N* solutions of $Na_2S_2O_3$ which has been twice recryst. from H_2O containing a small quantity of NaOH undergo a slow decrease in titre which is linearly proportional to their age when stored in amber bottles in the dark. A. R. Powell.

Determination of silver in colloids and organic compounds. V. R. Chertok (Farm. Zhur., 1929, 507—509).—Korndörfer's method (Apoth.-Ztg., 1914, 29, 901) is one of the simplest giving accurate results.

Chemical Abstracts.

Modifications of the micro-determination of calcium and potassium. M. Mousseron (Bull. Soc. Chim. biol., 1931, 13, 831—834; cf. A., 1930, 1011).—A colorimetric method based on the production of a green colour when $CaK_2Ni(NO_2)_6$ is treated with an aq. solution of antipyrine is described.

C. C. N. Vass.

Determination of calcium as oxalate. L. Velluz and R. Deschaseaux (Bull. Soc. Chim. biol., 1931, 13, 797—808).—The precipitated oxalate is washed first with an EtOH–Et_2O mixture, finally with Et_2O, dried, suspended in 5% H_2SO_4, and treated with cold 0·066*N*-$KMnO_4$, the excess being determined iodometrically after 5 min. This procedure allows the determination of 0·1—0·5 mg. of Ca with an error less than 3% or, in the presence of Mg, less than 5%.

C. C. N. Vass.

Determination of calcium with picrolonic acid. R. Dvorzak and W. Reich-Rohrwig (Z. anal. Chem., 1931, 86, 98—113).—Ca may be determined very accurately as picrolonate, the ppt. $Ca(C_{10}H_7O_5N_4)_2,8H_2O$ containing only 5·64% Ca and crystallising readily. The procedure is suitable for micro-determinations, giving an error of only 0·01 mg. with 2 mg. of Ca. A quant. separation from Mg can be effected, provided that the ratio Ca : Mg does not exceed 1 : 10. The method is particularly suitable for determining the hardness of potable and industrial waters.

E. S. Hedges.

Nephelometric determination of calcium. A. I. Polinkovski (Trans. State Inst. Test. Building Mat., 1929, No. 27, 11—26).—CaC_2O_4 is unsuitable for nephelometry; NH_3, NH_4 salts, excess of precipitant, and manner of introduction and mixing greatly affect the character of the ppt. Chemical Abstracts.

Determination of strontium in minerals and rocks. W. Noll (Z. anorg. Chem., 1931, 199, 193—208).—Various methods of determination of Sr, and especially of the separation from Ca, are reviewed. The usual method, of precipitation with Ca as oxalate and separation by EtOH and Et_2O, yields low results in presence of much Ca; *e.g.*, with a Sr : Ca ratio of 1 : 100 only about 60% of the Sr is recovered. The results are considerably improved if completely anhyd. EtOH and Et_2O are used, but the HNO_3 separation of Rawson is preferable. Sr may be precipitated quantitatively with $PbCrO_4$ from neutral solution, but separation of Sr and Ca cannot be effected by this method since the ppt. is insufficiently stable in slightly acid solution. H. F. Gillbe.

"Oxinate" precipitations. I. Magnesium Precipitation; titration of residue. F. L. Hahn (Z. anal. Chem., 1931, 86, 153—157; cf. A., 1927, 637).—In presence of NH_4Cl, aq. NH_3, and $COMe_2$, Mg is precipitated by 8-hydroxyquinoline. The excess of 8-hydroxyquinoline is determined by adding standard $KBrO_3$–KBr mixture and titrating back with KI and $Na_2S_2O_3$. Mg combines with 2 mols. of 8-hydroxyquinoline. E. S. Hedges.

Determination of magnesium as pyrophosphate. V. Njegovan and V. Marjanović (Arh. Hemiju, 1931, 5, 243—252).—The solution containing 0·2—0·3 mg. MgO is evaporated to dryness, 5 c.c. of conc. H_2SO_4 are added, and the vessel is heated at 100° to eliminate HCl and $H_2C_2O_4$, if present. On cooling, 15—20 c.c. of saturated aq. Na_2HPO_4 are added, and a few drops of phenolphthalein. A mixture of equal vols. of 25% NH_4NO_3 and conc. NH_3 solutions is added to alkalinity, when 150—200 c.c. of H_2O are added, and the solution is maintained for 1 hr. at 100°. On cooling, the ppt. is washed with 2·5% aq. NH_3 and ignited to const. wt. The mean error is 3—4%. R. TRUSZKOWSKI.

Potentiometric titration of zinc chloride solutions. M. PRYTZ (Z. anorg. Chem., 1931, **200**, 133—143).—From the potentiometric titration of aq. $ZnCl_2$ with NaOH by means of a Pt electrode at 25° the val. $1·53\times10^{-10}$ has been obtained for the equilibrium const. of the reaction $Zn^{\cdot\cdot}+H_2O=ZnOH^{\cdot}+H^{\cdot}$ in terms of activities, the value in terms of concentrations being $1·08\times10^{-9}$. The solubility product of $Zn(OH)_2$ is calc. to be $6·28\times10^{-18}$ in terms of activities, and $1·29\times10^{-17}$ in terms of concentrations. The point of inflexion on the titration curve occurs before 2 equivs. of NaOH have been added.
R. CUTHILL.

Determination of zinc as oxide, silicate, ferrite, sulphate, and sulphide. II. V. TAFEL and G. SILLE (Z. angew. Chem., 1931, **44**, 792—793).—Nissenson's method for the determination of Zn yields good results with pure Zn ferrite, but will not effect a quant. separation of ZnO,Fe_2O_3 and ZnS, as part of the latter dissolves also. The NaOH method previously described (A., 1930, 1545) is not entirely satisfactory for Zn residues, especially if org. materials are present, and has therefore been modified. The residue is mixed with NaOH and covered with EtOH in a crucible. By careful heating frothing can be avoided, and after being heated at 300° the melt may be analysed for Zn and Fe in the usual way. H. F. GILLBE.

Micro-determination of zinc. M. MOUSSERON and (MME.) M. MOUSSERON (Bull. Soc. Chim. biol., 1931, **13**, 821—830).—Zn is precipitated at 50° in presence of KNO_3 with an excess of $K_4Fe(CN)_6$ as $K_2ZnFe(CN)_6,Zn_2Fe(CN)_6$ which when boiled with aq. NH_3 yields NH_4CN which is titrated with $AgNO_3$ solution. Details are given which enable this technique to be employed in presence of Si, Co, Cu, Fe, Mn, and Al. C. C. N. VASS.

Potentiometric titration of zinc with potassium ferrocyanide. E. BRENNECKE (Z. anal. Chem., 1931, **86**, 175—182).—Potentiometric titration of Zn with $K_3Fe(CN)_6$ at 70° gives results which are uniformly low by 0·98%. The error is reduced to −0·73% by adding most of the reagent in the cold and finishing the titration at 65—75°. Titration of $K_4Fe(CN)_6$ with Zn salts gives an error of only −0·46%.
E. S. HEDGES.

Solid electrodes in electrometric analysis with precipitation reactions. J. A. ATANASIU and A. J. VELCULESCO (Z. anal. Chem., 1931, **85**, 120—138).—The value of two solid electrodes instead of the usual Pt–*N*-$HgCl_2$ system for electrometric analysis has been studied in cases involving titrations with $K_4Fe(CN)_6$ and with $AgNO_3$. The combinations Pt–Ni and Pt–SiC give very sharp potential changes at the end-point of all titrations with $K_4Fe(CN)_6$, whether in neutral or feebly acid solutions. Pt–platinised Pt, Pt–graphite, and Pt–Ta are suitable for titrations of Zn, Cd, Pb, Cu, Ce, Th, La, Ni, and Co, but not of Ag, with $K_4Fe(CN)_6$. For titrations of halogen or SCN ions with $AgNO_3$ only the systems Pt–Ni, Pt–SiC, and Pt–graphite give accurate results.
A. R. POWELL.

Quantitative separation of lead and iron. H. FUNK and O. VON ZUR-MÜHLEN (Z. anal. Chem., 1931, **85**, 435—438).—The Pb is precipitated as $PbCrO_4$ from the hot solution in presence of AcOH, and the Fe determined in the filtrate. R. CUTHILL.

Analysis of lead ores containing barium. L. GUZELJ.—See B., 1931, 978.

Qualitative analysis of small amounts of cations. A. SCHEINKMANN (Z. anal. Chem., 1931, **85**, 344—346).—The washed group I ppt. is treated with NH_4OAc to remove Pb, and after dissolving the AgCl in aq. NH_3, NH_4OAc is again poured through the filter-paper to dissolve the $HgClNH_2$. NH_4OAc can also be used to dissolve the $HgClNH_2$ and $Pb(OH)_2$ in group IIa. For the detection of Sb and Sn in group IIb, after dissolving the sulphides of these metals in HCl, a little $KMnO_4$ is added. Decolorisation shows the presence of $SbCl_3$ or $SnCl_2$. These are oxidised completely and then starch and aq. KI added. $SbCl_5$ is then reduced with liberation of I, but not $SnCl_4$. Sn in presence of Sb can be confirmed by adding a little Fe powder, warming, filtering, and adding a drop of $Hg_2(NO_3)_2$ and excess of NH_4OAc, when the grey ppt. is formed without the white ppt. normally obtained with Sb present. J. W. SMITH.

Separation and determination of copper and zinc. H. BRINTZINGER (Z. anal. Chem., 1931, **86**, 157—159).—Cu is determined by the KI and $Na_2S_2O_3$ method. The filtrate from the CuI is treated with NH_3 and AcOH and Zn is precipitated as $ZnNH_4PO_4$. The procedure is suitable for the analysis of Cu–Zn alloys. These are preferably dissolved in AcOH or H_2SO_4 with the addition of H_2O_2, which can be removed by boiling before adding KI. Dissolution in HNO_3 is not recommended. E. S. HEDGES.

Determination of metals in solution by means of their spark spectra. F. TWYMAN and C. S. HITCHEN (Proc. Roy. Soc., 1931, **A**, **133**, 72—92).—Details of the sparking vessel, the spectrographs, and the photometric apparatus are given. Experiments were carried out with chlorides of Cu, Zn, Bi, Pb, Ni, and Co in HCl solution, over a concentration range of 0·01—1·00%. The results are given in the form of curves connecting lengths of spectral lines with percentages of metals. It is claimed that the method offers as many advantages for the analysis of solutions of metals for minor constituents as those realised in the spectrographic analysis of alloys, and that the accuracy as regards amounts up to 0·50% equals that obtained by ordinary chemical methods. For percentages lower than 0·5, the spectrographic methods could usually be substituted with advantage for the chemical. L. L. BIRCUMSHAW.

Mercury ammonium derivatives in quantitative analysis. B. ŠOLAJA and V. MATOVINOVIĆ (Arh. Hemiju, 1931, **5**, 232—235).—$Fe^{\cdot\cdot\cdot}$ and $Co^{\cdot\cdot\cdot}$ can be quantitatively separated by double precipitation with $HgNH_2Cl$ in presence of NH_4Cl, or by single precipitation with $C_5H_5N,HgCl_2$ in presence of NH_4Cl.
R. TRUSZKOWSKI.

Determinations and separations of the cations of the hydrogen sulphide group. P. WENGER and C. CIMERMAN (Helv. Chim. Acta, 1931, **14**, 718—743).—A crit. study. N. H. HARTSHORNE.

Determination of the basicity relationships of samarium and gadolinium by quantitative X-ray analysis. P. GÜNTHER, A. KOTOVSKI, and H. LEHL (Z. anorg. Chem., 1931, **200**, 287—304).—Quant. X-ray analysis of rare-earth mixtures by comparison of the true intensities of the $L\alpha_1$ lines is possible in certain cases if the intensity is regarded as proportional to the at. concentration. Accurate analyses are possible with Pr and Nd mixtures, but with mixtures containing Ce the results are less satisfactory. X-Ray analysis of mixtures of Sm and Gd fractionated by aq. NH_3 shows that the basicities of these elements differ very little, that of Sm being the greater. H. F. GILLBE.

Determination of aluminium sulphate and sodium acetate. V. P. ZEMLIANITSIN (J. Chem. Ind. Russ., 1931, **8**, 629).—The aq. solution of $Al_2(SO_4)_3$ is filtered from insol. impurities, lime water is added, and excess of the latter is determined by titration with $0{\cdot}1N$-HCl. The no. of c.c. of lime water used multiplied by 0·000747 gives the Al_2O_3 content in g. NaOAc (2 g.) is ignited in a Pt crucible, and the Na_2CO_3 so formed is dissolved in H_2O and titrated with N-HCl. R. TRUSZKOWSKI.

Determination of gallium. A. BRUKL (Z. anal. Chem., 1931, **86**, 92—94).—A discussion of methods of procedure. E. S. HEDGES.

Modification of the silver salt–persulphate method for the determination of large quantities of manganese. R. LANG and F. KURTZ (Z. anal. Chem., 1931, **85**, 181—185).—The Mn is oxidised to $KMnO_4$ in boiling N-H_2SO_4 by the addition of 10 g. of HPO_3, 3—5 c.c. of $0{\cdot}1N$-$AgNO_3$, and 2 g. of $K_2S_2O_8$. Boiling is continued for 25 min. to destroy excess of $K_2S_2O_8$ and the cooled solution is titrated with $FeSO_4$ to a pale rose colour ($Mn^{\cdot\cdot\cdot}$ salt), 3 drops of a 1% solution of diphenylamine in H_3PO_4 are added, and titration is continued until the colour changes from violet to yellowish-green. The method is applicable to the determination of Mn in steels. A. R. POWELL.

Manchot's theory of formation of iron peroxide. F. VETTER (Z. anal. Chem., 1931, **86**, 134—140).—Experiments are described which show that the production of Cl_2 in the titration of $Fe^{\cdot\cdot}$ by $KMnO_4$ in presence of HCl is not due to the intermediate formation of a peroxide of Fe. E. S. HEDGES.

Application of hexamethylenetetramine as analytical reagent for the determination of metals of the ammonium [hydroxide] group in presence of manganese, nickel, cobalt, and magnesium. P. RÂY [with A. K. CHATTOPADHYA and D. BHADURI] (Z. anal. Chem., 1931, **86**, 13—24).—Hexamethylenetetramine precipitates quantitatively hydroxides from solutions of $Fe^{\cdot\cdot\cdot}$, Al, $Cr^{\cdot\cdot\cdot}$, Ti, U, Zr, and Th salts, but in presence of NH_4 salts Zn, Mn, Ni, Co, and Mg remain in solution. The procedure permits the quant. separation of Fe from all the metals in the latter group; Al is readily separated from all except Ni, although the separation from large quantities of Zn is incomplete, the separation of Ti is quant. except when large amounts of Zn are present, and the separation of U presents no difficulties. E. S. HEDGES.

Detection of iron. F. FEIGL and H. HAMBURG (Z. anal. Chem., 1931, **86**, 7—13).—2 : 2′-Dipyridyl in slightly acid solution gives a red coloration with $Fe^{\cdot\cdot}$ salts, the limiting concentration being 10^{-8}. Applied as a spot test, $Fe^{\cdot\cdot}$ may be recognised at a limiting concentration of $1{\cdot}66\times10^{-7}$. $Fe^{\cdot\cdot\cdot}$ salts give a yellow coloration which interferes with the test only if the ratio $Fe^{\cdot\cdot\cdot}/Fe^{\cdot\cdot}$ is very high; in such a case KF is added, converting $Fe^{\cdot\cdot\cdot}$ to $[FeF_6]'''$. Special directions are given for the detection of traces of Fe in fluorides, Hg salts, Al_2O_3, pyrolusite, and Ni. E. S. HEDGES.

Micro-titration of iron with permanganate. I. J. KNOP and O. KUBELKOVÁ (Z. anal. Chem., 1931, **85**, 401—428; cf. A., 1929, 670).—By micro-titration with $0{\cdot}001N$-$KMnO_4$, using various $CHPh_3$ dyes as indicators, as little as 0·1 mg. Fe may be determined with a precision of 0·3—0·4%. The titration can be carried out in presence of either H_2SO_4 or HCl, but a considerable excess of $MnSO_4$ should be present. R. CUTHILL.

Determination of iron in presence of manganese by hydrazine hydrate. A. JÍLEK and V. VICOVSKÝ (Coll. Czech. Chem. Comm., 1931, **3**, 379—384).—About 2 g. of NH_4Cl are added to a dil. solution of $Fe^{\cdot\cdot\cdot}$ and $Mn^{\cdot\cdot}$ salts and then dil. aq. NH_3 until the solution turns Me-red to yellow ($p_H=4{\cdot}4$—$6{\cdot}2$). The boiling solution is precipitated by a slight excess of aq. N_2H_4,H_2O (1 : 25) added in one portion. A granular ppt. is obtained which, after further boiling, must be filtered and washed with hot aq. NH_4Cl (1 g. per 100 c.c. and 1 c.c. N_2H_4,H_2O) and then with hot H_2O until the Cl′ is removed, and finally calcined and weighed as Fe_2O_3. The method compares satisfactorily with the determination by hydroxyquinoline or pyridine. The Mn may be determined in the filtrate by the phosphate, hydroxyquinoline, or sulphide method. M. S. BURR.

Polarographic studies with the dropping mercury cathode. XXIII. Simultaneous determination in the groups iron, chromium, aluminium and nickel, cobalt, zinc, manganese. J. PRAJZLER (Coll. Czech. Chem. Comm., 1931, **3**, 406—417).—The height of the "wave" in the current-voltage curve, obtained in the electrolysis, with a dropping Hg cathode, of solutions containing elements of the $(NH_4)_2S$ analytical group in the presence of indifferent salts may be taken as a measure of the concentration of the element and a method for the detection and determination of mixtures is based on it. In the sub-group Fe, Cr, and Al the three metals may be simultaneously determined in solution. The solution must be diluted to 10^{-4}—$10^{-3}M$ and be only slightly acidic. In the sub-group Zn, Ni, Co, and Mn, under similar conditions, Co and Mn may be determined directly, but Zn and Ni deposit together. After the addition of $(NH_4)_2C_2O_4$, however, Ni, Co, and Mn form more stable complexes than Zn. The Zn, in these circumstances, gives an easily measurable wave on the polarographic curve, and can thus be determined directly, Ni being found subsequently by difference. The degree of accuracy depends on the constancy of the height of a wave and the precision of measurement. It is within 5%, the precision remaining the same down to a concentration of $10^{-5}M$.

M. S. BURR.

Detection of cobalt in presence of elements of group III. T. BERSIN (Z. anal. Chem., 1931, 85, 428—433).—The following brown *compounds* have been obtained by interaction in solution of thioglycollanilide with Co^{III}, Ni, and Fe^{II} salts, respectively ($X = S\cdot CH_2\cdot CO\cdot NHPh$) : $CoX_3,4H_2O$, $[Co(S\cdot CH_2\cdot \dot{C}(\dot{O})\colon NPh)_3]Co$, NiX_2, and FeX_2. By means of the precipitation of the first compound as little as $0\cdot5\times10^{-6}$ g. Co may be detected in 5 c.c. of solution, and, as this compound, but not the others, is insol. in dil. acids, Co may be detected in presence of Fe^{II}, Ni, Al, Zn, Cr, and Mn, the sensitivity of the test being, however, diminished by these metals.

R. CUTHILL.

Iodometric determination of chromium and separation from iron and nickel. E. SCHULEK and A. DÓZSA (Z. anal. Chem., 1931, 86, 81—92).—$Cr^{\cdot\cdot\cdot}$ is oxidised to Cr_2O_7'' by means of NaOBr, excess of NaOBr is removed by PhOH, KI is added, and the liberated I titrated with $0\cdot1N$-$Na_2S_2O_3$. If Fe and Ni are present, a single oxidation does not suffice to separate Cr and the process must be repeated according to the amounts present. $Cr(OH)_3$ is readily occluded by $Fe(OH)_3$.

E. S. HEDGES.

Determination of uranous ion in presence of formic acid. C. OUELLET (Helv. Chim. Acta, 1931, 14, 967—971).—The addition of KCl as an antioxidant enables the precipitation and subsequent manipulation of uranous compounds to be carried out in the presence of air without danger of oxidation within 1—2 hr. Uranous salts in presence of HCO_2H may also be titrated with $KMnO_4$ in cold acid solution if only relative vals. are required. The actual results are too high.

F. L. USHER.

Determination of antimony in the presence of tin. D. BARKOVIĆ (Arh. Hemiju, 1931, 5, 236—238).—The mixed Sb and Sn sulphides are dissolved in boiling 20% HCl, and aq. H_2S is added gradually until a slight ppt. forms. The solution is boiled further until the ppt. redissolves and is cooled slowly, when a red ppt. appears in the presence of Sb (min. 0·01 mg. $Sb^{\cdot\cdot\cdot}$). This method allows 1 part of Sb to be detected in the presence of 100 of Sn.

R. TRUSZKOWSKI.

Detection of bismuth. G. LOCHMANN (Z. anal. Chem., 1931, 85, 241—242).—A large drop of 5% KI solution is placed on a piece of thin filter-paper; the hydroxide ppt. to be tested for Bi is dissolved in 10% HNO_3 and 1 drop of the solution is placed in the middle of the KI drop. If Bi is present a black spot surrounded by a yellow circle appears; on washing this spot with hot H_2O the dark centre suddenly turns bright red due to the formation of BiOI.

A. R. POWELL.

Adiabatic calorimetry at high temperatures. W. KANGRO and R. GRAU (Z. physikal. Chem., Bodenstein Festband, 1931, 85—92).—Details are given of the construction and operation of a high-temp. adiabatic calorimeter based on the principle previously described (A., 1928, 729). Measurement of the heat of conversion of opianoximic anhydride into hemipinimide yields 52·5±0·1 kg.-cal. per mol., in close agreement with the val. derived from the heat of combustion of the two compounds, viz. 52·5±0·8 kg.-cal. per mol.

H. F. GILLBE.

Combustion of substances containing chlorine in Berthelot's bomb. L. SMITH [and, in part, E. SCHJÅNBERG] (Svensk Kem. Tidskr., 1931, 43, 213—226).—Errors in the determination of heats of combustion of substances containing Cl by the Berthelot–Matignon method due to the presence of unreduced Cl_2 in the gaseous products are not satisfactorily eliminated by use of As_2O_3. The gaseous phase contains NOCl, Cl_2, and HCl and methods for their determination and the corresponding heat corrections are described. The proportion of Cl_2 decreases as the concentration of the As_2O_3 solution is increased from 0·07 to $0\cdot38N$, and if 99·7 instead of 96% O_2 is used. Addition of increasing amounts of paraffin to the substance causes first an increase and subsequently a decrease in the amount of Cl_2 in the gaseous phase. Correction for liquid products involves the determination of H_3AsO_3 (by $KMnO_4$ titration), total $HCl+HNO_3+As_2O_5$ (by titration with alkali and Me-orange to p_H 4·3), and of Cl′ by Volhard's method. Dissolved Au is determined by precipitation with H_2O_2 in alkaline solution, and Pt by precipitation with H_2S, the amount of these metals (from the bomb) dissolved increasing with increasing Cl content of the substance. An approx. determination of heat tone by this method is described. The use of quartz-wool slightly lowers the water equiv. The action of quartz-wool is not merely acceleration of the reduction of Cl by As_2O_3 since, under the same conditions more of the latter is oxidised when quartz-wool is absent (Cl remains in gas phase) than when it is present (no Cl remaining), but is also due to the sp. action of the moist wool, probably in displacing the equilibrium $2H_2O+2Cl_2 \rightleftharpoons 4HCl+O_2$. Using the above corrections the vals. of the heats of combustion of α- and β-chlorohydrin, αα′- and αβ-dichlorohydrin, and epichlorohydrin are 3641±1·3, 3647·4±2·1, 3152·8±2·2, 3187·9±1·7, and 4532·3±2·2, g.-cal. per g., respectively.

J. W. BAKER.

Use of a hot-cathode helium lamp as a source of monochromatic light for the polariscope. A. ROTHEN (Science, 1931, 74, 204—205).—With the He lamp described, polariscopic measurements can be made to ±0·003° and ±0·002°, respectively, with the yellow and red He lines.

L. S. THEOBALD.

Standardisation of turbidity values in nephelometric determinations. II. Simplified preparation of a turbidity standard. J. A. DE LOUREIRO (Biochem. Z., 1931, 239, 310—313; A., 1930, 1391).—By adapting the instrument used and plotting the curves on exponential paper (since the changes conform to the exponential law) the procedure previously described is improved and simplified.

W. MCCARTNEY.

Comparative spectrophotometric measurements. M. BARNARD and P. MCMICHAEL (J. Opt.

Soc. Amer., 1931, **21**, 588—614).—The American Photoelectric Corporation spectrophotometer is described. Data obtained with it are compared with the findings of the Bureau of Standards. A discussion is appended. J. Lewkowitsch.

Spectrophotometry. K. S. Gibson (J. Opt. Soc. Amer., 1931, **21**, 564—587).—The methods and apparatus in use at the U.S. Bureau of Standards are described in detail. The degree of agreement of visual, photo- and thermo-electric methods is illustrated. J. Lewkowitsch.

Applicability of photo-electric cells to colorimetry. H. E. Ives and E. F. Kingsbury (J. Opt. Soc. Amer., 1931, **21**, 541—563).—The accuracy and reproducibility of various types of photo-electric cell have been examined. Precision is obtainable only when a substitution method is used, as in visual photometry. J. Lewkowitsch.

Neutral ultra-violet lighting in investigation of structure. H. Langenbruch (Chem.-Ztg., 1931, **55**, 761—762)—A vertical illuminator has been constructed for ultra-violet photography. The "neutral" effect of this method of lighting is especially useful in forensic investigations such as the examination of paint films on metals, the effect obtained being independent of the direction of spreading the paint. E. S. Hedges.

Observation of striæ in chemical processes. III. Observation with the unaided eye ("visual method"). H. Alber and M. von Renzenberg (Z. anal. Chem., 1931, **86**, 114—127; cf. A., 1929, 24).—A simple method described for the observation of striæ in liquids is sensitive to a change of 0·0001—0·0002 in the value of *n* and has the advantage over the microscopical method that it is applicable up to changes of 0·025. E. S. Hedges.

Iron resistance lamps. C. Kröger (Chem. Fabr., 1931, **4**, 365—367).—The construction of Fe wire resistances for the automatic control of electric furnaces is described (cf. Ostwald and Luther, "Physikochemische Messungen," Leipzig, 1925, 452). N. H. Hartshorne.

Bridge for the measurement of the conductance of electrolytes. P. H. Dike (Rev. Sci. Instr., 1931, [ii], **2**, 379—395).—An improved bridge for d.c. and a.c. measurements is described. N. M. Bligh.

Direct electric heating of the micro-furnace in Pregl's method of organic micro-analysis. F. Engelhard (Z. anal. Chem., 1931, **85**, 61—64).—The furnace for heating the PbO_2 tube comprises a cylindrical Cu block covered with asbestos paper around which is wound the heating wire. The whole is covered with an insulating paste and several layers of asbestos and inserted in an unglazed porcelain tube. The temp. is regulated by an external resistance comprising lamps with Fe wire filaments in H_2. A. R. Powell.

Sodium coulometer. O. J. Stewart (J. Amer. Chem. Soc., 1931, **53**, 3366—3369; cf. A., 1925, ii, 921; 1927, 1049).—Each electrode is an evacuated glass tube 1·3 cm. in diameter and 9 cm. long through the wall of which is sealed a Pt wire brazed to a stout Ni wire extending to the bottom of the tube, and contains 15 g. of Cd; the anode also contains 0·5 g. of Na. Electrolysis in $NaNO_3$ baths at 340° leads to a slight etching of the cathodes, probably due to small electrolytic loss of silicate ions. The results of the anodic Na coulometer agree with those of the Ag coulometer and are accurate to 1 part in 10^4. J. G. A. Griffiths.

Measurement of the electrical resistivity of mineral waters at their source. A. Guillerd (Ann. Falsif., 1931, **24**, 411—422).—A portable "auditometer" is described; the electrical resistivity of H_2O can be measured with 200 c.c., using the principle of Kohlrausch's modification of the Wheatstone bridge. The H_2O is placed in an oblong vessel of ebonite, fitted with two parallel plates of Ag or Ag-plated Cu. A table is given so that all results may be calc. to 18°. The determination of the resistivity of H_2O is an accurate method of detecting pollution, whether this be from H_2O of a higher stratum or the surface. T. McLachlan.

Processes in electro-filtration. G. Mierdel and R. Seeliger (Naturwiss., 1931, **19**, 753—754).—The influence of the electric blast, the structure of macroscopic streams, and the radial transportation of particles to the precipitation electrodes are discussed. W. R. Angus.

Stirrer-condensers. J. Friedrichs (Chem. Fabr., 1931, 367—368).—Improved forms of combined reflux condenser and stirrer, in which wear at glass bearing surfaces is eliminated, are described. N. H. Hartshorne.

Effect of storage of distilled water in glass ampoules on the alkalinity and total solids content. A. O. Matthews (J. Amer. Pharm. Assoc., 1931, **20**, 767—770).—The corrosion of Jena glass ampoules by freshly distilled sterile H_2O (p_H 6·2, total solids 1·5 mg. per litre) when kept at 22—27° for 18 months was relatively slow. The inorg. solids rose from 1·5 to 3·7 mg. per litre and the average p_H was 6·7. No glass splinters or platelets were liberated. E. H. Sharples.

Fractionating heads. J. Erdös (Z. anal. Chem., 1931, **85**, 118—119).—Modifications of the Hempel fractionating head are illustrated; they permit intermediate fractions of the distillate to be collected from below the glass bead column. A. R. Powell.

Isolation of readily volatile substances in very dilute solution. A. A. Benedetti-Pichler and F. Schneider (Z. anal. Chem., 1931, **86**, 69—80).—The distillation flask described permits a highly conc. solution of the more volatile component to be obtained in a single distillation of 0·01% solutions of EtOH, $COMe_2$, $CHCl_3$, and Et_2O and 0·1% MeOH. E. S. Hedges.

Ionisation manometer. E. K. Jaycox and H. W. Weinhart (Rev. Sci. Instr., 1931, [ii], **2**, 401—411).—A gauge for pressure measurements of the order 10^{-9} mm. Hg, and free from Barkhausen oscillation difficulties, is described. N. M. Bligh.

Manometer for measuring low pressures of readily condensable gases. T. G. Pearson (Z. physikal. Chem., 1931, **156**, 86—88).—The apparatus consists essentially of a U-tube to the bend of which is sealed a vertical capillary. The Hg meniscus in one arm, which is closed, is always adjusted to a fixed point, and the displacement in the other arm when connected to the source of pressure is reproduced in magnified form by the meniscus in the capillary. A precision of 0·005 mm. is attainable. R. CUTHILL.

Improved McLeod gauge. S. D. BRYDEN, jun. (Rev. Sci. Instr., 1931, [ii], 2, 514—518).—The connexion to the vac. system is made through the top of the compression chamber, instead of by means of the usual T-joint below it. C. W. GIBBY.

Glass electrode determination of sodium in sodium chloride–potassium chloride mixtures. F. URBAN and A. STEINER (J. Physical Chem., 1931, 35, 3058—3062).—The determination of Na in mixtures of NaCl and KCl by means of the glass electrode is outlined. An equation for the mixed electrode potential is given. L. S. THEOBALD.

Glass electrode. D. A. MACINNES and D. BELCHER (J. Amer. Chem. Soc., 1931, 53, 3315—3331; cf. A., 1930, 423; 1929, 673).—With an improved apparatus, it is shown that between p_H 2 and 8 the H_2 and glass electrodes agree to within $\pm$0·0001 volt if corrections are made for the "asymmetry potential." Deviations depending on the nature of the positive ion are observed at $p_H > 8$, and at $p_H < 2$ deviations of an opposite kind, dependent on the negative ion, occur. Most of the apparent resistance of glass electrodes determined by d.c. measurements is due to polarisation. This resistance is increased greatly by drying even at room temp. Theories of the glass electrode are discussed. J. G. A. GRIFFITHS.

Apparatus for effecting exact micro-dilution. L. DEVILLERS (Bull. Biol. Pharm., 1931, 3, 309—310).—Exact dilutions of min. quantities of liquids can be effected by use of a modified Pasteur's pipette and a burette. C. C. N. VASS.

Sampling burette. E. SCHILLER (Chem.-Ztg., 1931, 55, 732).—A sampling tube, into the lower part of which is sealed an internal tube with graduated scale, has a stopcock near its upper end and can be closed by a stopper at the lower end. Into the ground upper end is fitted a detachable burette with top and bottom stopcocks, this being protected by a glass cap attached to the sampling tube. In operation, samples from various sources are collected in any desired, measured quantities in the sampling tube and mixed by inverting the tube. They are then drawn into the burette. Contamination by exposure to air is thus avoided. W. J. WRIGHT.

Syringe-pipette for precise analytical usage. A. KROGH and A. B. KEYS (J.C.S., 1931, 2436—2440).—The apparatus delivers rapidly a desired vol. of liquid (1—2 c.c.) with an accuracy of 0·1 cu. mm. By counteracting expansion with another expanding system the temp. error is eliminated. E. S. HEDGES.

Capillary viscosimeter with a device at the orifice to prevent the disturbing effect of surface tension on the determination. A. PARLOW (Chem.-Ztg., 1931, 55, 683).—The apparatus comprises a cylindrical glass reservoir terminating in a capillary tube the lower end of which opens out into a small glass bell from the bottom of which a thin glass rod protrudes upwards into the mouth of the capillary so that the drops of liquid run down the rod into the glass bell, from which they emerge through a small hole at the side. The whole is mounted in the usual water-jacket with stirrer and thermometer for maintaining a constant temp. A. R. POWELL.

Filtration of colloidal solutions. W. D. JANKOVSKI (Biochem. Z., 1931, 238, 101—103).—A simple method of filtering colloidal solutions is described. W. MCCARTNEY.

Simple muffle furnace with low gas consumption. R. HOEVERS (Chem. Weekblad, 1931, 28, 550—551).—A simple construction, in which special attention has been paid to heat insulation, is illustrated. S. I. LEVY.

Method of obtaining air currents of different humidities. J. B. SETH (Nature, 1931, 128, 638—639).—Any desired humidity can be produced by regulating the strengths of a current of dry air and of air saturated with H_2O. L. S. THEOBALD.

Conversion of the Mohr-Westphal balance for other normal temperatures and density units. W. BLOCK (Chem. Fabr., 1931, 374—376, 383).—The balance may be employed for determination of vals. of d_4, and of d^{15} and d^{20} of liquids, by modifying either the wt. of the rider of the volume of the float; the necessary calculations are given, together with a table of corrections for use when the balance is employed in its normal form. H. F. GILLBE.

Use of chromium steel vessels in analysis. A. KRÜGER (Chem.-Ztg., 1931, 55, 682—683).—Evaporating dishes of Cr steel are suitable for analytical operations involving strongly alkaline solutions, *e.g.*, the separation of Al from Fe with NaOH. The vessels also resist the action of aq. NH_3 and feebly alkaline Na_2S solution. A. R. POWELL.

Tables and charts of specific gravity and hardness for use in determination of minerals. J. L. ROSENHOLTZ and D. T. SMITH (Rensselaer Poly. Inst., Eng. and Sci. Series, no. 34, 83 pp.).—Alphabetical lists and charts for facilitating identification are given. C. W. GIBBY.

Applications of the Schlieren method of photography. D. B. GAWTHROP (Rev. Sci. Instr., 1931, [ii], 2, 522—531).—Photographs are given illustrating the uses of the method, which depends on the disturbances in density produced in air by heat, by the motion of projectiles, by the emergence of other gases from jets, etc. C. W. GIBBY.

Geochemistry.

Changes in the ozone concentration of the atmosphere. R. Ruedy (Physical Rev., 1930, [ii], 35, 295).—Increased O_3 has not been detected for the few days before or after strong magnetic storms.

L. S. Theobald.

Significance of the ozone content of the atmosphere. R. Mecke (Z. physikal. Chem., Bodenstein Festband, 392—404).—By consideration of existing spectroscopic data it is shown that the photochemical equilibrium between O_3 and O_2 is determined by two processes: the first is the formation of O atoms and O_3 from O_2 and O_2 excited by radiation of wavelength below 2025 Å., and the second the decomp. of the O_3 into excited O atoms and mols. under the influence of radiation of wave-lengths up to 2655 Å. At low O_3 concentrations and sufficiently low pressures the mass action relationship $k=[O_3]^2/[O_2]^3$ is valid. Calculation from the pressure and the intensity of de-ozonising radiation which exists at a height of 50 km. yields for the max. O_3 content of the atm. at that level 2×10^{-4}, compared with an observed content at ground level of about 10^{-8}. At higher or lower pressures the calc. O_3 content falls very rapidly. H. F. Gillbe.

Phenomena of the upper atmosphere. S. Chapman (Proc. Roy. Soc., 1931, **A**, **132**, 353—374).—Data relating to the upper atm. are summarised and correlated. Subjects dealt with are: solar ultraviolet radiation; absorption of solar radiation; separate absorbing layers in the earth's atm.; dissociative effects of solar radiation; O_3 layer; ionisation by ultra-violet radiation; absorption coeffs.; max. electron densities and corresponding gas densities; level of the layer ionised by ultra-violet radiation; ionising agent in the lower layer; nature of, and daily variation of, ionisation in the two layers; green light of the night sky. L. L. Bircumshaw.

Sea-water at Puget Sound Biological Station from Sept. 1928 to Sept. 1929. T. G. Thompson and M. W. Johnson (Pub. Puget Sound Biol. Sta., 1930, 7, 345—368). Chemical Abstracts.

Occurrence of fluorides in some waters of the United States. H. V. Churchill (Ind. Eng. Chem., 1931, 23, 996—998).—Traces of CaF_2 have been found in certain natural waters. The localities are those in which the dental defect known as "mottled enamel" is prevalent. The relative severity of the defect in the different areas appears to be correlated with the concentration of CaF_2, but a causal connexion is not definitely established. E. S. Hedges.

Specific gravities and vapour pressures of concentrated sea-water at 0—175°. K. Higashi, K. Nakamura, and R. Hara (J. Soc. Chem. Ind., Japan, 1931, 34, 72b).—The sp. gr. and v. p. were determined for ordinary up to nearly saturated concentrations of NaCl in the temp. range 0—175°. The stable modification of $CaSO_4$ in equilibrium with the brines and the effect of its saturation on the sp. gr. of the brines were taken into consideration. F. Salt.

Samelia meteorite. L. L. Fermor (Rec. Geol. Survey, India, 1931, 65, 161—162).—A section of this meteorite, polished and etched, confirms it as a coarse octahedrite. The lamellæ are 1—2·5 mm. wide and consist of broader bands of kamacite bordered by narrower bands of tænite. These cross one another, the interspaces being filled with plessite, which appears to be a eutectic mixture of kamacite and tænite.

C. A. Silberrad.

Unusual iron meteorite from Mexico. H. H. Nininger (Amer. J. Sci., 1931, [v], 22, 360—363).—The meteorite (wt. about 70·8 kg.) has an unusually high content of Ni (16·23%) and of Pt metals (0·014%), and is low in S (0·07%); Mg is present in traces.

C. W. Gibby.

Differentiation in the Shonkin Sag laccolith, Montana. F. F. Osborne and E. J. Roberts (Amer. J. Sci., 1931, [v], 22, 331—353).—A detailed petrological description is given. Differentiation into chemically dissimilar rocks is due principally to crystal settling. Its great extent is probably due to the alkalic nature of the magma. C. W. Gibby.

Twinned plagioclase felspars in rocks from Sirohi State, Rajputana. A. L. Coulson (Rec. Geol. Surv. India, 1931, 65, 163—172).

Diamonds with quartz intergrowths. C. W. Correns (Z. Krist., 1931, **80**, 37—44).—Diamonds with quartz intergrowths occur in the Campo do Sampaio mine (Diamantina, Minas Geraes, Brazil), in a conglomerate of coarse sandstone cemented by sericitised material. It has probably been deposited in fissures in the diamond, first formed by rock movements, and then enlarged by hot alkaline solutions or superheated steam, either of which would also cause the sericitisation. C. A. Silberrad.

Density and structure of millerite. N. H. Kolkmeijer and A. L. T. Moesveld (Z. Krist., 1931, **80**, 91—102).—Millerite, prepared according to Thiel and Gessner's method (cf. A., 1914, ii, 277), d^{18} 5·348, has a rhombohedral unit cell, r 5·636 Å., α 116° 35′, with 3 mols. The at. radius of S is 1·6, of Ni 0·7 Å. (cf. A., 1928, 390). C. A. Silberrad.

Acid volcanic rock of Kara-Dagh, Crimea. D. V. Sokolov and A. F. Fioletova (Trans. State Inst. Test. Building Mat., Moscow, 1930, no. 34, 33—45).—Liparite (K_2O+Na_2O 8·75, Fe 0·44, Ti 0·10%) should be suitable for glass manufacture. The presence of 0·050% V_2O_5 in andesite is recorded.

Chemical Abstracts.

Fergusite from Talasser Alatau, Turkestan. V. Nikolaiev (Zentr. Min. Geol., 1931, **A**, 33—42; Chem. Zentr., 1931, i, 2599).—The fergusite contains orthoclase 45, 37; nepheline 8·8, 16·9; granaphyre 9·7, 7·0; pyroxene 23·5, 12·0; biotite 6·0, 12·8; melanite 4·1, 10·8; apatite 0·5, 0·8; magnetite 2·1, 1·7; calcite 0·5, 0·6%. A. A. Eldridge.

Aegirite-augite glaucophane quartz schist from the province of Teshio, Hokkaido, Japan. J. Suzuki (Proc. Imp. Acad. Tokyo, 1931, 7, 283—286).—The schist obtained from the bed of the river Chirashibe shows microscopically successive layers of different mineralogical composition, thin layers of quartz and felspar grains, and others rich in glaucophane and aegirite-augite arranged in layers subparallel to the plane of schistosity.

C. C. N. VASS.

Danburite from Obira, Japan. Z. HARADA (Z. Krist., 1931, 79, 349—366; cf. this vol, 415).—Danburite occurs in good crystals exhibiting 72 forms; *d* 2·994±0·002; analysis: SiO_2 48·04, B_2O_3 27·80, CaO 21·97, MgO 0·76, $Fe_2O_3+Al_2O_3$ 1·00, loss on ignition 0·60%. n_α, n_β, n_γ were determined for numerous wave-lengths from λ 7082·0 (1·6267, 1·6296, 1·6324) to λ 2967·3 (1·6752, 1·6777, 1·6815).

C. A. SILBERRAD.

Constitution of mica. IX. Biotites. J. JAKOB (Z. Krist., 1931, 79, 367—378).—Analyses of single crystals of phlogopite from (1) Val Cannobino, Italy, (2) Burgess, Ontario, and of biotites (3) and (4) from Montido Daro, Bellinzona, (5) and (6) Claro, Ticino, and (7) St. Gotthard give, in this order: SiO_2 40·21, 40·82, 37·88, 37·71, 35·35, 35·30, 37·43; TiO_2 2·80, 1·15, 2·06, 1·64, 3·16, 2·71, 1·95; Al_2O_3 12·60, 12·79, 19·23, 19·29, 18·46, 18·86, 16·50; Fe_2O_3 0, 0, 4·09, 2·24, 4·03, 4·08, 5·03; FeO 2·52, 1·90, 10·47, 9·72, 16·26, 16·85, 15·84; MnO 0·02, 0·04, 0·30, 0·31, 0·61, 0·44, 0·22; MgO 25·45, 26·45, 13·19, 14·22, 8·46, 8·06, 11·17; Na_2O 1·78, 1·50, 1·40, 1·33, 1·34, 1·64, 1·69; K_2O 9·26, 10·80, 9·85, 9·33, 6·69, 8·97, 8·90; $H_2O(+110°)$ 4·58, 3·93, 1·56, 4·29, 5·72, 3·13, 2·22%; (1) contains also Cr_2O_3 0·76, and NiO 0·18; and (2) F 1·00. From (1) the Fe was readily removed by HCl, the colour changing from brown to the green of Cr_2O_3. On the basis of these analyses and a method of determining the amount of original FeO oxidised to Fe_2O_3 the composition of the biotites, like that of the muscovites (cf. A., 1930, 1016), can be expressed by varying nos., always totalling 25, of units containing the radicals $Al(SiO_4)_3$, $Mg(SiO_4)_3$, and $Mg(SiO_5)_3$, Si being partly replaced by Ti, Al by Fe^{III}, Cr^{III}, Mn^{III}, and Mg by Fe^{II}, Ca, etc. The number of possible varieties is 510.

C. A. SILBERRAD.

Physico-chemical properties of Japanese acid clay. VI. *X*-Ray studies. I. K. YAMAMOTO (J. Soc. Chem. Ind. Japan, 1931, 34, 244—247B).—Japanese acid clays of various origin give the same 7 characteristic *X*-ray diffraction lines as English fuller's earth or German activated clay, attributed to a cryst. kaolinite common to them all. This is stable at 600—900° and is unaffected by the extraction of 40% of the total SiO_2 by 20% NaOH.

C. HOLLINS.

Silberkiese as a solid solution. V. NIKITIN (Arh. Hemiju, 1931, 5, 184—192).—Crystallographic and analytical data indicate that silberkiese is a solid solution in FeS_2Ag of FeS or of $(FeS_2)_2Fe$.

R. TRUSZKOWSKI.

Vanadium in Chibiny. M. B. ZAPADINSKI (Ukrain. Chem. J., 1931, 6, [Tech.], 23—31).—Chibiny egerite and titanomagnetite contain about 0·5%, apatite 0·04%, and nepheline traces, of V_2O_5.

R. TRUSZKOWSKI.

Occurrence of the platinum metals in the earth's crust. I. NODDACK and W. NODDACK (Z. physikal. Chem., Bodenstein Festband, 1931, 890—894).—Various analyses are summarised. The ratio of the fractions of the Pt metals in meteorites to those in the earth's crust is for Ru 500, Pd 583, Pt 140, Os 122, Rh 86, and Ir 43. The crust thus appears to be impoverished with regard to these metals, but a probable cause is the preponderance of eruptive rocks in the crust. Below 16 km. considerable quantities of Ru, Os, and Pd may exist.

H. F. GILLBE.

Forest types in the south-west as determined by climate and soil. G. A. PEARSON (U.S. Dept. Agric. Tech. Bull., 1931, no. 247, 143 pp.).—The distribution of forest trees is largely controlled by the mean temp. and H_2O content of the soil. All species have approx. the same wilting point in the same soil. Soil conditions other than depth, texture, and org. matter content rarely become limiting factors in the distribution of species.

A. G. POLLARD.

Chemical composition of some chernozem-like soils of N. Dakota. T. H. HOPPER, L. L. NESBITT, and A. J. PINCKNEY (N. Dakota Agric. Exp. Sta. Tech. Bull., 1931, no. 246, 72 pp.).—Numerous analyses of various depth samples are recorded and their characteristics discussed.

A. G. POLLARD.

Phosphoric acid and lime contents of some arctic and Norwegian soils. E. G. DOERELL (Superphosphate, 1931, 4, 105—109).—The P content of the soils examined is the result of cultural operations and fertiliser treatments and is not dependent on the P content of the primitive rock.

A. G. POLLARD.

Organic Chemistry.

Possibility of detection of rotation isomerism. K. L. WOLF and W. BODENHEIMER (Z. physikal. Chem., Bodenstein Festband, 1931, 620—626).—A discussion.

H. F. GILLBE.

Biosynthesis. VI, VII, VIII. H. EMDE (Helv. Chim. Acta, 1931, 14, 881—911).—VI. The (empirical) formation of fats from sugars is discussed. γ-Fructose probably plays an important rôle in the synthesis of fatty acids from sugars. Glycerol and fatty acids are (reductive) products formed from sugars by oxidation–reduction processes.

VII. The possibility of various natural products (*e.g.*, carotene, cholesterol) being derived from straight-chain compounds (*e.g.*, lævulic acid, hexoses) instead of from isoprene is discussed.

VII. [With T. HORNEMANN.] A detailed study of the reaction between NH_4Cl and CH_2O solution (containing some MeOH and a trace of HCO_2H) shows that the following compounds are produced: CO_2, HCO_2H, HCO_2Me, MeOH, $CH_2(OMe)_2$, and mono-, di-, and tri-methylamine hydrochlorides; MeCl is not formed (cf. A., 1930, 453). $CH_2(OMe)_2$ and HCO_2Me are not obtained when MeOH-free CH_2O solution is used, or from hexamethylenetetramine (I) and conc. HCl. $CH_2(OMe)_2$ is prepared in almost quant. yield from (I). MeOH, and conc. HCl (cf. B.P. 338,624; B., 1931, 237); a little HCO_2Me is also produced. H. Burton.

Condensation of hydrocarbons by electrical discharge. VIII. S. C. Lind and G. R. Schultze.—See this vol., 1249.

Configurative relationship of hydrocarbons. III. Optical rotations of the hydrocarbons of the series methyl*iso*butylmethane. P. A. Levene and R. E. Marker (J. Biol. Chem., 1931, **92**, 455—460; cf. this vol., 931).—Et β-methylhexoate (free *acid*, $[M]_D^{24}$ +1·08°) by a Grignard reaction gave βδ-*dimethylheptan*-β-*ol*, b. p. 134—136°, which was distilled with $(CO_2H)_2$ to obtain the unsaturated *hydrocarbon*, b. p. 134—136°, $[M]_D^{24}$ −7·69°, hydrogenated to l-βδ-*dimethylheptane*, b. p. 131—131·5°, $[M]_D^{22}$ −4·49°. Similarly there were prepared: βδ-*dimethyloctan*-β-*ol* (from β-methylheptoic acid, $[M]_D^{24}$ +1·83, by way of the Et ester), *dimethyloctene*, b. p. 62°/30 mm. $[M]_D^{24}$ −5·04°, l-βδ-*dimethyloctane*, b. p. 70°/40 mm., $[M]_D^{24}$ −3·57°, βδ-*dimethylnonan*-β-*ol* (from β-methyloctoic acid, $[M]_D^{24}$ +2·47), *dimethylnonene*, b. p. 79°/30 mm., $[M]_D^{24}$ −4·76°, l-βδ-*dimethylnonane*, b. p. 75°/25 mm., $[M]_D^{24}$ −2·84°. The saturated hydrocarbons all rotate in the same direction and the val. falls with increasing mol. wt. in accordance with the authors' theory.

J. H. Birkinshaw.

Plant colouring matters. XXXVII. High-molecular hydrocarbons containing numerous methyl groups. P. Karrer, M. Stoll, and P. Stevens (Helv. Chim. Acta, 1931, **14**, 1194—1204).—Electrolysis of the Na salt of perhydrobixin in MeOH gives, in addition to various by-products, about 50% of an *ester* (I), $C_{44}H_{88}(CO_2Me)_2$, b. p. 265—270°/0·02 mm. Reduction of (I) with Na and EtOH to the corresponding glycol, conversion of this into the dibromide by aq. 33% HBr at 150°, and subsequent reduction with Cu–Zn and 60% AcOH gives *dibixane*, $C_{46}H_{94}$ (probably 4 : 8 : 12 : 16 : 23 : 27 : 31 : 35-*octamethyloctatriacontane*), b. p. 270—275°/0·2 mm. The mixture of about 70% of Me H ester and 30% of free acid, obtained by partial hydrolysis of (I) with MeOH–NaOH in $MeOH–Et_2O$, is electrolysed (as Na salt in MeOH), whereby some of the *ester*, $C_{88}H_{176}(CO_2Me)_2$, is produced. Treatment of this with MgMeI and subsequent reduction with red P and HI (*d* 1·7) at 200° gives a *hydrocarbon*, $C_{94}H_{190}$ (probably 2 : 5 : 9 : 13 : 17 : 24 : 28 : 32 : 36 : 41 : 45 : 49 : 53 : 60 : 64 : 68 : 72 : 75-*octadecamethylhexaheptacontane*), which does not resemble hydrocaoutchouc. H. Burton.

Action of radon on unsaturated hydrocarbons. G. B. Heisig.—See this vol., 1252.

Hydration of olefines to alcohols. A. V. Frost (J. Appl. Chem., Russia, 1930, 3, 1069—1076).—Free energies of formation of alcohols up to $C_6H_{13}\cdot OH$ are calc. High pressures, and temp. of 227—427°, favour the reactions. Chemical Abstracts.

Influence of substituents on the additive reactivity of ethylene derivatives. I. Addition of bromine in solution. C. K. Ingold and E. H. Ingold (J.C.S., 1931, 2354—2368).—The comparative effects of substituents on additive reactivity in ethenoid compounds, on substitution reactivity in the aromatic nucleus, and on tautomeric mobility are discussed on theoretical grounds. Measurements of the relative rates of addition of Br in competition experiments to C_2H_4 and some simple substituted ethylenes are recorded and these are shown to be consistent with theory. When several substituents are present, these may contribute in different ways and there is the possibility of inverted mutual action, a case of which is experimentally demonstrated.

F. R. Shaw.

Thermal chlorination reactions in the gaseous phase, with short heating periods. J. Mason and T. S. Wheeler (J.C.S., 1931, 2282—2293).—A high space velocity method, with high reaction-tube temp., has been developed for controlled chlorination in the gaseous phase. Tubes of a special refractory were used, either empty or (preferably) packed with pieces of the same material. Conditions must be adjusted to avoid pyrolysis, which occurs if the tube temp. is too high, even at high rates of flow. At temp. not exceeding 900° and with excess of CH_4 and suitable space velocities, the method is efficient for producing MeCl, with small amounts of CH_2Cl_2. The yield of MeCl is about 80% of the Cl_2 input. Using C_3H_8, $Pr^{\alpha}Cl$ was formed in greater amount than $Pr^{\beta}Cl$. Yields of CH_2Cl_2 slightly greater than 90% were obtained in the chlorination of MeCl.

E. S. Hedges.

Determination of alcohol in dilute solution by means of acid dichromate, compared with the sp. gr. method. S. G. Liversedge (Analyst, 1931, **56**, 595—596).—EtOH present in small amounts such as 0·1% of Et esters in org. acids, or EtOH in Et esters, after hydrolysis and/or separation from other org. matter, may be determined by oxidation with acid $K_2Cr_2O_7$ (90 c.c. of N-$K_2Cr_2O_7$ and 600 c.c. of H_2SO_4 per litre). The results are comparable with those given by the sp. gr. method.

T. McLachlan.

Reaction of bromine with *iso*propyl alcohol. J. F. J. Dippy, H. B. Watson, and E. D. Yates (J.C.S., 1931, 2508).—The main products of the action of Br on $Pr^{\beta}OH$ are $Pr^{\beta}Br$ and *as*-tetrabromoacetone, along with monobromo-, *as*-dibromo-, and ααα-tribromo-acetone. F. R. Shaw.

Alkyl peroxides. VII. Hydroxyalkyl hydrogen peroxides. A. Rieche [with R. Meister] (Ber., 1931, **64**, [*B*], 2328—2335).—The action of aldehydes with aq. H_2O_2 leads generally to dihydroxyalkyl peroxides. When MeCHO and H_2O_2 react at 0° in the presence of anhyd. Et_2O and Na_2SO_4 and the solvent is subsequently removed as rapidly as possible at room temp., α-*hydroxyethyl hydrogen peroxide*, $CHMe(OH)\cdot O\cdot OH$, *d* 1·160, remains as an almost odourless liquid which decomposes vigorously when heated. With aq. KI it liberates about 75% of the expected I, acid being simultaneously produced. With aq. $FeSO_4$ about half of the expected AcOH is formed; MeCHO is simultaneously produced and a part of the active O is consumed in oxidising the Fe^{II} salt. With aq. NaOH only about half of the expected acid is produced. H_2O appears to facilitate the conversion of α-hydroxyethyl hydrogen peroxide into di-α-hydroxyethyl peroxide, which furnishes ½ mol. of AcOH with $FeSO_4$, and AcOH and MeCHO with aq. NaOH. The yield of AcOH increases to 75% when the H peroxide in Et_2O is shaken with aq. $FeSO_4$ and to 86% if the solutions are allowed to rest in contact with one another. The C_7—C_{12} aldehydes are more readily isolated by reason of their cryst. nature. *α-Hydroxyheptyl*, m. p. 40° after softening, *α-hydroxyoctyl*, m. p. 46° after softening at 40°, *α-hydroxynonyl*, m. p. (indef.) 50—54°, *α-hydroxydecyl*, m. p. 61°, *α-hydroxyundecyl*, m. p. 62° after softening at 58°, and *α-hydroxydodecyl*, m. p. 65—67° after softening at 58°, *H peroxides* have been isolated. They are not explosive, and merely decompose vigorously when superheated. With HI they liberate 75—80% of the calc. amount of I and the corresponding quantity of O_2 when boiled with $TiCl_3$; with the latter reagent the higher dihydroxyalkyl peroxides yield the calc. amount of O_2. The H peroxides when treated with CH_2O or butaldehyde yield mixtures of the *s*-dihydroxyalkyl peroxides instead of the expected *as*-products. They tend to pass into acids by elimination of H_2O. H. Wren.

Alkyl peroxides. VIII. Ethylidene peroxide. A. Rieche and R. Meister (Ber., 1931, 64, [*B*], 2335—2340).—The formation of ethylidene peroxide is observed (1) by treatment of α-hydroxyethyl H peroxide in Et_2O with P_2O_5 and evacuation of the residue at 40°, (2) by action of P_2O_5 on dihydroxyethyl peroxide in Et_2O and subsequent warming of the product at 90°/vac., (3) by prolonged preservation or by warming (vac.) butylene ozonide, whereby MeCHO is evolved, and (4) by autoxidation of Et_2O. Immediately after prep. it is a very viscous oil, *d* 1·160—1·165, which explodes violently when heated, but is not markedly sensitive to friction. After some days in a closed vessel or some hr. if exposed to air it explodes with extraordinary violence when rubbed; only the portions actually touched are thereby affected. With warm, acidified KI it evolves 90% of the calc. amount of active O_2. It is hydrolysed by warm dil. H_2SO_4 to MeCHO and H_2O_2 and by alkali to AcOH in almost quant. yield. Mol. wt. determinations in freezing C_6H_6 give results varying from $[Me{\cdot}CHO_2]_4$ to $[Me{\cdot}CHO_2]_3$. H. Wren.

Esters of pyrophosphorous, hypophosphorous, and pyrophosphoric acids. II. Mechanism of action of bromine on sodium diethyl phosphite. A. E. Arbusov and B. A. Arbusov (J. pr. Chem., 1931, [ii], 131, 337—341; cf. this vol., 820).—The interaction of equiv. amounts of Br and $PO(OEt)_2{\cdot}O{\cdot}P(OEt)_2$ in light petroleum gives the *compound* $PO(OEt)_2{\cdot}O{\cdot}PBr_2(OEt)_2$, which can be preserved unchanged in a closed vessel for 24 hr., but evolves HBr in contact with atm. moisture. On addition of 1 mol. of $NaPO(OEt)_2$ a ppt. forms, but only a very small amount of substance volatile at 200°/11 mm. $[P(OEt)_3]$ is formed; addition of a further mol. of $NaPO(OEt)_2$ results in a marked reaction, with further precipitation, and $[P(OEt)_2]_2O$ can now be isolated in quantity. H. A. Piggott.

Colour reaction for soluble organic sulphur compounds. I. W. Grote (J. Biol. Chem., 1931, 93, 25—30).—Treatment of Na nitroprusside in $NaHCO_3$ solution with NH_2OH,HCl followed by Br yields a dark-coloured solution. The compound to be tested is dissolved in H_2O and excess of solid $NaHCO_3$ added, followed by the reagent. The following colour changes may occur. Purplish-red within 10 min. indicates C·SH, whilst an intense blue or green indicates E:S (where E is any single non-metallic element including S). Aq. KCN is added if no colour appears, when C·S·S·C compounds give a pink- to purplish-red within ½ hr. Thioacetic acid destroys the reagent, but a transient blue indicates the formula Me·CS·OH rather than Me·CO·SH. Ring compounds do not generally react. The use of the reagent for colorimetric determination of thiosulphate, thiocyanate, thiocarbamide, etc. is recommended. F. O. Howitt.

Stability of the carbon–sulphur linking in aliphatic sulphonic acids. F. C. Wagner and E. E. Reid (J. Amer. Chem. Soc., 1931, 53, 3407—3413).—When alkane-α- and -β-sulphonic acids are heated with aq. NaOH at 310—375° the main decomp. is $CH_2R{\cdot}SO_3Na+NaOH=CH_2R{\cdot}OH+Na_2SO_3$; this is probably followed by the change $CH_2R{\cdot}OH+NaOH=R{\cdot}CO_2Na+2H_2$. The (second order) velocity coeff. and heats of activation of the reactions studied are calc. The figures quoted after the following sulphonic acids are the % decomp. occurring when a *M*-solution of the Na salt is heated with an equal vol. of 3·7*N*-NaOH at 345° for 3 hr.: methane-, 1·5; ethane-, 62·7; propane-α-, 20·2, and -β-, 88·6; butane-α-, 17·3, and -β-, 75·2; pentane-α-, 13·3, and -β-, 64·2; hexane-α-, 11·7, and -β-, 54·9; $PhSO_3H$, 5; $CH_2Ph{\cdot}SO_3H$, 5. The stability of both α- and β-acids increases from C_2 to C_6; $MeSO_3H$ is very stable. The β-acids are less stable than the α-, but all are more stable than the corresponding mercaptans (this vol., 63). The acids are prepared either from alkyl iodides and $(NH_4)_2SO_3$ or by HNO_3-oxidation of mercaptans and purified through their *Ba* salts. H. Burton.

Isomeric isoprenesulphones. III. E. Eigenberger (J. pr. Chem., 1931, [ii], 131, 289—292).—*cis*-Isoprenesulphone is readily, and the *trans*-compound with greater difficulty, reduced by H_2 and colloidal Pt to the same *dihydro*-compound, m. p. 0·2°, b. p. 125—130°/12 mm. (some decomp.), thus confirming the view (this vol., 600) that the two forms are geometrical isomerides. The dibromo-compound reacts exothermally with Zn dust yielding isoprene, whilst Zn dust and EtOH affords only *cis*-isoprenesulphone. J. W. Baker.

Catalytic hydrogenation of the carboxyl group in organic compounds, particularly in those of high mol. wt. O. Schmidt (Ber., 1931, 64, [*B*], 2051—2053).—Contrary to Schrauth and others (this vol., 932), the use of high temp. and pressure is not essential for the hydrogenation of the CO_2H group if a sufficiently active contact is employed. The reduction of Et oleate to octadecyl alcohol is effected at 270—280°/atm. in the presence of a $CuCrO_4$ catalyst, whilst castor oil at 220°/200 atm. in presence of a Co catalyst yields octadecyl alcohol and octadecanediol. H. Wren.

Catalytic reduction of the carboxyl group. W. Normann (Z. angew. Chem., 1931, **44**, 714—717).—Aliphatic carboxylic acids can be reduced to the corresponding alcohols by H_2O under high pressure and in presence of a catalyst (Cu, Ni, etc.). The reaction may be carried out with the free acid or with an ester. Aldehydes and ketones are similarly reduced. J. W. Smith.

Acetylation in aqueous alkaline solutions. F. D. Chattaway (J.C.S., 1931, 2495—2496).—Many compounds containing OH or NH_2 groups can be easily acetylated by adding Ac_2O to their dil., ice-cold solution in alkali hydroxide. F. R. Shaw.

Monoglycerides of lower fatty acids. P. G. Gilchrist and H. A. Schuette (J. Amer. Chem. Soc., 1931, **53**, 3480—3484).—Direct esterification of glycerol in presence of H_3PO_4 and CCl_4 is impracticable with acids higher than butyric; *glyceryl mono*iso*butyrate*, b. p. 128—130°/2 mm., is prepared by this method. *Glyceryl* n-*valerate*, b. p. 129—131°/2 mm., iso*valerate*, b. p. 145—147°/3·5 mm., and n-*hexoate*, b. p. 132—134°/2 mm., are prepared from α-chlorohydrin and the Na salts of the fatty acids. The coeffs. of viscosity and surface tensions of the above esters and glyceryl acetate, propionate, and *n*-butyrate are determined. Other physical data are recorded. H. Burton.

Relation between ultra-violet absorption and structure of derivatives of acetic and malonic acids. R. Dolique (Ann. Chim., 1931, [x], **15**, 425—521).—The mutual influence on the absorption spectra of two neighbouring chromophores diminishes with separation, and ceases when they are separated by more than 3 C atoms. In the prep. of disubstituted malonic esters the yield is improved if that substituent which contains a Ph nucleus is introduced first. Excess of Et malonate improves the yield in the prep. of monoalkyl derivatives of Et malonate. Improvements in the prep. of several of the following compounds are recorded. The Na derivative of Et *n*-butylmalonate (b. p. 127°/12 mm.) with γ-phenylpropyl bromide gives *Et γ-phenylpropyl*-n-*butylmalonate*, b. p. 212—213°/15 mm. (35% yield), also obtained by reversing the order of introduction of the substituents (yield 33%), and purified by re-esterification of the *acid*, m. p. 137·5—138° (yield of acid 91%). The heated acid gives *α-(γ-phenylpropyl)hexoic acid*, m. p. 38°, b. p. 215°/19 mm. Similar reactions give Et ethyl-*n*-butylmalonate, b. p. 128°/13 mm., α-ethylhexoic acid, b. p. 222°/755 mm., 131°/18 mm. (*benzyl* ester, b. p. 150°/13 mm.) (cf. A., 1923, i, 81), Et *n*-butylbenzylmalonate, b. p. 187°/15 mm. (yield 35% from Et *n*-butylmalonate, or 52% from Et benzylmalonate) (A., 1922, i, 681) (*acid*, m. p. 104·5°), *α-benzylhexoic acid*, b. p. 185°/14 mm., 179°/10 mm. (yield 95%) [*Et* ester, b. p. 274°/756 mm., 156°/16 mm. (yield 82%); *benzyl* ester, b. p. 234—236°/28 mm., 222—223°/16 mm. (yield 80%)], Et di-*n*-butylmalonate, b. p. 151—152°/18 mm. (yield 55%; yield of acid 96%), α-*n*-butylhexoic acid, b. p. 149°/15 mm. {Et ester, b. p. 218°/752 mm., 110°/18 mm. (yield 84%), *benzyl* ester, b. p. 177°/15 mm., *amide*, m. p. 134·5° (sublimes 100—110°)] (cf. A., 1918, i, 250), *Et β-phenylethyl*-n-*butylmalonate*, b. p. 203°/15 mm., 205°/17 mm. (yield 34%, or 40%) [*acid*, m. p. 139° (yield 86%)], *α-(β-phenylethyl)hexoic acid*, b. p. 201—202°/17 mm., 238—239°/28 mm., Et dibenzylmalonate, b. p. 238°/22 mm. (yield 75%) [*acid*, m. p. 174° (yield 90%)], β-phenyl-α-benzylpropionic acid, m. p. 91° [Et ester, b. p. 202°/18 mm. (yield 75%); *benzyl* ester, m. p. 81° (yield 87%); amide, m. p. 129·5°]. Et phenylmalonate gives *Et phenyl*-n-*butylmalonate* (yield 58%), hydrolysed to the *acid*, m. p. 153°, and *α-phenylhexoic acid*, b. p. 182—183°/20 mm. (also obtained by heating phenyl-*n*-butylmalonic acid, and by hydrolysis of *α-phenylhexonitrile*, b. p. 151·1—152·5°/20 mm., obtained from $CH_2Ph\cdot CN$ by means of $NaNH_2$ and BuBr). Et α-ethylhexoate reduced by Bouveault's method gives β-ethylhexanol, b. p. 180°/758 mm., 96—97°/27 mm., 89—90°/18 mm. (yield 58%). Similarly are obtained β-butylhexanol (yield 63%; also obtained by similar reduction of α-butylhexoamide, yield 8%) (*phenylurethane*, m. p. 39°), *β-benzylhexanol*, b. p. 170—171°/27 mm. (yield 60%, also from the amide in small yield) (*phenylurethane*, m. p. 55·5°). β-Phenyl-α-benzylacetamide by similar treatment gives *γ-phenyl-β-benzylpropanol*, m. p. 27—28°, b. p. 197°/10 mm. (*phenylurethane*, m. p. 94°) (in better yield than from the ester), and a little γ-phenyl-β-benzylpropylamine (*Bz* derivative, m. p. 104°). α-Methyl-α-ethylpentanol, b. p. 79—80°/27 mm., α-methyl-α-benzylpentanol, b. p. 155°/27 mm., 144°/18 mm., *β-phenyl-α-benzyl-α-methylethanol* (from AcOEt and $CH_2Ph\cdot MgCl$), b. p. 182°/15 mm., and α-benzyl-α-methylpentanol (from $Me\cdot CO\cdot CH_2Ph$ and MgBuBr), b. p. 155°/27 mm., 144°/18 mm., could not be obtained optically pure. A. A. Levi.

Differing behaviour of α- and β-chloropropionic acids and of α- and β-chloroethylbenzenes during catalytic hydrogenation. C. Paal and C. Müller-Lobeck (Ber., 1931, **64**, [*B*], 2142—2150; cf. A., 1929, 1270).—The free chloropropionic acids are little attacked by activated H_2. Ca α-chloropropionate is quantitatively reduced to $CaCl_2$ and propionic acid, whereas the salt of the β-acid suffers only slight similar change. The action of the α-chloropropionate is considerably accelerated by the addition of MgO, which combines with the liberated HCl, but the oxide has little effect on the β-chloropropionate. Et α-chloropropionate is readily transformed into Et propionate in presence of MgO, whereas Et β-chloropropionate absorbs little H_2 before reaction ceases. The anticatalytic action of the liberated HCl is much more marked in the case of saturated than of unsaturated acids, probably owing to the negativing action of the ethylenic linking in the latter and the consequent loosening of the C–Cl linking.

In presence of the requisite quantity of MgO, α-chloroethylbenzene is quantitatively converted into PhEt, whereas under similar conditions β-chloroethylbenzene suffers only slight reduction. With larger amounts of Pd and prolonged period of action, the β-derivative yields PhEt. Reduction of α-chloroethylbenzene proceeds more rapidly than that of Ca α-chloropropionate or α-chlorobutyrate. The *semi-hydrated Ca* and the *Ag* salts of α- and β-chloropropionic acid are incidentally described.

H. Wren.

Highly-polymerised compounds. LV. Polyacrylic acid. H. Staudinger and H. W. Kohlschütter (Ber., 1931, 64, [*B*], 2091—2098).—Polymerisation of acrylic acid by irradiation occurs more rapidly in CO_2 than in O_2, and is particularly rapid when the operation is commenced in O_2 or air and continued in CO_2. The influence of O_2 is marked with 30% and 5% aq. solutions. Below 100°, individual specimens of acrylic acid show individual behaviour towards polymerisation, but at 110° or above polymerisation occurs rapidly in all cases, yielding non-homogeneous products varying from glassy, transparent masses to hard, porcelain-like materials. All are amorphous. Polymerisation is considered to follow the scheme: $\cdots CH(CO_2H)\cdot CH_2 \cdots + xCO_2H\cdot CH{:}CH_2 \longrightarrow CH(CO_2H)\cdot CH_2\cdot[CH(CO_2H)\cdot CH_2-]_{x-1}\cdot CH(CO_2H)\cdot CH_2\cdot$. Solid polyacrylic acids swell strongly in H_2O without dissolving completely at low temp.; at 100—120° homogeneous sols. are more or less rapidly obtained. They are polybasic acids of unknown mol. wt. They are weaker than the monomeric acid and the Na salts are feebly alkaline. Titration of the acids with NaOH in presence of phenolphthalein shows about 96% of the CO_2H group, but exact results are obtained potentiometrically. The conductivity of the poly-acids and their salts is lower than that of the monomeric substances. The viscosity of polyacrylic acid sols depends on p_H in the same manner as that of the proteins. Viscosity is at a max. at the neutral point and decreases with increase of NaOH. With heteropolar compounds such as the polyacrylic acids, high $\eta_{sp}c$ vals. do not necessarily imply a high mol. wt., since viscosity varies with p_H and there is no evidence of the identity of the dissolved particles and the mols. The changes of viscosity are due to causes other than those operative with homopolar mol. colloids. Since the behaviour of the admittedly highly-polymerised acrylic acids resembles that of the proteins, it is probable that the latter also are highly polymerised and not specially structured. Depolymerisation of polyacrylic acids can be effected by contact with H_2O at different temp. or with aq. NaOH. H. Wren.

Configurative relationships of the α-bromo-acids obtainable from the optical isomerides of *iso*leucine and of *allo*leucine to the amino-acids obtainable from these by amination. Walden inversion. E. Abderhalden and W. Zeisset (Z. physiol. Chem., 1931, 200, 179—190).—By known reactions (bromination with NOBr, chlorination with $SOCl_2$, amination with aq. NH_3, etc.), the following were obtained: chloroacetyl-*l*(+)-*iso*leucine, m. p. 71—73°, $[\alpha]_D^{20}$ +26·0° in EtOH, *glycyl*-l(+)-iso*leucine*, m. p. 242—243° (decomp.), $[\alpha]_D^{20}$ −14·1° in H_2O; chloroacetyl-*d*(−)-*iso*leucine, m. p. 72—74°, $[\alpha]_D^{20}$ −26·1° in EtOH, glycyl-*d*(−)-*iso*leucine, m. p. 240—242° (decomp.), $[\alpha]_D^{20}$ +13·6° in H_2O; *chloroacetyl*-l(+)-allo*leucine*, m. p. 80—86°, $[\alpha]_D^{20}$ +19·1° in EtOH, *glycyl*-l(+)-allo*leucine*, m. p. 245—247° (decomp.), $[\alpha]_D^{19}$ −9·4° in H_2O; *chloroacetyl*-d(−)-alloiso*leucine*, *glycyl*-d(−)-alloiso*leucine*, m. p. 244—246° (decomp.), $[\alpha]_D^{18}$ +9·2° in H_2O; [d]-(+)-allo-*α-bromo-β-methylvaleric acid*, b. p. 107—108°/2—3 mm., $[\alpha]_D^{18}$ +12·80° from *d*(−)-alloiso*leucine*; [d](+)-allo-α-*bromo*-β-*methylvaleryl chloride*, b. p. 76—78°/12—13 mm.; [l](−)-*allo-α-bromo-β-methylvaleric acid*, b. p. 124—126°/7 mm., $[\alpha]_D^{19}$ −12·90°, from *l*(+)-*alloiso*leucine [*phenylcarbimido*-derivative, m. p. 151°, $[\alpha]_D^{20}$ +31·6°], [l](−)-allo-α-*bromo*-β-*methylvaleryl chloride*, b. p. 51°/3 mm.; [d](+)-α-*bromo*-β-*methylvaleric acid*, m. p. 40—41°, $[\alpha]_D^{19}$ +24·2° in C_6H_6, giving *d*(−)-*iso*leucine (*phenylcarbimido*-derivative, m. p. 125—130°, $[\alpha]_D^{20}$ −32·1° in EtOH), [d](+)-α-*bromo*-β-*methylvaleryl chloride*, b. p. 57—59°/3 mm.; [l](−)-α-*bromo*-β-*methylvaleric acid*, m. p. 38—40°, $[\alpha]_D^{17}$ −22·3° in C_6H_6 [*chloride*, b. p. 69—71°/10 mm.], giving *l*(+)-*iso*leucine (*phenylcarbimido*-derivative, m. p. 123—127°, $[\alpha]_D^{20}$ +32·4° in EtOH); [l](−)-allo-α-*bromo*-β-*methylvalerylglycine*, m. p. 77—79°, $[\alpha]_D^{20}$ −48·1° in EtOH, giving d(−)-iso*leucylglycine*, m. p. 212—214° (decomp.), $[\alpha]_D^{21}$ −18·8° in H_2O; [d](+)-allo-α-*bromo*-β-*methylvalerylglycine*, m. p. 81—82°, $[\alpha]_D^{20}$ +49·4° in EtOH (α-*bromo-fatty acid*, $[\alpha]_D^{18}$ +12·80°), giving l(+)-iso*leucylglycine*, m. p. 220° (decomp.), $[\alpha]_D^{19}$ +16·6° in H_2O; [*d*](+)-α-bromo-β-methylvalerylglycine, m. p. 107—108°, $[\alpha]_D^{20}$ +62·7° in EtOH (α-*bromo-fatty acid*, $[\alpha]_D^{19}$ +24·2°), giving *l*(+)-*alloiso*leucylglycine, m. p. 260—261° (decomp.), $[\alpha]_D^{20}$ +57·0° in H_2O (*phenylcarbimido*-derivative, m. p. 151°, $[\alpha]_D^{20}$ +30·4° in EtOH); [l](−)-α-*bromo*-β-*methylvalerylglycine*, m. p. 105—106°, $[\alpha]_D^{20}$ −60·9° in EtOH (α-*bromo-fatty acid*, $[\alpha]_D^{17}$ −22·3°), giving d(−)-alloiso*leucylglycine*, m. p. 252—255° (decomp.), $[\alpha]_D^{21}$ −62·7° in H_2O. J. H. Birkinshaw.

Behaviour of octoic, hexoic, valeric, *iso*valeric, and benzoic acids on extraction from aqueous solution with light petroleum. J. Grossfeld and A. Miermeister (Z. anal. Chem., 1931, 85, 321—330).—The partition coeffs. of the above acids between H_2O and light petroleum have been determined, and all follow the law $k=c/\sqrt{c_2}$. The % extracted when solutions of different concentration are agitated with equal vols. of light petroleum are tabulated. J. W. Smith.

Hydrogenation of unsaturated lactones to deoxy-acids. II. W. A. Jacobs and A. B. Scott (J. Biol. Chem., 1931, 93, 139—152).—Catalytic reduction (Adams) of ααβ-trimethyl-Δ^{β}-angelicalactone in EtOH at 20—25° gives ααβ-*trimethylvaleric acid* (about 50%), b. p. 137—138°/43 mm., and ααβ-*trimethyl-γ-valerolactone*, b. p. 121—123°/33 mm. Similarly, β-methyl-Δ^{β}-angelicalactone affords β-methylvaleric acid (about 50%), b. p. 197—198° (corr.)/758 mm. (*Ag* salt), and β-methyl-γ-valerolactone; ααβ-trimethyl-Δ^{β}-butenolide yields ααβ-trimethylbutyric acid (21%) and (mainly) ααβ-trimethylbutyrolactone; β-phenyl-αα-dimethyl-Δ^{β}-butenolide furnishes β-*phenyl*-αα-*dimethylbutyric acid* (about 25%), m. p. 61—62°, and β-*phenyl*-αα-*dimethylbutyrolactone*, m. p. 91—92°, whilst complete hydrogenation gives the same proportions of β-cyclo*hexyl*-αα-*dimethylbutyric acid*, m. p. 39—40°, and β-cyclo*hexyl*-αα-*dimethylbutyrolactone*, m. p. 51—52°. The yield of deoxy-acid formed during reduction of βγ-unsaturated γ-lactones (cf. A., 1930, 1162) is diminished by β-substitution. α-Anisylidene-Δ^{β}-angelicalactone undergoes a preliminary 1 : 4-addition of H_2 and finally gives (mainly) α-*anisyl*-γ-*valerolactone*, m. p. 60—61°, and 17% of α-*anisylvaleric acid*, m. p.

50—52°. Δ^{α}-Butenolide (prepared by thermal decomp. of γ-chlorocrotonic acid) affords butyrolactone (90%) and butyric acid (10%); the acid is probably formed from Δ^{β}-butenolide which may arise during the reduction or is present in the original material. Reduction of δ-keto-β-phenylhexoic acid with Na–Hg in EtOH gives β-*phenyl*-δ-*hexolactone*, b. p. 197—200°/19 mm., reduced catalytically to a *mixture*, b. p. 194—198°/20 mm., of stereoisomeric β-*cyclo*hexyl-δ-hexolactones. H. BURTON.

Synthesis of straight-chain unsaturated acids. R. BHATTACHARYA and J. L. SIMONSEN (Proc. XV Indian Sci. Cong., 1928, 153).—λ-Iodododecoic acid, prep. from castor oil by way of undecenoic, λ-bromoundecoic, cyanoundecoic, decamethylenedicarboxylic, and λ-hydroxylauric acids, was condensed with decin to yield behenolic acid.
CHEMICAL ABSTRACTS.

Alcoholysis. I. M. GOSWAMI and S. RAMANUJAM (J. Indian Chem. Soc., 1931, 8, 413—416).—The conversion of fat (coconut oil) into the Me esters of its fatty acids by boiling with MeOH in presence of various catalysts is studied. $POCl_3$ is as effective as, and more readily manipulated than, dry HCl (cf. A., 1907, i, 9; 1919, i, 308). Benzene- (I) and naphthalene-stearosulphonic acids (II), pyridine, piperidine, and piperidine hydrochloride have little or no effect. When (I) and (II) contain traces of mineral acid catalytic activity is observed. H. BURTON.

Unsaturated fatty acids and their derivatives. III. Four stereoisomerides of dihydroxy- and dibromo-stearic acids. IV. Mechanism of forming stearolic acid from dichlorostearic acid. Y. INOUE and B. SUZUKI (Proc. Imp. Acad. Tokyo, 1931, 7, 261—264, 265—268).—III. The hydroxy-acids are prepared by the action of 1% aq. $KMnO_4$ on a 1% solution of oleic or elaidic acid in 1% aq. KOH, at 1—3°; *elaido-* and *oleo-dihydroxystearic acid* have m. p. 100° and 130°, respectively. The acids were resolved through the strychnine salts; the active *elaidodihydroxystearic acids* have $[\alpha]_D^{22}$ −27·45° and +27·6° in MeOH, whilst the corresponding oleic acids have $[\alpha]_D$ −23·6° and +23·0° in MeOH. All the stereoisomerides were readily racemised. The dibromides were readily prepared by the action of Br in the cold and were separated by the strychnine salts. l-*Oleodibromostearic acid* had $[\alpha]_D$ −18·5°. Inactive dihydroxy-acids were obtained on treatment of the dibromo-compounds with Ag_2O.

IV. Treatment of oleodichlorostearic acid with 20% KOH in EtOH for 12 hr. at 100° and oxidation of the Me esters by Armstrong and Hilditch's method showed that in addition to stearolic acid, $\Delta^{\zeta\theta}$-octadecadienoic acid, $C_{18}H_{32}O_2$ (*Me* ester, b. p. 192—193°/4 mm.; *Zn* salt, m. p. 85°), was obtained. Treatment of the second acid with 20% KOH in EtOH at 150° converted it almost quantitatively into stearolic acid. Sorbic acid with 10% KOH in EtOH gave Δ^{β}-*pentinenecarboxylic acid*, m. p. 128°. C. C. N. VASS.

Oxidation of oleic acid by means of hydrogen peroxide with and without the addition of copper sulphate: a possible analogy with its oxidation *in vivo*. I. S. MACLEAN and M. S. B. PEARCE (Biochem. J., 1931, 25, 1252—1266).—When oleic acid was oxidised by H_2O_2 at 95° (A., 1908, i, 119) a fraction agreeing in composition with that of diketostearic acid was formed. An α-keto-derivative of nonoic or decoic acid and some dihydroxystearic acid were also present. The yields of H_2CO_3, AcOH, and HCO_2H corresponded with the complete oxidation of 5—10% of the total oleic acid. Increasing the proportion of H_2O_2 increased the proportion of dihydroxystearic acid present. Small amounts of Cu^{II} salts greatly increased the extent of oxidation. At 95° with a large excess of H_2O_2 more than 70% of the original oleic acid was completely broken down to H_2CO_3, HCO_2H, and AcOH. Succinic and δ-keto-η-hydroxyoctoic acids were also formed at the same time. Oxidation in the presence of Cu^{II} salt at 60° produced amounts of H_2CO_3, HCO_2H, and AcOH corresponding with complete oxidation of about 20% of the total oleic acid. The product obtained in greatest amount was δ-keto-η-hydroxyoctoic acid. Succinic acid and a mixture of various oxygenated derivatives of stearic acid were also present. Among the products of oxidation of octoic acid succinic and δ-keto-η-hydroxyoctoic acid were found.
S. S. ZILVA.

Action of concentrated sulphuric acid on oleic acid and oleyl alcohol. C. RIESS (Collegium, 1931, 557—588).—A max. amount of H_2SO_4 is combined at the point of unsaturation during the first hr. of its action at room temp. on oleic acid. The amount of organically combined SO_3 is reduced by more prolonged action and hydroxystearic acid is formed, the amount being greater as the amount of reacting H_2SO_4 is increased or the temp. raised. Most of the hydroxystearic acid is esterified. The combination of the H_2SO_4 is much slower at 0°, and it is practically the only reaction which occurs, since very little hydroxystearic acid is formed even after 24 hr. The sulphonation proceeds furthest at low temp., whilst the hydrolysis of the H_2SO_4 esters proceeds only very slowly. Oleyl alcohol is sulphonated at the point of unsaturation and at the OH group, but the reaction is slower than with oleic acid. Within the limits 0—40°, the reaction of the H_2SO_4 with the unsaturated atoms is almost independent of the temp. The reaction of the H_2SO_4 with the OH group proceeds very slowly at low temp. and is accelerated appreciably as the temp. is raised. The H_2SO_4 is eliminated again at still higher temp., especially if 40% of H_2SO_4 is used. D. WOODROFFE.

Preparation and purification of linoleic acid. H. I. WATERMAN and J. A. VAN DIJK (Verfkroniek, 1931, 4, No. 2, 15—19; Chem. Zentr., 1931, i, 2740).—Linoleic acid, prepared from sesamé oil fatty acids by bromination and debromination, distilled in a cathode-light vac., freed from oleic and saturated acids by cooling in $COMe_2$, and finally cryst. from $COMe_2$ by cooling, had I val. 179·9, CNS′ val. 91·2, d_4^{20} 0·9031, n_C 1·46643, n_D 1·46944, n_F 1·47642, n_G 1·48228; $[M]_C$ 86·02, $[M]_D$ 86·49, $[M]_F$ 87·60, $[M]_G$ 88·51.
A. A. ELDRIDGE.

Polymerisation of the methyl esters of higher unsaturated fatty acids. VIII. Polymerisation of methyl linolenate and linoleate. IX. Hydrogenation of the methyl esters assumed to be

intrapolymerised [cyclic monomerides]. K. Kino (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, **16**, 127—132, 133—135; cf. this vol., 602).—Me linoleate and linolenate, obtained from linseed and sesamé oils through the Pb salts and bromides, are heated in H_2 at 290—300° for varying times. Distillation of the product at 6—7 mm. removes monocarboxylic esters, which from the I val. and mol. wt. are considered to contain *cyclo*butane derivatives, formed by intramol. condensation, the proportion increasing with time of heating, and being less for the linoleate than for the linolenate. The residue from the distillation, which increases with time of heating, consists mainly of dimeride from Me linoleate, but contains higher polymerides in the case of Me linolenate.

IX. More H_2 is absorbed in the catalytic hydrogenation of the above monocarboxylic esters than that calc. from the I val., the velocity of absorption diminishing after the quantity corresponding with the I val. has been absorbed. The ester $C_{19}H_{31}\cdot CO_2Me$ (A., 1930, 1272) after reduction gives an acid having the same m. p. as arachidic acid, the theoretical quantity of H_2 to reduce the assumed *cyclo*butane ring being absorbed. The ester $C_{21}H_{33}\cdot CO_2Me$ (*loc. cit.*) is not completely reduced, the resulting acid after repeated purification having a lower m. p. than behenic acid. A. A. Levi.

Conversion of erucic acid into brassidic acid by nitrous acid. G. Rankoff (J. pr. Chem., 1931, [ii], **131**, 293—300).—Smooth isomerisation of erucic acid, $Me\cdot[CH_2]_7\cdot CH\dot{:}CH\cdot[CH_2]_{11}\cdot CO_2H$, into brassidic acid, $Me\cdot[CH_2]_{18}\cdot CH\dot{:}CH\cdot CO_2H$, occurs when it is treated in 30% HNO_3 with 0·2 of its wt. of $NaNO_2$ at 54—58°. With larger quantities of $NaNO_2$ oxidation affords by-products which prevent crystallisation of the product and under such conditions were isolated arachidic (*n*-eicosoic acid), brassylic, $HO_2C\cdot[CH_2]_{11}\cdot CO_2H$, and *n*-nonoic acids, and a nitrogenous substance which affords *n*-nonoic acid on steam-distillation. J. W. Baker.

Lignoceric acid and lignoceryl alcohol from "sulphate soap." H. Sandqvist, J. Gorton, and E. Bengtsson (Ber., 1931, **64**, [*B*], 2172—2174).—Extraction of the Na salts from "Tallöl" with Et_2O, ligroin, etc. removes phytosterols and lignoceryl alcohol, $C_{24}H_{50}O$, which are separated from one another by fractional crystallisation and destruction of the unsaturated sterols by treatment of their acetates in $CHCl_3$ with an excess of Ac_2O and conc. H_2SO_4. Treatment of the sulphate soap with H_2O leaves the sterols in solution, whereas the lignoceryl alcohol is found in the filter residue. After removal of the alcohol by Et_2O, the remaining Na salts yield lignoceric acid identical with the product obtained by oxidising the alcohol. For lignoceric acid and its Me ester the m. p. 80·3—81° after softening at 77° and 58—59·8°, respectively, are recorded, whereas synthetic *n*-tetracosoic acid and its Me ester have m. p. 85° and 60°, respectively. Lignoceryl alcohol, m. p. 76°, and its acetate, m. p. 56°, are compared with synthetic *n*-tetracosanol, m. p. 77·5°, and its acetate, m. p. 57°. H. Wren.

Optical rotation of lactic acid. W. D. Bancroft and H. L. Davis (J. Physical Chem., 1931, **35**, 2508—2529).—Sarcolactic acid should be designated *l*-(+)-lactic acid to show that, although its dil. aq. solutions are dextrorotatory, the lævorotations of its salts and esters show it to be the *l*-form of lactic acid. As in the case of malic acid (A., 1930, 892), there is a fourth tautomeric modification involved. The evidence indicates this to be a dextrorotatory ethylene oxide form. The equilibria involving the anhydride or lactide are reached slowly, whilst that between the normal and the ethylene oxide forms is reached rapidly. The changes in rotation shown by solutions of sarcolactic acid on concentration or dilution can then be satisfactorily interpreted. L. S. Theobald.

Lævulic acid. II. Vapour pressure of alkyl esters (C_1—C_6). H. A. Schuette and M. A. Cowley (J. Amer. Chem. Soc., 1931, **53**, 3485—3489).—Equations are derived expressing temp.–v. p. relationships for the Me, Et, Pr, Pr^β, Bu, Bu^β, *iso*amyl, n-*amyl*, b. p. (calc.) 253·2°/760 mm., and n-*hexyl*, b. p. (calc.) 266·8°/760 mm., esters of lævulic acid. The entropies of vaporisation indicate that all these esters are associated. Other physical data are recorded.

H. Burton.

Oxidation by ozone. Preparation of ι-hydroxydecoic acid by oxidation of undecenyl acetate. M. Mottier (Helv. Chim. Acta, 1931, **14**, 1080—1090).—Details are given for the prep. of ι-hydroxydecoic acid in about 80% yield by ozonolysis of Δ^κ-undecenyl acetate and subsequent hydrolysis with H_2O in presence of air. The effects of temp. and time of heating on the decomp. of the ozonide by H_2O and AcOH are studied. Decomp. of the ozonide with alkali gives mainly aldehydic condensation products one of which is probably the aldol (*semicarbazone*, m. p. 71—72°) derived from 2 mols. of ι-hydroxydecaldehyde.

H. Burton.

Preparation of ethyl oxalate. P. W. Jewel and J. S. Butts (J. Amer. Chem. Soc., 1931, **53**, 3560—3561).—Cryst. oxalic acid (1 kg.) is heated with EtOH (2 litres) until dissolved, and the mixture distilled at 80°/25 mm. until the vapour temp. is 60°. The residue is heated with EtOH (2 litres) for 3 hr., H_2O and EtOH are removed as above, the resultant product is dried, and then distilled. The yield of Et oxalate is about 85%. H. Burton.

Additive components of ethyl sodiomalonate and related compounds. N. E. Holden and A. Lapworth (J.C.S., 1931, 2368—2375).—When benzylideneacetophenone is heated in C_6H_6 with Et sodiomethylmalonate, Et α-methylcinnamate and Et sodiobenzoylacetate are produced. This cannot be explained by the hypothesis advanced by Thorpe (*ibid.*, 1900, 77, 923) and by Michael and Ross (this vol., 67), which overlooks the possibility of exchange of positions of H and CN or H and CO_2Et; it is, however, capable of interpretation on the basis of analogy with well-known reactions which are consistent with electrochemical conceptions of the behaviour of sodio-derivatives of weak acids or ψ-acids.

F. R. Shaw.

Di*iso*propylmalonic acid and its derivatives. F. C. B. Marshall (J.C.S., 1931, 2336—2338).—The prep. of *Et diisopropylmalonamate*, m. p. 62° (from the Ag salt and EtI); *Et*, b. p. 246·2°/751 mm., *Et H*, m. p. 66°, and *Me diisopropylmalonate*, m. p. 32°; and diisopropylmalonic acid, m. p. 198° (from Me ester), which is converted by $SOCl_2$ into *diisopropylacetyl chloride*, b. p. 63°/15 mm. (*anilide*, m. p. 148—149°) (cf. A., 1908, i, 602), is described.

F. R. Shaw.

Electrolysis of hydrogen esters of unsaturated dicarboxylic acids. P. Karrer and M. Stoll (Helv. Chim. Acta, 1931, 14, 1189—1194).—Electrolysis of Na Et fumarate in presence of MeOH and NaOAc gives no muconate (cf. Bloch, Diss., München, 1902); the main product is an ester, b. p. 98—101°/12 mm., hydrolysed by 10% KOH to fumaric acid and an oil. In absence of NaOAc, the same ester and a trace of Me muconate are produced. *Me H muconate*, m. p. 163°, prepared by partial hydrolysis of the Me_2 ester, does not undergo the Kolbe synthesis when electrolysed as the K salt in presence of aq. MeOH and KOAc; the main reaction is hydrolysis.

H. Burton.

Digitalonic acid and the corresponding trihydroxymethoxyglutaric acid. H. Kiliani (Ber., 1931, 64, [*B*], 2027—2028; cf. A., 1916, i, 493).—The isolation of trihydroxymethoxyglutaric acid, m. p. 122°, $[\alpha]_D$ −27·4° in H_2O, from the products of the action of HNO_3 (*d* 1·4) on digitalonolactone is effected through the Ca and Zn salts. A ketonic acid is formed in considerable amount as by-product.

H. Wren.

Action of potassium cyanide on potassium mannosaccharate. H. Kiliani (Ber., 1931, 64, [*B*], 2018—2026; cf. A., 1928, 741).—The view that the attack of KCN on K mannosaccharate occurs between the ββ′-C atoms requires modification, since the acids, $C_7H_{10}O_{10}$, are converted by boiling HI into adipic and unsaturated C_6 acids instead of butane-αβδ-tricarboxylic acid and when boiled in H_2O lose CO_2 (indicating thus the presence of the $C(CO_2H)_2$ group) and yielding an unknown *acid*, $C_6H_{10}O_8$ or $C_6H_8O_7$, analysed as the *mono-* and *penta-hydrated Ca* salts. An improved method for the isolation of the $C_7H_{10}O_{10}$ acids is described. H. Wren.

Preparation of ellagic acid. M. Nierenstein (Helv. Chim. Acta, 1931, 14, 912).—Attention is directed to the author's method (J.C.S., 1921, 119, 279) of prep. of ellagic acid, the Ac_4 derivative of which has m. p. 343—346° and not 317—319° (cf. this vol., 351). H. Burton.

Polymerisation of acetaldehyde. W. H. Hatcher and B. Brodie (Canad. J. Res., 1931, 4, 574—581).—The polymerisation to paracetaldehyde of MeCHO alone or in C_6H_6 in presence of H_3PO_4 has been followed dilatometrically. At low concentrations the reaction is of the third order, but at high concentrations the reaction velocity increases with time. The velocity is directly proportional to the quantity of catalyst. Powdered glass has a slight variable influence on the reaction, but it is considered to be without theoretical significance. The equilibrium concentration of paracetaldehyde is 94·3% for the partial depolymerisation in presence of H_3PO_4.

J. D. A. Johnson.

αβ-Ethylenic straight-chain aldehydes. R. Delaby and S. Guillot-Allègre (Compt. rend., 1931, 192, 1467—1469).—β-Alkylacraldehydes are obtained by oxidation with CrO_3 of the corresponding alcohols, obtained by the isomerisation of alkylvinylcarbinols under the influence of PBr_3. Optimum conditions for oxidation are described. β-*Ethylacraldehyde* [Δ^α-*pentenal*], b. p. 125° (*semicarbazone*, m. p. 180°; p-*nitrophenylhydrazone*, m. p. 115°; β-ethylacrylic acid, m. p. 4°); β-*propylacraldehyde*, b. p. 150—152° (*semicarbazone*, m. p. 175—176°; p-*nitrophenylhydrazone*, m. p. 139°; β-*propylacrylic acid*, m. p. 33°); β-butylacraldehyde, b. p. 165—167° (*semicarbazone*, m. p. 169°; p-*nitrophenylhydrazone*, m. p. 154°), and β-iso*amylacraldehyde* (impure), b. p. 76—79°/13 mm. (*semicarbazone*, m. p. 179°; p-*nitrophenylhydrazone*, m. p. 152—156°), are described.

G. Discombe.

Conjugated double linkings. XIX. Hexadienal and octatrienal. R. Kuhn and M. Hoffer (Ber., 1931, 64, [*B*], 1977—1979; cf. A., 1930, 1406).—The isolation of homogeneous hexadienal and octatrienal from the products of the action of piperidine on a mixture of croton- and acet-aldehyde is readily effected through the $NaHSO_3$ *compounds*. Hexadienal can be distilled unchanged in NH_3 and the crude material is readily purified by the action of NH_3 in Et_2O (whereby crotonaldehyde, aldol, etc. are precipitated) and subsequent distillation; it has b. p. 173—174° (corr.)/754 mm., 64—66°/11 mm., d_D^{22} 0·9087 [*oxime*, m. p. 159·5—160·5° (corr., partial decomp.); *phenylhydrazone*, m. p. 101—102° (corr.)]. Octatrienal, m. p. 55°, readily becomes polymerised to a yellow, amorphous mass even in an indifferent gas. The aldehydes readily reduce Fehling's and Ag solution. The green coloration with Schiff's reagent, imputed to octatrienal (*loc. cit.*), is due to an impurity.

H. Wren.

Oxygen absorption by fission products of the hexoses and active catalysts thereof. L. Ahlström and H. von Euler (Z. physiol. Chem., 1931, 200, 233—245).—The rate of oxidation of dihydroxyacetone, glyceraldehyde, and methylglyoxal increases with rising p_H between 6·5 and 8. Methylglyoxal is much more slowly oxidised, but the rate is considerably increased in presence of hæmin. Oxidation of glyceraldehyde is slightly stimulated by $CuSO_4$ and not inhibited by KCN. Dihydroxyacetone and glyceraldehyde show stimulation by hæmin in pyridine, further increased by KCN. Mesohæmin ester produces slight stimulation, deuteroporphyrin ester inhibition. $FeSO_4$ produces an increase in rate, $Fe_2(SO_4)_3$ none. Mesoporphyrin hydrochloride shows inhibition with glyceraldehyde. Pyruvate oxidation is strongly stimulated by $FeSO_4$.

J. H. Birkinshaw.

Action of thiocarbimides on oximes. C. V. Gheorghiu (Ann. Sci. Univ. Jassy, 1931, 16, 389—458).—A more detailed account of work previously reviewed (A., 1927, 229). H. Burton.

Detection of acetone in presence of acetaldehyde. L. Klinc (Arh. Hemiju, 1931, 5, 212—216).—The Scott–Wilson reagent, for both $COMe_2$ and MeCHO, can be made sp. for $COMe_2$ by adding 5 c.c.

of the reagent to the solution examined, allowing the ppt. to form, adding a few c.c. of H_2O, and evaporating to half vol. 5 c.c. of Scott–Wilson acid mixture are then added, and the solution is distilled through a boiling 30% KOH solution into 5 c.c. of Scott–Wilson reagent, when a ppt. indicates the presence of $COMe_2$. Should the MeCHO content exceed 2 mg., 2 c.c. of 3% H_2O_2 should be added to the original solution together with the reagent, and the mixture is at once distilled through KOH into fresh reagent.
R. TRUSZKOWSKI.

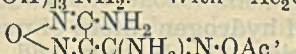
Reductions with lead–sodium [alloys]. I. F. FICHTER and I. STEIN (Helv. Chim. Acta, 1931, **14**, 1205—1211).—Alloys containing 10—30% Na reduce $COMe_2$ in dil. H_2SO_4 solution at 45° to pinacol and small quantities of one or more unstable Pb *iso*propyls. F. L. USHER.

Chemistry of the three-carbon system. XXVII. Homomesitones, $C_{10}H_{18}O$ and $C_8H_{14}O$. G. A. R. KON and E. LETON (J.C.S., 1931, 2496—2507).—The action of alkaline condensing agents on $COEt_2$ gives no homomesitones (cf. A., 1928, 1218), but evidently a cyclic *compound*, b. p. 124—128°/12—18 mm.; acid agents behave similarly. The expected condensation products, δ-*methyl*-ε-*ethyl*-Δ^{δ}-*hepten*-γ-*one*, b. p. 80°/10 mm. (*semicarbazone*, m. p. 153°), and δ-*methyl*-ε-*ethyl*-Δ^{ϵ}-*hepten*-γ-*one*, b. p. 74°/10 mm. (*semicarbazone*, m. p. 109°), are obtained synthetically from the corresponding acids. $COMePr^{a}$, in presence of NaOEt, undergoes condensation to a mixture of αβ and βγ isomerides of ξ-methylnonen-δ-ones, in the proportion of 3 : 1, *i.e.*, ξ-*methyl*-Δ^{ϵ}-, b. p. 90—92°/16 mm., and ξ-*methyl*-Δ^{η}-*nonen*-δ-*one*, b. p. 94°/18 mm., which may also be obtained from the corresponding acids. The homomesitone condenses with Et malonate to give 1-*methyl*-4-*ethyl*-1-n-*propyl*cyclo*hexane*-3 : 5-*dione*, m. p. 106°. The action of acid condensing agents on $COMePr^{a}$ gives crude ketones with branched chains, but synthesis from the corresponding acids is required to give pure products: δ-*methyl*-γ-*ethyl*-Δ^{γ}-(αβ), b. p. 83°/14 mm. (*semicarbazone*, m. p. 123°), and δ-*methyl*-γ-*ethyl*-Δ^{δ}-*hepten*-β-*one* (βγ), b. p. 69°/11 mm. (*semicarbazone*, m. p. 154°).

The equilibria and mobilities of the foregoing have been determined under standard conditions. The great influence of the α-alkyl substituent in retarding mobility and also in shifting the equilibrium towards the βγ-form is shown. It is indicated that *cis–trans*-isomerism affects the equilibration of $CMeEt{:}CMe{\cdot}COMe$ and its βγ-isomeride, and the change between the two forms of the βγ-isomeride passes through the αβ-ketone. F. R. SHAW.

Mono-methyl and -ethyl ether of dihydroxyacetone. I. S. NEUBERG (Biochem. Z., 1931, **238**, 459—460).—By oxidation of α-Me and -Et ethers of glycerol with hypobromite the corresponding ethers of dihydroxyacetone are obtained, the m. p. of the 2 : 4-dinitrophenylhydrazones being 175° and 171°, respectively. The same reaction may be carried out biochemically by fermentation with *Acetobacter suboxidans*. P. W. CLUTTERBUCK.

[Reasons for the difference in the behaviour of analogous compounds of bivalent cobalt, nickel, and copper containing diacetyldioxime.] S. PONZIO (Ber., 1931, **64**, [*B*], 2346).—A reply to Thilu and Heilborn (this vol., 938). H. WREN.

Dioximes. LXXVIII. G. LONGO (Gazzetta, 1931, **61**, 575—583).—αγ-*Diamino*-αβγ-*trioximinopropane*, m. p. 154° [Ni salt, $C_3H_6O_3N_5)_2Ni$], is prepared by the reaction $CH_2(CN)_2 \xrightarrow{HNO_2} NC{\cdot}C({:}NOH){\cdot}CN \xrightarrow{2NH_2OH} H_2N{\cdot}[C({:}NOH)]_3{\cdot}NH_2$. With Ac_2O it gives the substance  $O<\begin{matrix}N{:}C{\cdot}NH_2\\N{:}C{\cdot}C(NH_2){:}N{\cdot}OAc\end{matrix}$, m. p. 193—194° (cf. Wieland, A., 1930, 482). Dicyanoglyoxime, m. p. 145° (decomp.) [trihydrate, m. p. 98—99°; *Ac_2* derivative, m. p. 181—182°; *Bz* derivative, m. p. 143—144° (decomp.); *Bz_2* derivative, m. p. 225° (decomp.); *Na* salt; *Ag* salt], prepared by the action of KCN on dichloroglyoxime, reacts with NH_2OH giving αδ-*diamino*-αβγδ-*tetraoximinobutane*, m. p. 181—182° (decomp.) [Ac_6 derivative, darkens at 190°, m. p. 230° (decomp.)]. E. E. J. MARLER.

Bromonitroso-derivatives of oximino-compounds. I. DE PAOLINI (Gazzetta, 1931, **61**, 551—557).—The following radicals are classified with regard to their favourable effect on the reaction $CRR'{:}NOH \longrightarrow CRR'Br{\cdot}NO$ $(C_nH_{2n+1},\ RC_nH_{2n},\ CO_2Et) > (COC_nH_{2n+1},\ Bz) > (C_6H_4R,\ CO_2H,\ CN)$. Class 3 completely inhibits the reaction. The anomaly of the formation of a bromonitroso-derivative by the form of α-oximinopropionic acid which has additive properties is explained by suggesting a ψ-acid structure $-(OH)C{:}O$ (A., 1918, ii, 4), the ordinary form of the acid which forms no bromonitroso-derivative being a true carboxylic acid. E. E. J. MARLER.

Ferricyanide method for the determination of reducing sugars. Modification of the Hagedorn–Jensen–Hanes technique. A. C. HULME and R. NARAIN (Biochem. J., 1931, **25**, 1051—1061).—This modification gives a linear relation between the amount of sugar and the amount of ferricyanide reduced over a range of 0·2—3·0 mg. in the case of dextrose, lævulose, and invert-sugar, and of 0·2 to 3·5 mg. in the case of maltose. In a mixture of sugars the ferricyanide-reducing power of one sugar is unaffected by the presence of others. Invert-sugar prepared by acid hydrolysis of sucrose has a slightly higher reducing value than a mixture of equal amounts of dextrose and lævulose. Sucrose inverted by HCl hydrolysis gives accurate results. The results are high when citric acid is used. S. S. ZILVA.

Hydrazones and osazones of sugars. E. VOTOČEK and F. VALENTIN (Arh. Hemiju, 1931, **5**, 155—162).—The sugar of which a given hydrazone is a derivative can be identified by distilling the hydrazone with 12% HCl, when the production of furfuraldehyde indicates the presence of pentose, and of methylfurfuraldehyde methylpentose, whilst neither is evolved by hexoses. This reaction can be applied to determine whether the pentose or methylpentose component of a disaccharide is responsible for its reducing action. Lactosephenylosazone exhibits mutarotation in MeOH, whilst the rotation of the phenylosazone of anhyd. lactose is constant. *p*-Nitrobenzaldehyde can conveniently be substituted for PhCHO in the regeneration of sugars from their hydrazones, in view of the greater insolubility of its hydrazone. Fructosephenylmethylosazone yields the corresponding phenylosazone on heating with excess NHPh·NH$_2$, whilst with *p*-bromophenylmethylhydrazone a mixed osazone is obtained. The mutarotation of osazones is not due to tautomerism between the dihydrazone and azo-forms, as fructosephenylmethylosazone, which does not possess a labile H atom, exhibits mutarotation.

R. TRUSZKOWSKI.

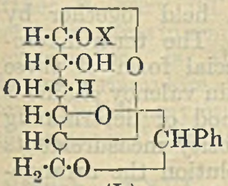
***X*-Ray examination of arabinose, xylose, and rhamnose.** E. G. Cox (J.C.S., 1931, 2313—2323).—*X*-Ray examination, by which unit cells and space-groups have been determined, indicates that β-*l*-arabinose and α-*d*-xylose [the latter described by Wherry (A., 1919, i, 65) as monoclinic] are orthorhombic, bisphenoidal, space-group Q_4. The space-group of *d*-rhamnose hydrate is C_2^2. Possible structures for arabinose and xylose are suggested and a tentative suggestion as to the configuration of the mols. in the cryst. state is put forward.

F. R. SHAW.

Alterations in the rotation and mutarotation of dextrose. I. Effect of concentrating [solutions]. H. N. NAUMANN (Biochem. Z., 1931, 239, 434—440).—When aq. solutions of pure dextrose are conc. (even slightly) at atm. pressure mutarotation occurs and persists for 3—4 hr. Concentration on the water-bath does not cause reduction in the final val. of the rotation. Concentration under reduced pressure causes mutarotation similar to that produced at atm. pressure. When evaporation is carried out under reduced pressure the temp. should not exceed 40° after the solution has become syrupy.

W. McCARTNEY.

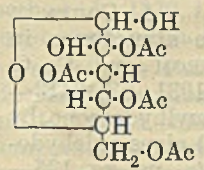
Benzylideneglucose and its application to syntheses; 1-benzoylglucose. L. ZERVAS (Ber., 1931, 64, [*B*], 2289—2296).—Interaction of dextrose and PhCHO in presence of anhyd. ZnCl$_2$ gives a mixture from which 4 : 6-*benzylidene*-α-d-*glucose* (I; X=H) m. p. 188° (corr.), $[\alpha]_D^{22}$ −4·0° in MeOH (equilibrium). It exhibits downward mutarotation and reduces Fehling's solution slowly when cold unless excess of alkali is present, rapidly when hot. According to conditions it affords a *phenylhydrazone*, m. p. 181° (corr.), or *phenylosazone*, decomp. 210° (corr.). With alkali and 1 mol. of Me$_2$SO$_4$ it gives benzylidenemethylglucoside, identical with that derived from PhCHO and β-methylglucoside. Acetylation of benzylideneglucose yields a mixture from which β-*benzylideneglucose triacetate*, m. p. 201° (corr.), $[\alpha]_D^{22}$ −51·7° in CHCl$_3$, is isolated, converted by catalytic hydrogenation into a glucose triacetate, which further yields β-glucose penta-acetate. Benzylideneglucose is sol. in aq. NaOH to a *Na* derivative (I; X=Na), $[\alpha]_D$ −19·1° (initial val.), which slowly decomposes in aq. solution, but regenerates α-benzylideneglucose if immediately acidified with AcOH. With Me$_2$SO$_4$ it affords benzylidenemethylglucoside and with Ac$_2$O almost exclusively β-benzylideneglucose triacetate. It is transformed by BzCl in anhyd. CHCl$_3$ into 1-*benzoyl*-4 : 6-*benzylidene*-β-*glucose*, m. p. 208° (corr.), $[\alpha]_D^{22}$ −44·2° in COMe$_2$, catalytically hydrogenated to 1-*benzoyl*-β-*glucose*, m. p. 193° (corr.), $[\alpha]_D^{22}$ −26·8° in H$_2$O (*tetra-acetate*, m. p. 145° (corr.); $[\alpha]_D^{21}$ −26·6° in CHCl$_3$), which is hydrolysed by technical emulsin to BzOH.



(I.)

H. WREN.

Crystalline acetates of glucosone and the products of their transformation. K. MAURER and W. PETSCH (Ber., 1931, 64, [*B*], 2011—2017; cf. A., 1929, 428).—Treatment of oxyglucal tetra-acetate in anhyd. Et$_2$O with Cl$_2$ followed by agitation of the product with NaHCO$_3$ and a little H$_2$O leads to the separation of glucosone hydrate tetra-acetate (I), whilst the filtrate when preserved deposits *glucosone hydrate triacetate* (II), m. p. 76°, $[\alpha]_D^{19}$ +104·2° to +84·2° in 40% EtOH in 14 days, which reduces cold Fehling's solution and yields glucosazone after treatment with NaOH and NHPh·NH$_2$. It is transformed by P$_2$O$_5$ at 18° or in CHCl$_3$ at 0° into *glucosone triacetate* (III), $[\alpha]_D^{21}$ +105° in 40% EtOH.



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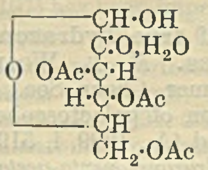

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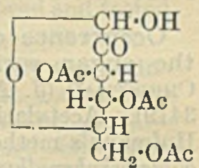
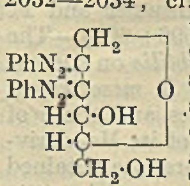


(III.)

Examination of the substances by Zerevitinov's method shows the evolution of the expected vol. of CH$_4$ when *s*-tetrachloroethane is used as solvent, whereas high results are obtained in pyridine (in which the rotation rapidly sinks to 0°) owing to the production of diacetylkojic acid; the change occurs also in aq. solution containing 1—2% of pyridine.

H. WREN.

Unsaturated reduction products of sugars. XVII. Products of the dismutation of sugars. M. BERGMANN and L. ZERVAS (Ber., 1931, 64, [*B*], 2032—2034; cf. this vol., 939). Re-examination of the phenylosazone $C_{18}H_{22}O_3N_4$ or $C_{18}H_{20}O_3N_4$ (*loc. cit.*) shows that the second formula is correct and that the substance is identical with the osazone obtained from the product of the action of hypobromite on styracitol. The annexed formula is therefore established and also the persistence of oxyglucal in the product of the hydrolysis of hydroxyglucal tetra-acetate.



H. WREN.

Dicarbonyl sugars. II. New oxidation product of dextrose. B. HELFERICH and N. M. BIGELOW (Z. physiol. Chem., 1931, 200, 263—276; cf. A., 1929, 1280).—Treatment of triacetyl-β-methylglucoseenide (I) with Pb(OAc)$_4$ in C$_6$H$_6$ gives *penta-acetyl*-β-*methylgluconoside* (II), m. p. 146—149° (decomp.), $[\alpha]_D^{20}$ −85·9°. (II) on shaking with H$_2$O yields *tetra-acetylgluconose* (III), m. p. 103—106° (slow heating), $[\alpha]_D^{20}$ −39·8°. (III) is also formed as by-product in the prep. of (I), with a *substance*, m. p. 88—90°. (III), after 10 min. hydrolysis with 0·2*N*-NaOH, affords *gluconose* (a syrup) (*bis*-p-*nitrophenylhydrazone*, m. p. 121—126°). Catalytic hydrogenation of (I) gives triacetyl-β-methyl-*d*-*iso*rhamnoside (IV) and a small amount of a *product*, $[\alpha]_D^{20}$ $-49{\cdot}0°$. Hydrolysis of (IV) in $CHCl_3$ with Na in MeOH yields β-methyl-*d-iso*rhamnoside, which when hydrolysed by 5% H_2SO_4 affords *isor*hamnose (V). Acetylation of (V) with Ac_2O and NaOAc gives β-*tetra-acetyl*iso*rhamnose* (VI), sinters at 142°, m. p. 147°, $[\alpha]_D^{20}$ $+21{\cdot}3°$. (VI) is also obtained by catalytic hydrogenation of β-tetra-acetylglucoseen. J. H. BIRKINSHAW.

Ring structure of di*iso*propylidenegalactose. P. A. LEVENE and G. M. MEYER (J. Biol. Chem., 1931, **92**, 257—262).—*Trimethyl*-d-*galactose* iso*propylidene ether*, b. p. 105°/0·3 mm., $[\alpha]_D^{20}$ $-31{\cdot}4°$ in MeOH, obtained by methylation of *d-iso*propylidenegalactose (A., 1925, i, 1043), is hydrolysed by acid to *trimethyl*-d-*galactose*, $[\alpha]_D^{20}$ $-4{\cdot}3°$ in MeOH, which is oxidised by Br and converted into *trimethyl-δ-galactonolactone*, $[\alpha]_D^{20}$ $+46{\cdot}8°$ in H_2O (*Na* salt, $[\alpha]_D^{25}$ $+29{\cdot}4°$ in H_2O). From the dextrorotation of the lactone and the rate of its formation from the free acid, mono- and di-*iso*propylidenegalactose possess a pyranose structure. A. COHEN.

Occurrence of true hydrazone structures in the sugar series. M. L. WOLFROM and C. C. CHRISTMAN (J. Amer. Chem. Soc., 1931, **53**, 3413—3419).—Acetylation of galactosephenylhydrazone by Hofmann's method (A., 1909, i, 519) gives aldehydo-*galactosephenylhydrazone penta-acetate*, m. p. 135—136°, $[\alpha]_D^{17}$ $+41{\cdot}7°$ in pyridine (cf. *loc. cit.*), also formed from *aldehydo*-galactose penta-acetate or its alcoholate (A., 1930, 1023) and NHPh·NH_2. The α-*phenyl*-α-*benzylhydrazone*, m. p. 128—129°, $[\alpha]_D^{28}$ $+91°$ in pyridine, α-*phenyl*-α-*methylhydrazone*, m. p. 138—139°, $[\alpha]_D^{28}$ $+27{\cdot}3°$ in pyridine, and the p-*nitrophenylhydrazone*, m. p. 194—195° (corr.; decomp.), $[\alpha]_D^{26}$ $+21{\cdot}2°$ in $CHCl_3$, of *aldehydo*-galactose penta-acetate are also prepared by both methods. The hydrazones are assigned open-chain structures. H. BURTON.

Carbohydrates and polysaccharides. XXXVI. Structure of the lævan synthesised by the action of *B. subtilis* on sucrose. H. HIBBERT and F. BRAUNS (Canad. J. Res., 1931, 4, 596—604).—The lævan obtained by the action of *B. subtilis* on sucrose is identical with that obtained using *B. mesentericus* (this vol., 827), its physical properties and those of the lævulose obtained by hydrolysis, of its Me_3 derivative, of the 1 : 3 : 4-trimethylfructofuranose obtained by hydrolysis of the latter, and of lævan triacetate being in agreement with those recorded for the lævan obtained using the latter culture. The necessity for the use of an ash-free lævan in methylation experiments is emphasised, the presence of 0·5% of ash leading to a methylated product insol. in $CHCl_3$ or MeI. J. D. A. JOHNSON.

Strophanthin. XXIV. Isomeric hexahydrodianhydrostrophanthidins and derivatives. W. A. JACOBS, R. C. ELDERFIELD, A. HOFFMANN, and T. B. GRAVE (J. Biol. Chem., 1931, **93**, 127—138).—Catalytic reduction (Adams) of oxidodianhydrostrophanthidin ethylal in EtOH gives mainly α-*hexahydro-oxidodianhydrostrophanthidin ethylal* (I), m. p. 128—129°, $[\alpha]_D^{20}$ $+21°$ in 95% EtOH, hydrolysed by dil. AcOH to α-*hexahydrodianhydrostrophanthidin* (II), m. p. 178—180° after softening at about 112°, $[\alpha]_D^{25}$ $+41°$ in $CHCl_3$ (*oxime*, m. p. 258—260°, formed only with difficulty); (II) reacts in the aldehydic and the lactol forms. (I) is isomerised (not homogeneously) by HCl in EtOH. Clemmensen reduction of (II) affords a *mixture*, m. p. 196—202°, of octahydrotrianhydrostrophanthidins (cf. A., 1925, i, 566), whilst the *Bz* derivative, m. p. 213—215° (*oxime*, m. p. 242—243°), of (II) gives, similarly, indefinite products. Oxidation of (II) with Kiliani's CrO_3 solution in AcOH yields mainly a *dilactone* (III), $C_{23}H_{32}O_4$, m. p. 192—194°, $[\alpha]_D^{26}$ $+19{\cdot}4°$ in $CHCl_3$, and a little of the isomeric hexahydrodilactone (IV), m. p. 265—267°, previously described (A., 1926, 73); (III) is converted into (IV) by HCl in AcOH. Re-investigation of the reduction of the dianhydrodilactone, $C_{23}H_{26}O_4$ (*loc. cit.*), shows that (IV) and an *isomeride*, m. p. 196—199° (from EtOH), 204° (from Et_2O), $[\alpha]_D^{26}$ $+18°$ in $CHCl_3$, are produced. Catalytic reduction (Adams) of anhydrodihydrostrophanthidin (*Bz* derivative, m. p. 190—192°) in EtOH proceeds with difficulty, giving *dihydroanhydrodihydrostrophanthidin*, m. p. 217—219°, $[\alpha]_D^{20}$ $+28°$ in pyridine, converted by EtOH containing 5% of HCl into *dihydro-oxidodianhydrodihydrostrophanthidin ethylal*, m. p. 174—176°, $[\alpha]_D^{25}$ $-108°$ in $CHCl_3$. This is hydrolysed to *dihydrodianhydrodihydrostrophanthidin*, m. p. (indef.) 247° after softening above 215°, and reduced catalytically (Pt or Pd) to β-*hexahydro-oxidodianhydrostrophanthidin ethylal*, m. p. 131—132°, $[\alpha]_D^{24}$ $+13{\cdot}4°$ in EtOH. Hydrolysis of this affords β-*hexahydrodianhydrostrophanthidin* (V), m. p. 155—156° after softening, $[\alpha]_D^{20}$ $+20°$ in $CHCl_3$ [*oxime*, m. p. 262° after softening; *Bz* derivative, m. p. 209—211° (*oxime*, m. p. 252°)], which also reacts in aldehydic and lactol forms. Oxidation of (V) (as II) gives mainly IV.

The results of Windaus *et al.* (A., 1926, 73) on the reduction of dianhydrostrophanthidin could not be confirmed. H. BURTON.

Structure of highly-polymerised compounds. K. H. MEYER and H. MARK (Ber., 1931, 64, [*B*], 1999—2002).—The authors and Staudinger agree in the view that highly-polymerised, natural materials consist of long, chain-like mols. held together by normal, chemical main valencies. The term macromols. scarcely expresses the special form of these structures. The length of the main valency chains is controversial; Staudinger's method of determining mol. wt. by extrapolition of viscosity measurements does not find acceptance. In solution the arrangements are very complicated and, in general, neither homogeneous micelles nor isolated main valency chains are present. It is beyond doubt that, owing to the marked action of the solvent, the dissolved particles differ from the micelles in the solid state and the propriety of speaking of "dissolved micelles" is doubtful. Causes other than cracking are operative in causing dependence of viscosity of solutions on temp. Staudinger's criticisms of changes in the authors' point of view and his historical treatment of the subject are discussed. H. WREN.

Starch. XXV. Diamylose and tetra-amylose; triamylose and hexa-amylose. H. PRINGSHEIM, A. WEIDINGER, and H. SALLENTIEN (Ber., 1931, 64, [*B*], 2117—2125).—Mainly a re-investigation of the substances in consequence of the criticisms of Miekeley

(A., 1930, 1414), in agreement with whom the val. $[\alpha]_D^{20}$ + 148° in H_2O for α-tetra-amylose is accepted. The substance loses H_2O and EtOH of crystallisation very slowly and on desiccation yields a product of approx. const. wt. with the composition $C_6H_{10}O_5,0·5H_2O$. Diamylose has $[\alpha]_D^{20}$ +136° in H_2O, the val. being unchanged by intensive desiccation. Under like conditions, α-hexa-amylose has $[\alpha]_D$ +136°. Repeated crystallisation of diamylose from H_2O leads to its conversion into tetra-amylose. This effect is not due to the heating in H_2O. Tetra- and di-amylose when cryst. from aq. EtOH retain about 2% of EtOH, the presence of which is not betrayed by cryoscopic determinations of mol. wt.; it must therefore be firmly combined in the mol. It is removed when aq. solutions of the carbohydrates are boiled or when the substances are intensely desiccated. Tetra-amylose then remains as tetra-amylose, whereas di- is converted into tetra-amylose. Similarly, α-amylosan is stabilised by a slight EtOH content. Miekeley's production of two acetates from tetra-amylose is due to degradation by either method resulting in diamylose acetate, hydrolysed to diamylose, which is converted by H_2O into tetra-amylose. Re-examination of the difference between tri- and β-hexa-amylose is rendered difficult by the sparing solubility in H_2O, which is too small to permit direct determination of mol. wt. A difference between $[\alpha]_D$ for these compounds similar to that now established between di- and tetra-amylose has been noted. Triamylose acetate, $[\alpha]_D^{20}$ +120° in $CHCl_3$, and β-hexa-amylose acetate, $[\alpha]_D^{20}$ +143° in $CHCl_3$, differ distinctly in solubility in PhMe. The acetate of the hexa-compound appears to be present in AcOH and PhOH as that of the tri-substance. In C_6H_6 hexa-amylose acetate persists, whereas the triamylose derivative gives uncertain vals. In camphor the triamylose derivative behaves non-uniformly, whereas the hexa-amylose compound exhibits the corresponding mol. wt. In $C_{10}H_8$ and dioxan the hexa- is transformed into the tri-compound. In $CHBr_3$ the triacetate passes into the hexa-stage or further in very dil. solution, whereas the hexa-acetate remains in a much greater state of aggregation. Hexa-amylose is almost tasteless and "dark," whereas triamylose tastes sweet and "bright." Tetra- and di-amylose are almost equally sweet, but the former is "brighter" and the latter "darker."

H. Wren.

Starch. XXVI. New polyamyloses. H. Pringsheim, A. Weidinger, and P. Ohlmeyer (Ber., 1931, **64**, [*B*], 2125—2130).—α-Tetra-amylose, dried over P_2O_5 at 78°, passes in boiling formamide into α-allo*amylosan*, $C_6H_{10}O_5$, $[\alpha]_D^{20}$ +139° in H_2O; β-allo*amylosan*, $[\alpha]_D^{20}$ +146° in pyridine–H_2O (7 : 3), is derived similarly from β-hexa-amylose. The substances show the typical polyamylose property of giving with org. solvents, *e.g.*, C_2HCl_3, additive products sparingly sol. in H_2O. The iodo-product of the α-series is depicted, whereas that of the β-compound could not be obtained homogeneous. When heated with H_2O both compounds pass into the colloidal state. α-allo*Amylosan acetate*, $[\alpha]_D^{20}$ +112° in $CHCl_3$, and β-allo*amylosan acetate*, $[\alpha]_D^{20}$ +124° in $CHCl_3$, both trimeric in dioxan, are described. β-Hexa-amylose, dried until const. in wt., has $[\alpha]_D^{20}$ +159° in H_2O, increased to +172° by further heating, and subsequently remaining const. After crystallisation from H_2O or aq. EtOH, $[\alpha]_D^{20}$ sinks to +159° and cannot again be raised by further heating. Similar observations are recorded for α- and β-*iso*amylosan, but not for the amylosans. α-Amylosan is very faintly sweet, almost tasteless, whereas β-amylosan is decidedly sweet. α-Amylosan is transformed by AcBr into acetobromomaltose, converted by Ag_2CO_3 in EtOH into maltose hepta-acetate, m. p. 178—179°, $[\alpha]_D^{20}$ + 76° in $C_2H_2Cl_4$; β-amylosan behaves similarly, but yields the biose acetate in smaller amount. The amylosans and *iso*amylosans are not fermented by the α-glucosidase of yeast, the β-glucosidase of emulsin, or malt amylase; takadiastase affects the β-compounds much more readily than those of the α-series.

H. Wren.

Iodometric determination of starch by Paloheimo's method. L. Paloheimo and I. Paloheimo (Biochem. Z., 1931, **238**, 391—400).—The authors' method (A., 1930, 1167) has been improved and tested under various conditions. P. W. Clutterbuck.

Use of the Pulfrich photometer in the iodometric determination of starch. L. Paloheimo and I. Antila (Biochem. Z., 1931, **238**, 401—407).—Comparative determinations were carried out, using the simplified spectrophotometer of Heilmeyer and Krebs (A., 1930, 1201) and the authors' dilution method (*ibid.*, 1167). The former is simpler in that standard solutions are not used, but if a colour-filter is employed instead of the standard, the methods are equally simple. P. W. Clutterbuck.

Plant colloids. XXX. Phosphorus-containing degradation products of potato-starch. M. Samec [with S. Seliškar and V. Zitko] (Kolloid-chem. Beih., 1931, **33**, 449—459).—An examination of several methods of isolating derivatives of starch rich in P indicates that the best yield is obtained by the procedure of Northrop and Nelson (A., 1916, i, 373). Experiments with one of these derivatives showed its mol. size and P content to lie between the vals. for a compound of H_3PO_4 with a di- and a tri-saccharide. Electrometric and conductometric titration gave two discontinuities in the neutralisation curve, as with H_3PO_4, and the same behaviour is shown by potato-amylopectin. E. S. Hedges.

Glycogen. II. Preparation of glycogen from yeast, and identity of glycogen from different sources. III. Nature of the carbohydrate constituents of the cell membrane of yeast. K. M. Daoud and A. R. Ling (J.S.C.I., 1931, **50**, 365—368T, 379—382T).—II. The method of preparing glycogen from yeast is much the same as that described by Ling, Nanji, and Paton (A., 1925, i, 1011) up to the stage at which the mannan is precipitated with Fehling's solution. The filtrate from the Cu cloth is then rendered slightly acid with HCl and the Cu removed by dialysis in running H_2O for 6 days. The final product was a white powder containing 1·59% of ash; $[\alpha]_D$ (corrected for ash)+179°. The authors have compared glycogen prepared from yeast by Harden and Young's method (J.C.S., 1902, **81**, 1224; 1912, **101**, 1928); prepared from yeast by their own method; prepared from liver, and prepared from horse-flesh. They conclude that glycogen from different sources is identical, and that the differences in [α], opalescence of solutions, and coloration with I are probably to be explained by differences in the degree of esterification with H_3PO_4 and of polymerisation.

III. Repeated extraction of dried yeast with boiling 2% NaOH yielded an insol. residue, having moisture 12·95, ash 7·2, protein 13·6, carbohydrate (by difference) 66·16%. The nitrogenous matter is of the nature of protein; chitin is absent. The carbohydrate constituents of yeast-cell membrane are glycogen and mannan, partly esterified with phosphoric and silicic acids and thus rendered insol. Glycogen and mannan are probably the only reserve polysaccharides of the plasma, and they are utilised in building up the membrane of the yeast-cell, this being in accordance with Becker's observation on the thickening of the yeast-cell membrane in a highly conc. wort.

Action of Grignard reagent (magnesium methyl iodide) on cellulose. F. C. Wood (J.S.C.I., 1931, 50, 257—258T).—Hydrocellulose dried over P_2O_5 at room temp., or ordinary cotton cellulose dried at 120°, does not react with MgMeI in Et_2O at room temp. or in $NPhMe_2$ at 120°. It is very difficult to free the material from Mg; as much as 15% of MgO was found in one sample ashed. If any compound be formed it is of the additive type and does not involve the elimination of gaseous hydrocarbon.

Production and solubility of different highly hydrolysed cellulose acetates. A. Deripasko (Cellulosechem., 1931, 12, 254—263).—Secondary cellulose acetate sol. in $COMe_2$ is obtained from the primary (sol. in $CHCl_3$) material by treatment of the acetylation product with H_2O or dil. AcOH at const. temp. This process is described as hydrolysis. When insufficient H_2O to convert the residual Ac_2O into AcOH is added, a secondary acetate richer in OAc than the original primary acetate is obtained, but with larger amounts of H_2O a product poorer in OAc is formed. The OAc content also falls with increasing time of hydrolysis. High OAc content is accompanied by low H_2SO_4 content and *vice versa*, and the higher OAc content is ascribed to the greater solubility or the quicker decomp. of the cellulose sulphuric ester present. The stability of secondary acetates increases with decreasing H_2SO_4 content. Hydrolysis with larger amounts of H_2O gives products of high viscosity. When 7½% instead of 15% of H_2SO_4 is used as catalyst in preparing the primary acetate the effect of concentration of the hydrolysis mixture on the viscosity of the secondary acetate is the same, but the rate of hydrolysis is very slow and must be accelerated by the addition of more H_2SO_4. Secondary acetates are sol. in $COMe_2$ when the yield of AcOH is between 60 and 49%. Technical cellulose acetates are manufactured by nearly identical processes and have nearly the same chemical composition and solubility. Factors governing the solubility in different solvents (H_2SO_4 content, particle size, etc.) are discussed, and results of an investigation of solubility by titrating $COMe_2$ solutions of the acetates with org. liquids that have no solvent power for the acetate show that this varies with the OAc content. B. P. Ridge.

Lignin. III. Sulphonation in the hydroaromatic series. Preparation of *cyclo*hexanol-*o*-sulphonic acid. IV. Reaction of phenolic derivatives with acetic anhydride–acetic acid–sulphuric acid. H. Friese.—See this vol., 1286, 1289.

Lignin. Action of bromine on lignin from pine wood. A. Friedrich and E. Pelikan (Biochem. Z., 1931, 239, 461—472; B., 1926, 151).—When pine-wood lignin is brominated 30% of its OMe content is lost, and since no elimination of OMe takes place, it follows that rearrangement occurs. The OMe groups which do not undergo this change must be in a different form of combination from those which do. Four bromination products can be isolated. Of these, two, which constitute 90% of the yield, are similar in composition but differ in their solubility in AcOH. The other two also contain Br and OMe, but differ in composition from the chief products. Of the Br taken up by lignin only 28% is firmly bound; any Br above this amount is removed by alkylation, and when the alkylated lignin is again brominated the amount of Br taken up is less than that originally absorbed. W. McCartney.

Pine-wood lignin. B. Rassow and H. Gabriel (Cellulosechem., 1931, 12, 249—254; cf. this vol., 1041).—Lignin is most probably formed by the condensation of coniferyl alcohol and aldehyde, and is therefore aromatic. The presence of an aromatic complex explains the fact that lignin has a higher C content than has cellulose. On this assumption, and from certain analytical results, a structural formula for glycol-lignin is deduced (corresponding with $C_{30}H_{34}O_{10}$) which shows that this substance should have 3 OMe groups, mol. wt. 554, and a OMe content of about 17%, and the experimentally determined values for the C, H, O, and OMe contents of this substance are in agreement with the calc. vals. Extraction of the wood with numerous solvents and examination of the extracts and residues by means of the phloroglucinol test show that it is impossible to effect complete separation of the substance sensitive to this reaction, and it is therefore highly probable that lignin is identical with this substance. By treatment of wood with cuprammonium solution a product much richer in lignin can be obtained. Glycerol gives a red coloration with phloroglucinol, but this may be distinguished from that given by lignin by its behaviour towards NaOH and conc. H_2SO_4. B. P. Ridge.

Lignin, coniferyl alcohol, and saligenin. K. Freudenberg, F. Sohns, W. Dürr, and C. Niemann (Cellulosechem., 1931, 12, 263—276).—The results of optical and *X*-ray investigations of wood and cellulose in connexion with the ultimate structure and morphology of wood fibres and lignin show that the earlier conceptions of the structure of lignin are justified. In the formation of lignin two stages are assumed, first condensation of (on the average) 12 mols. of hydrated γ-3 : 4 dihydroxyphenyl-αβ-propylene glycol to form a chain in which the free phenolic groups may be methylated, and, secondly, conversion of these chains into larger aggregates by polymerisation or condensation, which occurs as a result of chemical action or of a *post-mortem* process. The assumed structure—especially its aromatic and permutoid character—is supported by the results of investigations with coniferyl and salicylyl alcohols. The formation of cellulose is also discussed.

B. P. Ridge.

Action of magnesium ethyl bromide on chloroacetdiethylamide. S. P. Ti (Compt. rend., 1931, **192**, 1462—1466).—The reaction product of MgEtBr and $CH_2Cl·CO·NEt_2$ (this vol., 77) is diethyl-β-hydroxy-β-ethylbutylamine (obtained also from $NHEt_2$ and the corresponding chlorohydrin) (*acetate*, b. p. 97—98°/13 mm.; *phenylurethane*, m. p. 78°; *picrate*, m. p. 130—131°), dehydrated by $SOCl_2$, PCl_5, and 48% HBr to *diethyl-γ-methyl-Δ^β-pentenylamine*, b. p. 169° (*picrate*, m. p. 74°; *chloroplatinate*, m. p. 142—143°; *chloroaurate*, m. p. 100—102°), and *diethyl-β-ethyl-Δ^α-butenylamine* decomposed at once to $CHEt_2·CHO$ and $NHEt_2$. G. Discombe.

Synthesis of methionine. G. Barger and T. E. Weichselbaum (Biochem. J., 1931, **25**, 997—1000).—The product of interaction of Et sodiophthalimidomalonate and β-chloro-α-methylthiolethane was hydrolysed with NaOH to the phthalamidomalonic acid and then with HCl to methionine. The yield was 58% against 6% obtained by Strecker's method (A., 1929, 175). S. S. Zilva.

Resolution of synthetic methionine. W. Windus and C. S. Marvel (J. Amer. Chem. Soc., 1931, **53**, 3490—3494).—The *formyl* derivative, m. p. 99—100°, of *dl*-methionine (A., 1930, 1026) (*Bz* derivative, m. p. 143—145°) is resolved by brucine into *d*-, $[\alpha]_D^{25}$ +10·62±0·5° in H_2O (*brucine* salt, m. p. 144—145°), and l-*formylmethionines*, $[\alpha]_D^{25}$ −10·0±0·5° in H_2O. These are hydrolysed by 10% HCl to *d*-, $[\alpha]_D^{25}$ +8·12—8·76±0·5° in H_2O, and l-*methionine*, $[\alpha]_D^{25}$ −7·5 to −8·11±0·5° in H_2O (p-*tolylcarbimide* derivative, m. p. 157—158°). H. Burton.

Fungus poisons. I. Muscarine. I. F. Kögl, H. Duisberg, and H. Erxleben (Annalen, 1931, **489**, 156—192).—A physiological method of determining muscarine, based on its influence on the heart-beats of the frog, is described. With its aid pure muscarine is isolated, new steps in the purification being the removal of other bases by filtration through permutit, and precipitation and crystallisation of its salt with the radical $[(NH_3)_2Cr(SCN)_4]'$, analysis of which indicates the formula $[C_8H_{18}O_2N]^+$ for the muscarine ion. The *chloroaurate* is also described. Muscarine is unaffected by 0·1*N*-NaOH in N_2, or by H_2 and PtO_2–Pt at room temp.; it is stable to air at p_H 9·8, but not at p_H 4·0. It contains an OH group [*benzoylmuscarine chloroplatinate*, m. p. 256—257° (decomp.)], and gives the Schiff and Angeli–Rimini aldehyde reactions. The Hofmann degradation (Ag_2O on the chloride) gives NMe_3, an unidentified volatile substance, m. p. 70°, and d-αβ-*dihydroxy*-n-*valeric acid*, m. p. 72°, $[\alpha]_D^{20}$ +180·7° in H_2O [p-*phenylphenacyl* ester, m. p. 207°; identified by direct comparison (mixed m. p. and $[\alpha]_D$) with the *l*-isomeride]. Muscarine is therefore considered to be $OH·CHEt·CH(CHO)·NMe_3·OH$ or $CHO·CH(OH)·CHEt·NMe_3·OH$, probably the former on account of its stability to alkalis; the formation of a carboxylic acid in the Hofmann degradation is due to the oxidising action of the Ag_2O. *dl*-αβ-Dihydroxy-*n*-valeric acid (p-*phenylphenacyl* ester, m. p. 207°), obtained by oxidation of Δ^α-pentenoic acid with $AgClO_3$–OsO_4 (cf. A., 1930, 1271), was resolved by means of its brucine salt, but only the l-*acid*, m. p. 72° (*brucine* salt, $[\alpha]_D^{20}$ −260·8° in $CHCl_3$; p-*phenylphenacyl* ester, m. p. 207°), was obtained optically pure. β-*Methyl-αβ-dihydroxybutyric acid*, m. p. 94° (p-*phenylphenacyl* ester, m. p. 182°), was prepared by the action of boiling 0·4*N*-KOH on Et dimethylglycidate (this vol., 604), and *αγ-dihydroxybutane*-β-*carboxylic acid*, m. p. 167°, obtained by reduction of Et hydroxymethyleneacetoacetate with Na and EtOH, were also synthesised for comparison.

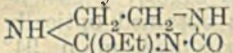
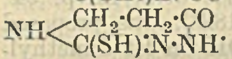
H. A. Piggott.

Hydrolysis of chitin by hydrochloric acid. I. L. Zechmeister and G. Toth (Ber., 1931, **64**, [*B*], 2028—2032).—When chitin is treated for 15 hr. at 20° with aq. HCl saturated at 0° the yields are approx. 25% of acetylglucosamine, 15% of material insol. in H_2O, but sol. in dil. acids, and 60% of intermediate fractions of complex composition which immediately give horny, amorphous products. Mild acetylation of them in pyridine yields a mixture of cryst. acetates of which the simplest member is a biose octa-acetate, $C_{28}H_{40}O_{17}N_2$, m. p. 305° (corr.), $[\alpha]_D$ +55° in AcOH, probably identical with the chitobiose octa-acetate of Bergmann and others (this vol., 250) and characterised by free solubility in cold $CHCl_3$. More complex cryst. acetates sparingly sol. in cold $CHCl_3$ and with lower $[\alpha]_D$ have been isolated. H. Wren.

Formation of glycine from serine. B. H. Nicolet (Science, 1931, **74**, 250; cf. this vol., 638).—The mechanism is discussed. No glycine has been detected when cysteine is hydrolysed with alkali.

L. S. Theobald.

Physico-chemical behaviour of polypeptides derived from *l*(+)-alanine. E. Abderhalden and W Gohdes (Ber., 1931, **64**, [*B*], 2070—2073).—*l*(+)-Alanine polypeptides have been prepared from *l*(+)-alanine and *d*(+)-α-bromopropionyl chloride. Compounds more complex than *d*-α-bromopropionyl-di-*l*-alanyl-*l*-alanine are extraordinarily voluminous and gelatinous and, after desiccation, swell to some extent in H_2O. The penta- and hexa-peptides are obtained exclusively as strongly swollen, hydrated gels from H_2O or aq. NH_3; this behaviour is not shown by the corresponding glycine peptides. They are markedly hygroscopic and retain $1H_2O$ which cannot be removed by desiccation in high vac. without alteration to the polypeptide. Marked diminution in solubility is exhibited by the tetrapeptide; the penta-compound is sparingly sol. and the hexapeptide completely insol. in H_2O. Decrease in solubility is accompanied by increase in colloidal properties which predominate in the case of the pentapeptide and are exclusive with the hexa-derivative. The colloidal particles are negatively charged. The following vals. are recorded for $[\alpha]_D^{20}$ in 2*N*-HCl; *l*-alanine, +14·5°; *l*-alanyl-*l*-alanine, −37·6°; di-*l*-alanyl-*l*-alanine, −77·5°; tri-*l*-alanyl-*l*-alanine, −115°; tetra-*l*-alanyl-*l*-alanine, −133°. H. Wren.

***cis–trans* Isomerism in ethyl carbethoxythiocarbamate. Synthesis of four-, five-, six-, and seven-membered heterocyclic compounds from ethyl carbethoxythiocarbamate.** P. C. Guha and N. C. Dutt (Proc. XV Indian Sci. Cong., 1928, 157).—Et carbethoxythiocarbamate, m. p. 144°, is converted by boiling with dil. aq. HCl into a form, m. p. 44°; with ethylenediamine the latter gives  $\mathrm{NH}{<}\begin{array}{l}\mathrm{CH_2{\cdot}CH_2{-}NH}\\ \mathrm{C(OEt){:}N{\cdot}CO}\end{array}$ and the former gives  $\mathrm{NH}{<}\begin{array}{l}\mathrm{CH_2{\cdot}CH_2{\cdot}CO}\\ \mathrm{C(SH){:}N{\cdot}NH}\end{array}$. Chemical Abstracts.

Guanidine and nitrous acid. I. W. D. Bancroft and B. C. Belden (J. Physical Chem., 1931, 35, 2684—2688).—Treatment of a cold, acid solution of guanidine with N_2O_3 yields cyanamide. The product obtained after a 73% conversion contained no carbamide, cyanide, or dicyanodiamide. L. S. Theobald.

Extension of Michael's reaction. P. C. Guha and M. N. Chakladar (Proc. XV Indian Sci. Cong., 1928, 150).—Compounds, *e.g.*, $CS(NRNa){\cdot}CH(CO_2Et)_2$, formed from thiocarbimides and Na derivatives of Et acetoacetate, malonate, and cyanoacetate are easily decomposed by acids to yield compounds of the general formula NHR·CSMe, CO_2, and alcohol. Carbimides afford compounds NHR·COMe. Chemical Abstracts.

Isomerism of hydrocyanic acid. L. Reichel and O. Strasser (Ber., 1931, 64, [*B*], 1997—1999).—Comparison of the absorption spectra of *iso*amyl cyanide and -carbylamine and HCN in *n*-heptane shows that the acid exists mainly in the nitrile form. H. Wren.

Valency problem of boron. VI. Valency manifestations of boron in boron tri-*p*-anisyl, tri-*tert*.-butyl, and tri-*sec*.-propyl. Possible existence of mixed boron trialkyls. E. Krause and P. Nobbe (Ber., 1931, 64, [*B*], 2112—2116).—*Boron tri*-p-*anisyl*, m. p. 128° (vac., corr.), from Mg, *p*-bromoanisole, and BF_3 in Et_2O, forms an additive *product*, $C_{21}H_{24}O_3NBr$, m. p. 191° (decomp.), with NH_3, combines with pyridine and Na, and is converted by air into boron tri-*p*-anisyl oxide. BF_3 and Mg-*tert*.-BuCl in Et_2O afford *B tri*-tert.-*butyl*, b. p. 71°/12 mm., readily oxidised by air, which does not unite with Na and gives a non-cryst. *ammonate* which loses NH_3 at about 85°/atm. It is transformed by regulated oxidation into tert.-*butylboric acid*, m. p. 113° (corr.), stable to light and air. *B tri*-sec.-*propyl*, b. p. 33—35°/12 mm., resembles the *tert*.-butyl derivative. BPhO and MgEtBr react vigorously and the product when distilled gives BEt_3 and BPh_3. The prep. of suitable mixed B trialkyls appears possible, but there is a very pronounced tendency towards the the production of symmetrical compounds. H. Wren.

Applications of thallium compounds in organic chemistry. VI. Thallium and dialkylthallium derivatives of tetra-acetylethane and tetra-acetylpropane. R. C. Menzies and E. R. Wiltshire (J.C.S., 1931, 2239—2243).—*Thallium, dimethylthallium,* and *diethylthallium tetra-acetylethane* decompose when heated, are sol. in H_2O, but not in organic solvents, and hence belong to the type of salts (cf. Sidgwick and Brewer, A., 1926, 71), whereas thallium and *dimethylthallium tetra-acetylpropane*, m. p. 98°, behave as chelate compounds. The decreased stability of the non-alkylated compound as compared with the alkylated one may be due to a diminution of the labile co-ordinating capacity of the metal in the latter case. F. R. Shaw.

Reaction between tin trimethyl hydroxide and methyl iodide. T. Harada (Bull. Chem. Soc. Japan, 1931, 6, 240—241).—The compound $(SnMe_3)_3OI,H_2O$, previously obtained from $SnMe_3OH$ and $SnMe_3I$ (A., 1925, i, 1254; 1927, 685), is also formed from $SnMe_3OH$ (2 mols.) and MeI (1 mol.) in Et_2O (cf. A., 1930, 1565); conductivity measurements indicate that it is a salt. H. Burton.

Hydrocarbons, benzylidene*cyclo*hexane, and 1-benzyl-Δ^1-*cyclo*hexene. D. Kursanov (Ber., 1931, 64, [*B*], 2297—2301).—PhCHO and Mg *cyclo*hexyl bromide afford phenyl*cyclo*hexylcarbinol with considerable amounts of $CH_2Ph{\cdot}OH$. The K derivative of the carbinol and CS_2 afford *K* cyclo*hexylbenzyl xanthate*, $C_6H_4{\cdot}CH(CH_2Ph){\cdot}O{\cdot}CS_2K$ (corresponding *Pb* salt), transformed by MeI in C_6H_6 into the *Me* ester, m. p. 54—55°. The last-named compound decomposes at 160—175°/15 mm. into *benzylidene*cyclo*hexane*, b. p. 117—118·5°/10 mm., the structure of which is confirmed by its oxidation to *cyclo*hexanone and BzOH. The hydrocarbon differs from the isomeric product, b. p. 127·2—128·4°/15 mm., derived from $CH_2Ph{\cdot}OH$ and *cyclo*hexene, and P_2O_5, which must therefore be regarded as benzyl-Δ^1-*cyclo*hexene (cf. A., 1915, i, 789). H. Wren.

Catalytic hydrogenation of aromatic hydrocarbons under high pressure and high temperature. I. Kagehira (Bull. Chem. Soc. Japan, 1931, 6, 241—254).—Hydrogenation of aromatic hydrocarbons in presence of 8% of their wt. of reduced Ni is studied. C_6H_6 at 200°/76 atm. (all pressures quoted are the initial pressures at 0°) gives an almost quant. yield of *cyclo*hexane. Similarly, Ph_2 at 200°/95 atm. affords di*cyclo*hexyl (I), but at 250°/95 atm. phenyl*cyclo*hexane is produced [by dehydrogenation of (I)]. $C_{10}H_8$ at 200°/91 atm. yields tetrahydronaphthalene, reduced further at 160°/91 atm. to a mixture of 90% of *cis-* and 10% of *trans*-decahydronaphthalenes. Decahydroacenaphthene is obtained at 200°/94 atm., but at 270°/102 atm. tetrahydroacenaphthene results. Anthracene at 200°/97 atm. gives a mixture of octa- (1 pt.), solid (m. p. 60·5—61°) *tetradeca-* (3 pts.), and liquid (b. p. 150—155°/13 mm.) *tetradeca*-hydro-derivatives (2 pts.), whilst phenanthrene (containing a trace of a S compound) at 260°/83 atm. affords only 6% of tetrahydrophenanthrene. This is reduced at 175°/87 atm. to mainly octa- (II) and a little tetradeca-hydrophenanthrene (III); (III) is obtained from (II) in 13% yield at 160°/77 atm. Pyrene is reduced at 300°/82 atm. to hexahydropyrene, which at 210°/92 atm. gives decahydropyrene, converted at 240°/107 atm. into a mixture of isomeric *hexadecahydropyrenes*, m. p. 87—88° and b. p. 162—166°/9·5 mm. H. Burton.

Nitration of benzene. P. S. Varma and K. A. Joshi (Proc. XV Indian Sci. Cong., 1928, 151).—The

presence of Sn during nitration of C_6H_6 by HNO_3 in absence of H_2SO_4 slightly increases the yield of $PhNO_2$.
CHEMICAL ABSTRACTS.

Diphenyl series. C. COURTOT and C. C. LIN (Bull. Soc. chim., 1931, [iv], 49, 1047—1065).—Sulphonation of 4 : 4′-dibromodiphenyl with $ClSO_3H$ in $CHCl_3$ affords 4 : 4′-*dibromodiphenylene*-2 : 2′-*sulphone*, m. p. 315°, and 4 : 4′-*dibromodiphenyl*-3-*sulphonic acid* (Ca and Na salts; *chloride*, m. p. 131°; *amide*, m. p. 200°); with $ClSO_3H$ alone at 60°, 42% of 4 : 4′-dibromodiphenylenesulphone, 41·5% of 4 : 4′-*dibromodiphenyl*-3 : 3′-*disulphonic acid* (*Na* salt; *diamide*, m. p. 332°), and 12·5% of 4 : 4′-*dibromodiphenyl*-3 : 3′-*disulphonyl chloride*, m. p. 210°, are obtained. Sulphonation with H_2SO_4 at 80° for 4 hr. yields the same disulphonic acid; with 16% oleum, 21% of 4 : 4′-dibromodiphenylenesulphone, 21% of an isomeric *sulphone*(?), sinters about 450°, and 45% of the 3 : 3′-disulphonic acid; and with 30% oleum, 73% of the 3 : 3′-disulphonic acid and 13·5% of a 4 : 4′-*dibromodiphenylenesulphonedisulphonic acid* (?3 : 6) (*Na* salt). 4 : 4′-Dibromodiphenylenesulphone, m. p. 315°, is not identical with the product obtained by bromination of diphenylene sulphide and oxidation (A., 1928, 896), and since with 22% aq. NH_3 in presence of Cu_2Cl_2 at 250° for 10 hr. it is converted into 4 : 4′-diaminodiphenylenesulphone, m. p. 327—328° (Ac_2 derivative, m. p. 406—407°; Bz_2 derivative, m. p. 413—414°), affording diphenylenesulphone on diazotisation and decomp. with EtOH, the latter must be the 3 : 3′-Br_2-derivative. 75% yields of diphenyl are obtained by Job and Reich's method from PhBr and Mg in presence of $FeCl_3$, and a 95% yield of 4 : 4′-dibromodiphenyl on aq. bromination.

The following are obtained from the corresponding benzidinesulphonic acids by the Sandmeyer reaction; yields of 95—98% for the I-, 80—85% for the Br-, and 65—70% for the Cl-derivatives are obtained: 4 : 4′-*dichloro-acid* (Na salt; *dichloride*, m. p. 148°; *diamide*, m. p. 308°), 4 : 4′-*dibromo-* (Na salt; *dichloride*, m. p. 190°; *diamide*, m. p. 296°), and 4 : 4′-*di-iodo-diphenyl*-2 : 2′-*disulphonic acid* (*dichloride*, m. p. 232°; *diamide*, m. p. above 400°); 4 : 4′-*dichloro-* (Na salt; *dichloride*, m. p. 172°; *diamide*, m. p. 286—287°), 4 : 4′-dibromo-, and 4 : 4′-*di-iodo-diphenyl*-3 : 3′-*disulphonic acid* (Na salt; *dichloride*, m. p. 254°; *diamide*, m. p. 316°); 4 : 4′-*dichloro-* (Na salt; *chloride*, m. p. 104°; *amide*, m. p. 189°), 4 : 4′-dibromo-, and 4 : 4′-*di-iodo-diphenyl*-3-*sulphonic acid* (Na salt; *chloride*, m. p. 157°; *amide*, m. p. 192°).
R. BRIGHTMAN.

Action of aliphatic oxides on aromatic compounds. Preparation of substituted dibenzyls. R. A. SMITH and S. NATELSON (J. Amer. Chem. Soc., 1931, 53, 3476—3479).—Addition of ethylene oxide (1 mol.) to a mixture of $AlCl_3$ (1 mol.) and C_6H_6 (6 mols.) gives dibenzyl (65%) and β-phenylethyl alcohol (5%) (cf. A., 1925, i, 1278). 4 : 4′-Dibromodibenzyl is prepared similarly from PhBr in 70% yield. Propylene oxide and C_6H_6 afford α-methyldibenzyl (46%) and α-phenyl*iso*propyl alcohol (8%); with PhBr 32% of 4 : 4′-*dibromo-α-methyldibenzyl*, m. p. 95°, is produced.
H. BURTON.

Action of bromine on substituted ethylenes. F. ARNDT and L. LORENZ (Ber., 1931, 64, [*B*], 2073—2075; cf. this vol., 234).—A reply to Bergmann (A., 1930, 1569; this vol., 949).
H. WREN.

Naphthalene model. N. NAKATA (Ber., 1931, 64, [*B*], 2059—2069).—Measurements of the dipole moments of a series of derivatives show that only the α-positions in the $C_{10}H_8$ mol. are truly aromatic. Substituents in the β-position are in aliphatic or less markedly aromatic union, thus explaining the difference between 2 : 3-dihydroxy- and other *o*-dihydroxy-naphthalenes. Centrosymmetry, ascribed to the $C_{10}H_8$ mol., is exhibited by 1 : 5-difluoro-, 1 : 4-dichloro-, 1-bromo-5-nitro-, and 1 : 7-dichloronaphthalenes but the possession of a small moment by 2 : 6-dichloronaphthalene is remarkable. The following observation appear new: α-*naphthalenediazonium fluoborate*, decomp. 110°; β-*naphthalenediazonium fluoborate*, decomp. 116°; 2-*fluoronaphthalene*, m. p. 58°; 2 : 8-dichloronaphthalene, m. p. 134° (modified prep.); 1 : 5-*naphthalenebisdiazonium fluoborate*, decomp. 190°, and 1 : 5-*difluoronaphthalene*, m. p. 70°; 1-*bromonaphthalene-2-diazonium fluoborate*, decomp. 98—99°, and 1-*bromo-2-fluoronaphthalene*, m. p. 49°; 1-bromo-2-iodonaphthalene, m. p. 94°; 2-*chloro*-1-*bromonaphthalene*, b. p. 110°/21 mm., m. p. 60°.

The observation that 2 : 6-dichloronaphthalene has a finite dipole moment has led to unsuccessful attempts to resolve the naphthoic acids and naphthylamines into optically active components, during which the following substances have been prepared: *brucine α-naphthoate* (+H_2O), m. p. 182° (decomp.), $[\alpha]_D$ −27·0° in $CHCl_3$, and *brucine β-naphthoate*, m. p. 139° (decomp.), $[\alpha]_D$ −13·7° in $CHCl_3$; *quinine β-naphthoate*, decomp. 130—131°, $[\alpha]_D$ −152·9° in $CHCl_3$; *α-naphthylamine camphorsulphonate*, m. p. 186°, $[\alpha]_D$ +23·4° in EtOH, and *β-naphthylamine camphorsulphonate*, m. p. 200°, $[\alpha]_D$ +29·2° in EtOH; *α-naphthylamine bromocamphorsulphonate*, m. p. 219°, $[\alpha]_D$ +60·6° in $COMe_2$ and *β-naphthylamine bromocamphorsulphonate*, m. p. 192°, $[\alpha]_D$ +38·1° in EtOH.
H. WREN.

Dihydro-derivatives of 1- and 2-methylnaphthalene. V. VESELÝ and J. KAPP (Coll. Czech. Chem. Comm., 1931, 3, 448—455).—Reduction of 1-$C_{10}H_7Me$ (I) by Na and 96% EtOH is only partial. The product, when treated with Br in $CHCl_3$, gives *ar-dibromo*-5 : 6 : 7 : 8-*tetrahydro*-1-*methylnaphthalene*, m. p. 86—87°, and a liquid mixture of dibromide and unchanged (I). When this mixture is distilled in steam, partial removal of HBr occurs. The dibromide (? the cryst. portion), when treated with Zn in boiling MeOH, followed by MeOH saturated with HCl, gives an autoxidisable mixture (II) of *ar*-dihydro-1-methylnaphthalenes, b. p. 116—117°/11 mm. Reduction is proved to have affected the *ar*-nucleus because (II) gives hemimellitic acid on oxidation with $KMnO_4$. (II) contains 10% of 6 : 8-dihydro-1-methylnaphthalene, isolated as $Hg(OAc)_2$ compound, m. p. 160—162°, whilst the remainder, being oxidised by $Hg(OAc)_2$ to liquid glycols, is either the 5 : 6- or 7 : 8-dihydroderivative. 2-$C_{10}H_7Me$, however, affords more 5 : 8-dihydro-derivative; by similar treatment *ar-dibromo*-5 : 6 : 7 : 8-*tetrahydro-2-methylnaphthalene* (III), m. p. 90—91°, was obtained, which gives a mixture of *ar*-dihydro-2-methylnaphthalenes, b. p. 107—108°/

14 mm., giving benzene-1 : 2 : 4-tricarboxylic acid on oxidation; this mixture contains 58% of 6 : 8-dihydro-derivative (IV), isolated as $Hg(OAc)_2$ compound, m. p. 124—126°. When regenerated from the latter by conc. HCl, (IV) provides (III) on bromination.

2-Methyl-α-naphthylamine, when treated with Na in amyl alcohol, gives 2-*methyl*-5 : 6 : 7 : 8-*tetrahydro-α-naphthylamine*, b. p. 158—161° (*hydrochloride*; *Ac* derivative, m. p. 185—186°), which, when diazotised and warmed in dil. H_2SO_4, gives 2-*methyl*-5 : 6 : 7 : 8-*tetrahydro-α-naphthol*, m. p. 41—42°, in poor yield.
R. S. Cahn.

1 : 5- and 1 : 8-Dimethylnaphthalene. V. Veselý and F. Šturso (Coll. Czech. Chem. Comm., 1931, 3, 430—431).—Mg 1-methyl-5-naphthyl bromide (prepared from Mg activated by MeI) with Me_2SO_4 in presence of N_2 gives 1 : 5-*dimethylnaphthalene*, m. p. 77—78° (*picrate*, m. p. 137—138°). 1 : 8-*Dimethylnaphthalene*, an oil (*picrate*, m. p. 141 142°), is similarly prepared.
R. S. Cahn.

2 : 8-Dimethylnaphthalene. V. Veselý and A. Medvedeva (Coll. Czech. Chem. Comm., 1931, 3, 440—447).—7-Methyl-α-naphthol could not be converted into 1-chloro-7-methylnaphthalene. When 2-methylnaphthalene-8-sulphonic acid is heated with conc. H_2SO_4 at 100° for 1·5 hr., poured into H_2O, and treated successively with $NaNO_2$ and conc. HNO_3, first at room temp., and then at 100°, 2 : 4-*dinitro*-7-*methyl-α-naphthol* (I), m. p. 166—166·5°, is obtained, which with *p*-toluenesulphonyl chloride in $NPhMe_2$ or $NPhEt_2$ at 100° gives 8-*chloro*-5 : 7-*dinitro*-2-*methylnaphthalene*, m. p. 155·5—156°. This with Et sodiomalonate in Et_2O yields Et_2 5 : 7-*dinitro*-2-*methylnaphthalene*-8-*malonate*, m. p. 103—106°, converted by H_2SO_4 in Ac_2O into 5 : 7-*dinitro*-2-*methylnaphthalene*-8-*acetic acid*, m. p. 160—176° (decomp.), which when heated in pyridine at 40°, loses CO_2 to form 5 : 7-*dinitro*-2 : 8-*dimethylnaphthalene*, m. p. 163—165·5°. Reduction of this by $SnCl_2$ and alcoholic HCl at 100° gives a poor yield of 5 : 7-*diamino*-2 : 8-*dimethylnaphthalene*, m. p. 114—116° (hydrochloride), which on diazotisation in aq. EtOH affords 2 : 8-*dimethylnaphthalene*, m. p. 84—85° (*picrate*, m. p. 114—117°). (I) is partly reduced by $SnCl_2$ (3 mols.) and alcoholic HCl at room temp. to 3-*nitro*-4 : 6-*dimethyl-α-naphthylamine*, m. p. 151—153° (*perchlorate*; *Ac* derivative, m. p. 220—222°), and 4-nitro-1 : 7-dimethyl-β-naphthylamine (not obtained pure). The former amine, when diazotised and treated with EtOH, gives 2-*nitro*-1 : 7-*dimethylnaphthalene*, m. p. 56·5—58°, reduced by Fe and AcOH to 1 : 7-*dimethyl*-β-*naphthylamine*, an oil (*Ac* derivative, m. p. 207—208°). The diazonium salt of this base, when treated with EtOH, gives a *substance*, m. p. 42—43°, and, when decomposed by dil. H_2SO_4, gives 1 : 7-*dimethyl*-β-*naphthol*, m. p. 138—140°. This does not couple with diazotised *p*-nitroaniline; the constitutions of this and the preceding substances are thus established.

[With M. J. Páč.] 7-Methyl-α-naphthol, NaOAc, NH_4Cl, and Ac_2O at 270° give 7-methyl-α-naphthylamine.
R. S. Cahn.

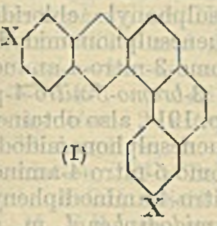
[Polynuclear, aromatic hydrocarbons and their derivatives. IX. Constitution of anthracene.] O. Diels and K. Alder (Ber., 1931, 64, [*B*], 2116—2117; cf. Clar, this vol., 1044).—The authors have shown previously (this vol., 848) that anthracene and 9 : 10-dibromoanthracene add crotonic and maleic acids or their anhydrides etc. in the 9 : 10-position and have interpreted the reaction with respect to the constitution of anthracene.
H. Wren.

Synthesis of anthracene homologues. III. 2 : 3 : 6 : 7-Tetramethylanthracene. G. T. Morgan and E. A. Coulson (J.C.S., 1931, 2323—2331).—2 : 3 : 6 : 7-*Tetramethylanthracene* (I), m. p. 308°, and -*anthraquinone* (II), m. p. 338°, have been synthesised by independent methods. (*a*) 3 : 4-*Dimethylbenzoyl chloride*, b. p. 188°/140 mm. (*anilide*, m. p. 108°), condenses alone by Friedel–Crafts reaction to form (II) in small yield, and with ψ-cumene to give 2 : 4 : 5 : 3′ : 4′-*pentamethylbenzophenone*, m. p. 90°, which on pyrolysis affords 2 : 3 : 6 : 7-*tetramethyl*-9-*anthrone*, m. p. 271—272° (when boiled with Ac_2O gives a *substance*, m. p. 233—234°, a complex containing 1 mol. each of 2 : 3 : 6 : 7-tetramethylanthrone and 2 : 3 : 6 : 7-tetramethylanthranyl acetate), readily oxidised to give (II), and reduced by Na to 2 : 3 : 6 : 7-*tetramethyl*-9 : 10-*dihydroanthracene* (III), m. p. 217—219°. (*b*) Condensation of *p*-benzoquinone with βγ-dimethyl-$\Delta^{\alpha\gamma}$-butadiene affords 2 : 3 : 6 : 7-*tetramethyl*-$\Delta^{2:6}$-*octahydroanthraquinone*, m. p. 202—203°, which can be transformed into an *isomeride*, m. p. 307°, the constitution of which is discussed. When O_2 is passed through an alcoholic suspension of this compound, (II) is formed. (II) is reduced by Al powder to 2 : 3 : 6 : 7 : 2′ : 3′ : 6′ : 7′-*octamethyl*-10 : 10′-*dihydroanthranol*, m. p. 319°, and by Na in amyl alcohol to (III), which is dehydrogenated with Se to (I). (I) is contained in the heavy neutral oils of low-temp. tar and can be oxidised to (II).
F. R. Shaw.

Anthracene series. Halogenation and nitration. P. S. Varma and A. Subramanyam (Proc. XV Indian Sci. Cong., 1928, 151).—Mono- and di-iodoanthraquinone are obtained by the action of $NaNO_2$ and fuming H_2SO_4 on anthracene and I.
Chemical Abstracts.

Synthesis of 4-methylphenanthrene. C. B. Radcliffe, I. R. Sherwood, and W. F. Short (J.C.S., 1931, 2293—2297).—4-Methylphenanthrene, prepared by dehydrogenation with Se of the product of the action of MgMeI on 4-keto-1 : 2 : 3 : 4-tetrahydrophenanthrene (from β-naphthyl bromomethyl ketone and Et sodiomalonate), is identical with methanthrene obtained from podocarpic acid either by distillation with zinc dust (Oudemans, A., 1874, 73) or by dehydrogenation with Se. Each hydrocarbon is oxidised to 4-methylphenanthraquinone (*quinoxaline* derivative, m. p. 177°).
F. R. Shaw.

Polynuclear aromatic hydrocarbons and their derivatives. X. Naphtho-2′ : 3′ : 3 : 4-phenanthrene and its quinones. E. Clar and H. D. Wallenstein (Ber., 1931, 64, [*B*], 2076—2082).—1-*Bromo*-2 : 7-*dimethylnaphthalene*, m. p. 48°, is prepared from the hydrocarbon and Br in CS_2, whilst 1-*iodo*-2 : 7-*dimethylnaphthalene*, m. p. 62°, is obtained by means of I and HIO_3 in boiling AcOH. Treatment of the compounds with Na or Cu powder regenerates the hydrocarbon with possibly a little tetramethyldinaphthyl. The action of $AlCl_3$ on 2 : 7-$C_{10}H_6Me_2$ or its bromo-derivative yields fluorescent products from which a perylene derivative could not be isolated. 2-$C_{10}H_7Me$ and Cl_2 at 250—286° afford 2-$C_{10}H_7{\cdot}CH_2Cl$ (transformed by Na into αβ-di-2-naphthylethane dehydrogenated by Pt–C to αβ-di-2-naphthylethylene) and much tar; analogous results are obtained with 2 : 7-$C_{10}H_6Me_2$. Distillation of the tars with Zn dust yields, respectively, 2′ : 3′-*naphtho*-3 : 4-*phenanthrene* (I; X=H), m. p. 261° (*dipicrate*, m. p. 213°) and 7 : 7′-*dimethyl*-2′ : 3′-*naphtho*-3 : 4-*phenanthrene* (I; X=Me), m. p. 228° (*monopicrate*), neither of which could be dehydrogenated according to Zelinski. The hydrocarbons are oxidised by CrO_3 in AcOH to mixtures of mono- and di-quinones from which 3 : 4-*phthalylphenanthrene*, m. p. 240—241° after darkening, and *dimethyl*-3 : 4-*phthalylphenanthrene*, m. p. 294° after darkening, are isolated. H. WREN.



(I)

Influence of substitution on the oxidation of side-chains in the benzene nucleus. P. S. VARMA and P. B. PANICKER (Proc. XV Indian Sci. Cong., 1928, 150—151).—In the *p*-series (C_6H_4MeX) the order of decreasing degree of oxidation by neutral aq. $KMnO_4$ is: X=CO_2H, NO_2, Br, Cl, OMe, I, NHAc, and in the *o*-series: NO_2, CO_2H, Br, Cl, NHAc, I. CHEMICAL ABSTRACTS.

Principle of induced alternate polarity in relation to the reactions of derivatives of *p*-dichlorobenzene and other compounds with sodium methoxide. T. DE CRAUW (Rec. trav. chim., 1931, 50, 753—792).—Numerous examples of the replacement of Cl and NO_2 in chloronitro- and nitrobenzenes under the influence of NaOMe are discussed with reference to the theory of alternate polarities; the steric effect is discussed particularly. The effects of various groups on the replacement of Cl in numerous substituted chlorobenzenes are also discussed.

p-$C_6H_4Cl_2$ and BzCl in presence of $AlCl_3$ at 150—170° give 2 : 5-*dichlorobenzophenone* (I), m. p. 88° [*oxime*, m. p. 135° (rapid heating), 207° (slow heating), converted by conc. H_2SO_4 into 2 : 5-*dichlorobenzanilide*, m. p. 122°]. 2 : 5-*Dichloroacetophenone* (II) has b. p. 251°/756 mm., m. p. 14°, when regenerated from its *oxime*, m. p. 130°. Reduction of 2 : 5-dichloronitrobenzene by Lapworth and Pearson's method (J.C.S., 1921, **119**, 765) gives 2 : 5-*dichlorophenylhydroxylamine* (III), m. p. 93°, oxidised by $K_2Cr_2O_7$ and dil. H_2SO_4 to 2 : 5-*dichloronitrosobenzene* (IV), m. p. 101°. 2 : 5-*Dichlorothiophenol*, m. p. 24° (*Pb* salt), prepared by the xanthate method, is similarly oxidised to 2 : 5 : 2′ : 5′-*tetrachlorodiphenyl disulphide*, m. p. 129°. Chlorination of acet-*o*-toluidide by methods other than Chattaway and Orton's gives a mixture of 3- and 5-chloro-derivatives; 3-*chloro*-o-*toluidine* (*Ac* derivative, m. p. 110°) has b. p. 252—254°/750 mm., m. p. 9°. 2-Acetamidodiphenyl and Cl_2 in AcOH give (after hydrolysis) 3-, m. p. 15° (*Ac* derivative, m. p. 97°), 4′-, m. p. 71° (*Ac* derivative, m. p. 122°), and 5-*chloro*-2-*aminodiphenyls*, m. p. 54° (*Ac* derivative, m. p. 125°), converted by the usual method into 2 : 3-, b. p. 172°/30 mm., 2 : 4′-, b. p. 191°/30 mm., and 2 : 5-*dichlorodiphenyls* (V), b. p. 182°/3 mm. NH_2Ph and (IV) in AcOH afford 2 : 5-*dichloroazobenzene*, m. p. 64°, reduced by Zn dust and alkali to 2 : 5-*dichlorohydrazobenzene*, m. p. 74°. This is converted into 2 : 5-*dichlorobenzidine*, m. p. 95°, and thence into (V).

The action of NaOMe on numerous 2 : 5-dichlorobenzene derivatives, including the following, is described (the products formed are given in parentheses): I (2 : 5-*dichlorobenzhydrol*, m. p. 66°); II (2 : 5-*dichlorophenylmethylcarbinol*, b. p. 222°/757 mm., and a *compound* $C_{16}H_{12}OCl_4$, m. p. 157°); III (2 : 5 : 2′ : 5′-tetrachloroazoxybenzene and a little 2 : 5 : 2′ : 5′-*tetrachlorohydrazobenzene*, m. p. 124° [also formed by reduction of the *tetrachloroazobenzene*, m. p. 189°]); IV (tetrachloroazoxybenzene); V (5-*chloro*-2-*hydroxy*-, m. p. 46°, and 2-*chloro*-5-*hydroxy-diphenyl*, m. p. 63°); 2 : 5-dichlorobenzenesulphonic acid (5-*chlorophenol*-2-*sulphonic acid*, decomp. about 150°); 2 : 5-dichlorobenzonitrile (5-*chloro*-2-*methoxybenzonitrile*, m. p. 101°); 2 : 5-dichlorotoluene (mainly 6-chloro-*m*-cresol). The action of NaOMe on polyhalogenobenzenes is reinvestigated. H. BURTON.

Mechanism of nitration with nitrates. G. BACHARACH and W. BRECKSTONE (Ber., 1931, 64, [*B*], 2136; cf. Menke, A., 1925, i, 386, 655).—Diacetylorthonitric acid, $(OH)_3N(OAc)_2$, b. p. 45°/15 mm., isolated by the action of Ac_2O on $Cu(NO_3)_2,3H_2O$ whereby $Cu(OAc)_2$ is also produced, is the active agent in Menke's nitration process. The conversion of NH_2Ph into *p*- and *o*-nitroacetanilide is described. H. WREN.

Derivatives of anilinesulphonyl chloride and aminothiophenol. J. POLLAK, R. POLLAK, and E. RIESZ (Monatsh., 1931, 58, 118—128).—*Anilinedisulphonyl chloride*, m. p. 94—95° (*dianilide*, m. p. 280°), is obtained with difficulty from sulphanilic acid or PhNHAc and $ClSO_3H$ (Jarsch and Nadel, Diss., Vienna, 1929).

[With A. E. WITTELS.] Chloroacetanilide (I), when heated with $ClSO_3H$ (II) at 60° for 2 hr., gives *chloroacetanilide*-p-*sulphonyl chloride* (III), m. p. 112° (*anilide*, m. p. 187°), which with NH_3 gas yields the *sulphonamide*, m. p. 216°, with liquid or warm conc. aq. NH_3 *glycylanilide*-p-*sulphonamide*, m. p. 259°. (III), when heated with AcOH, Ac_2O, NaOAc, and Zn dust, gives *p*-acetylmercaptoacetanilide, and with Zn dust and 10% HCl at 100° *p*-acetamidophenyl disulphide. When (I) and (II) are heated at 150° for 3 hr., anilinetrisulphonyl chloride is obtained, hydrolysis accompanying sulphonation. The SH group in acetylmercaptoacet-*p*-toluidide (IV) [obtained by reductive acetylation of acet-*p*-toluididesulphonyl chloride (*amide*, m. p. 242°)] is in the *o*-position, since this substance is also formed by reductive acetylation of *p*-nitrotoluene-*o*-sulphonyl chloride. Chloroacet-*p*-toluidide (V), when heated with (II) at 60° for 2 hr., gives the o-*sulphonyl chloride*, m. p. 87° (*amide*, m. p. 231°), which on reductive acetylation yields (IV). (V), when heated with (II) and NaCl at 150° for 3 hr., gives the same *p*-toluidinedisulphonyl chloride (VI) as *p*-toluidine or acet-*p*-toluidide; this chloride, on reductive acetylation, gives 4-*acetylmercapto*-1 : 5-*dimethylbenzthiazole* (VII), m. p. 86—87°, which, when warmed with Me_2SO_4 and subsequently with *p*-dimethylaminobenzaldehyde and a little piperidine, gives 4-*acetylmercapto*-1-(p-*dimethylaminostyryl*)-2 : 5-*dimethylbenzthiazolium methosulphate* (VIII), violet, m. p. 205—206°. The position of the second SO_3H group in (V) is confirmed by the transformation of (V) into 4-chlorotoluene-2 : 5-disulphonyl chloride. (VII) was also prepared from *p*-toluidinedisulphonyl chloride by treatment first with Zn dust and 20% HCl, and then with Ac_2O or AcCl.

[With A. Nadel.] *o*-Toluidine, when heated with (II) and NaCl at 120—130° for 1 hr., gives the 3 : 5-*disulphonyl chloride*, m. p. 153° (*anilide*, m. p. 188°).

R. S. Cahn.

Preparation of *p*-chloroaniline. K. H. Hasan (Proc. XV Indian Sci. Cong., 1928, 158).—Chattaway and Orton's method is criticised.

Chemical Abstracts.

Lability of fluorine in 4-fluoro-3-nitroaniline. A replacement of fluorine by the ethoxyl group in acid solution. H. H. Hodgson and J. Nixon (J.C.S., 1931, 2272—2274).—The mechanism of the above replacement is discussed. Diazotisation of 4-fluoro-3-nitroaniline gives 2-nitrobenzene-4-diazo-1-oxide, decomp. 178° (*ibid.*, 1915, **109**, 645), brominated to 6-*bromo*-2-*nitrobenzene*-4-*diazo*-1-*oxide*, decomp. 185°, which gives 4-chloro-6-bromo- and 4 : 6-dibromo-2-nitrophenol (also obtained by the action of $CuSO_4$ and KBr on 2-nitrobenzene-4-diazo-1-oxide) by the Sandmeyer reaction, 6-bromo-2-nitrophenol when heated with KOH in EtOH, and 6-*bromo*-4-*iodo*-2-*nitrophenol*, m. p. 85°, when heated with KI and a little $CuSO_4$. 4-Fluoro-3-nitroaniline diazotised in EtOH and H_2SO_4 gives *o*-nitrophenetole, reduced to *o*-phenetidine hydrochloride, which is oxidised by Caro's acid to o-*nitrosophenetole*, m. p. 93°.

A. A. Levi.

Substituted quaternary azonium iodides. V. Molecular state of phenyl-dimethyl-, -methylethyl-, -diethyl-, -methylbenzyl-, and -propylbenzyl-azonium iodides in solution. B. K. Singh and M. R. Sud (Proc. XV Indian Sci. Cong., 1928, 148).—For all except phenylethylazonium iodide the degree of dissociation is greater in EtOH than in H_2O. That in H_2O, but not in EtOH, increases with increasing formula wt.; the degree of dissociation increases with dilution in both solvents.

Chemical Abstracts.

Condensation of β-naphthylamine with oxalyl derivatives. G. Gallas and G. Bermúdez (Anal. Fís. Quím., 1931, 29, 464—469).—When β-naphthylamine is heated with $(COEt)_2$ at 150—200° or refluxed with $(COCl)_2$ in CS_2 derivatives of β-naphthyloxamic acid are obtained. Aceto-β-naphthylamide and $(COCl)_2$ with $AlCl_3$ in CS_2 yield (?)2-*acetamidoacenaphthenequinone*, m. p. 232° (*base*, m. p. 196°, yielding *quinoxaline*, m. p. above 250°, with *o*-phenylenediamine), and a *substance*, m. p. 181°.

R. K. Callow.

Diphenyl series. X. Bromination of 4-*p*-toluenesulphonamidodiphenyl. F. Bell (J.C.S., 1931, 2338—2343; cf. A., 1930, 904).—Bromination of 4-*p*-toluenesulphonamidodiphenyl in pyridine gives 3 : 5-dibromo- (this vol., 629), and in $CHCl_3$ 3 : 4′-dibromo-4-*p*-toluenesulphonamidodiphenyl, converted (*a*) by HNO_3 in AcOH into 3 : 4′-*dibromo*-5-*nitro*-4-p-*toluenesulphonamidodiphenyl*, m. p. 229°, hydrolysed to the amino-compound, and (*b*) by Br in pyridine into 3 : 5 : 4′-*tribromo*-4-p-*toluenesulphonamidodiphenyl*, m. p. 218°, which gives with *p*-toluenesulphonyl chloride 3 : 5 : 4′-*tribromo*-4-*di*-p-*toluenesulphonamidodiphenyl*, m. p. 274°, also obtained from the tribromoaminodiphenyl and *p*-toluenesulphonyl chloride. Bromination of 3-nitro-4-*p*-toluenesulphonamidodiphenyl in AcOH gives 5 : 4′-dibromo-3-nitro-4-aminodiphenyl, and in pyridine gives 3-*bromo*-5-*nitro*-4-p-*toluenesulphonamidodiphenyl*, m. p. 191°, also obtained by nitration of 3-bromo-4-*p*-toluenesulphonamidodiphenyl, and hydrolysed to 3-bromo-5-nitro-4-aminodiphenyl (A., 1928, 996). 4′-Nitro-4-aminodiphenyl gives 4′-*nitro*-4-p-*toluenesulphonamidodiphenyl*, m. p. 144°, which with Br in pyridine gives 3 : 5-*dibromo*-4′-*nitro*-4-p-*toluenesulphonamidodiphenyl*, m. p. 274°, and in AcOH gives 3-*bromo*-4′-*nitro*-4-*p*-*toluenesulphonamidodiphenyl*, m. p. 144°, converted by HNO_3 in AcOH into 3-*bromo*-5 : 4′-*dinitro*-4-p-*toluenesulphonamidodiphenyl*, m. p. 250°. 2-*p*-Toluenesulphonamidodiphenyl with Br in pyridine gives 3 : 5-*dibromo*-2-*p*-*toluenesulphonamidodiphenyl*, m. p. 118°, hydrolysed to 3 : 5-dibromo-2-aminodiphenyl (A., 1927, 236). 4′-Bromo-4-*p*-toluenesulphonamidodiphenyl with HNO_3 in AcOH gives 4′-*bromo*-3 : 5-*dinitro*-4-p-*toluenesulphonamidodiphenyl*, m. p. 233°. A. A. Levi.

Diazotisation of difficultly diazotisable amines. S. Krishna and R. L. Bhatia (Proc. XV Indian Sci. Cong., 1928, 152).—Pyridine is used as solvent.

Chemical Abstracts.

Organic sulphur–nitrogen linking. VI. E. Riesz, R. Pollak, and R. Zifferer (Monatsh., 1931, 58, 147—169; cf. A., 1930, 1573).—The quinonoid formula for the products of oxidation of arylthiolarylamines (*i.e.*, substances of the type Ar·S·NHAr′) by CrO_3 is supported by the fact that these products are formed only when an oxidisable substituent is present in the *o*- or *p*-position of the Ar′ nucleus. A quinone has been obtained from a substance not containing a NO_2 group; hence this group does not take part in the reaction, and, consequently, the valency of the S atom is unchanged. In attempts to elucidate the mechanism of the oxidation in cases in which unimol. quinonoid compounds are not formed, a number of substances were prepared and oxidised. If Ar′ is replaced by an aliphatic radical, no oxidation takes place. If Ar′ is replaced by CH_2Ph (or a substitution product of this), oxidation gives the disulphide $(ArS\cdot)_2$; this reaction doubtless occurs by way of the arylidenethiolamines, ArS·N:CHAr′, since such compounds have been found also to oxidise to form disulphides. No cases were found, when *p*-, or *p*- and *o*-non-oxidisable constituents were present, in which oxidation takes a simple course. Oxidation by PbO_2 in Et_2O or C_6H_6 takes place only when CrO_3 is also effective, and is considered to be due to production of free radicals with subsequent linking of two mols. in two points of each. Many types of product are possible. Attempts to cause the free radicals to react with diazomethane were unsuccessful. Two of the possible bimol. types were synthesised, but found to differ from the oxidation products.

4-Chloro-2-nitro-1-chlorothiolbenzene (I) and *p*-aminodiphenylamine in Et_2O at 0° give N-4-*chloro-2-nitrophenylthiol*-N'-*phenyl*-p-*phenylenediamine*, reddish-brown, m. p. 104°, which with $Na_2Cr_2O_7$ in AcOH yields N-4-*chloro-2-nitrophenylthiol*-N'-*phenylbenzoquinonedi-imine*, dark red, m. p. 140—150°. *o*-Aminodiphenylamine and (I) afford similarly N-4-*chloro-2-nitrophenylthiol*-N'-*phenyl*-o-*phenylenediamine*, red, m. p. 122°, and *N*-4-*chloro-2-nitrophenylthiol*-N'-*phenyl*-o-*benzoquinonedi-imine*, reddish-brown, m. p. 140—142°. *p*-Aminobenzyl alcohol and (I) give p-(4-*chloro-2-nitrophenylthiolamino)benzyl alcohol*, reddish-yellow, m. p. 154°, which is decomposed by oxidation. *N*-*p*-Tolylthiolaniline and 30% H_2O_2 in hot AcOH yield a bimol., brown substance, $C_{26}H_{24}N_2S_2$, m. p. 187—190°. *p*-Chlorothioltoluene and *p*-aminophenol in dry Et_2O form 4-N-p-*tolylthiolaminophenol*, red, m. p. 68°, yielding on oxidation N-p-*tolylthiolbenzoquinoneimine*, red, m. p. 104°. Shaking (I) in Et_2O with 40% aq. NH_2Me gives 4-*chloro-2-nitrophenylthiolmethylamine*, yellow, m. p. 74°, stable to H_2O_2 and CrO_3, even on warming. Ethylenediamine affords similarly *di-(4-chloro-2-nitrophenylthiol)ethylenediamine*, yellow, m. p. 185—186°, stable to CrO_3 and H_2O_2. Nitrophenylthiol-glycine and -*dl*-leucine esters, chloronitrophenylthiol-*dl*-leucine ester, and chloronitrophenylthiol-leucylglycine and its ester are also stable to H_2O_2 and $Na_2Cr_2O_7$ in AcOH, even on warming. (I) and $CH_2Ph{\cdot}NH_2$ in Et_2O yield 4-*chloro-2-nitrophenylthiolbenzylamine*, yellow, m. p. 104°, which is unchanged by H_2O_2, but on long heating with CrO_3 in AcOH gives 4-chloro-2-nitrophenyl disulphide (III). Benzylidene-4-chloro-2-nitrophenylthiolamine is stable to CrO_3 in cold AcOH, but when heated gives (III). 4-Chloro-2-nitrophenylthiolamine (IV) and *p*-dimethylaminobenzaldehyde give the p-*dimethylaminobenzylidene* derivative, red, m. p. 157°, similarly oxidised to the disulphide. 5-Bromo-*m*-4-xylidine and (I) in Et_2O give 5-*bromo*-N-4'-*chloro-2'-nitrophenylthiol*-m-4-*xylidine*, yellow, m. p. 157°; this is oxidised by warm H_2O_2 or CrO_3 in AcOH, but no products were isolated. N-4'-*Chloro-2'-nitrophenylthiolaminoacetophenone*, yellowish-orange, has m. p. 196°. (IV) and picryl chloride in EtOH (with or without NaOAc) give *di-(4-chloro-2-nitrophenylthiol)imide*, yellow, m. p. 232° (cf. A., 1918, i, 537).

The following substances were prepared for comparison with the bimol. oxidation products of 4'-chloro-2'-nitrophenylthiolaniline and similar substances. *NN'*-Di-(4'-chloro-2'-nitrophenylthiol)-*o*-phenylenediamine and pyrocatechol, with or without P_2O_5, at 110° or 150° give a dark, insol. product with too low a C content. 2 : 2'-Dinitrodiphenyl disulphoxide and warm NH_2Ph give a dark product, which was different from the *substance*, $C_{24}H_{18}O_4N_4S_2$, bluish-violet, m. p. 190°, obtained by oxidation of *p*-nitrophenylthiolaniline with CrO_3 in AcOH.

o-Phenylenediamine, *p*-toluenesulphonyl chloride, and NaOAc in boiling EtOH form p-*toluenesulphonyl*-o-*phenylenediamine*, m. p. 114°, which with HNO_2 affords 1-p-*toluenesulphonylbenztriazole*, m. p. 133°.

R. S. CAHN.

cycloHexanonephenylcyclohexylthiosemicarbazone. R. STOLLÉ and F. HANUSCH (Ber., 1931, 64, [*B*], 1979—1980; cf. A., 1930, 1427).—The by-product, m. p. 157°, obtained during the action of *s*-di*cyclo*hexylhydrazine on phenylthiocarbimide in Et_2O (*loc. cit.*) is probably cyclo*hexanonephenyl*cyclo*hexylthiosemicarbazone*, $C_6H_{10}{:}N{\cdot}N(C_6H_{11}){\cdot}CS{\cdot}NHPh$; its production is ascribed to the partial oxidation of the hydrazine to its peroxide during the change. Its prep. from *cyclo*hexylhydrazine, *cyclo*hexanone, and phenylthiocarbimide is described. H. WREN.

Benzene- and naphthalene-azo-*o*-coumaric acids. D. CHAKRAVARTI (J. Indian Chem. Soc., 1931, 8, 391—396).—When a dil. alkaline solution of a benzene- or naphthalene-azocoumarin is boiled with a little HgO, the first-formed coumarinate undergoes inversion to the coumarate (cf. A., 1930, 913); the following *o*-coumaric acids are prepared: *benzeneazo*- (I), decomp. 205°; o-, decomp. 223°, m-, decomp. 213°, and p- (II), decomp. 236°, -*nitrobenzeneazo*-; *naphthalene*-α- (III), decomp. 198—200°, and -β-*azo*-, decomp. 210°; *benzeneazo*-β : 5-*dimethyl*-, decomp. 186°. *Diphenylbisazodicoumarin*, not melted at 280° (from coumarin and tetrazotised benzidine in alkali), is similarly converted into *diphenylbisazodi*-o-*coumaric acid* (IV), decomp. 315°. *Naphthalene*-α- and -β-*azocoumarins* have m. p. 217° and 271°, respectively. (I), (II), (III), and (IV) are also prepared from *o*-coumaric acid and the requisite diazonium salt in alkali. Benzeneazocoumarin is reduced by $SnCl_2$ and HCl to 6-aminocoumarin. With conc. acids the azo-*o*-coumaric acids become more deeply coloured, probably owing to the formation of a salt of the quinonephenylhydrazone form.

H. BURTON.

New azo dyes. E. JUSA and E. RIESZ (Monatsh., 1931, 58, 137—146).—Azo dyes, having also the properties of vat dyes, and isomerides of naphthol-AS have been prepared.

[With L. STEINHARDT.] When 6-mercaptocarbethoxy-β-naphthol is boiled with aq. KOH and $CH_2Cl{\cdot}CO_2K$, β-*naphthol*-6-*thioglycollic acid*, m. p. 156°, is obtained; this on prolonged treatment with $ClSO_3H$ at room temp. gives a dark *substance*, which, since it is sol. in H_2O and is reduced by $Na_2S_2O_4$, appears to contain SO_3H groups and a thionaphthene ring. This product dyes animal fibres dark brown shades (fast to washing and boiling, but not to alkalis), gives a ppt. with metallic salts, and is oxidised by $K_3Fe(CN)_6$ solution to a less sol. compound, which dyes animal fibres bluish-green. Both dyeings give light reddish-brown shades when coupled with diazotised *p*-nitroaniline. β-Naphthol-3-carboxyl chloride with 2-aminoanthraquinone in $PhNO_2$ at 160° gives the 2-*anthraquinonylamide*, m. p. 275—280°, which dyes cotton yellowish-brown and gives fast red shades when treated with diazotised *p*-nitroaniline. Anthraquinone-2-sulphonyl chloride with 2-aminoanthraquinone yields a *substance*, $C_{28}H_{14}O_6N_2S$, m. p. 335—338°, which dyes cotton fast dark brown shades. Salicoyl-α- and -β-naphthylamides (the α-compound has m. p. 187°, lit. 182—183°), give azo dyes sensitive to alkali. 4-p-*Nitrobenzeneazosalicoyl*-α- and -β-*naphthylamides* have m. p. 264—265° and 274—275°, respectively. The N-*Bz* derivative of 3-amino-β-naphthol, m. p. 231°, with

diazotised *p*-nitroaniline gives a light red *azo* compound fast to chlorine when coupled on the fibre. 3-Benzamido-β-naphthol has no affinity for cotton.
R. S. Cahn.

Action of diazonium salts, nitrous acid, and hypochlorous acid on *O*-alkylhydroxylamines. A. B. Boese, jun., L. W. Jones, and R. T. Major (J. Amer. Chem. Soc., 1931, 53, 3530—3541).—Treatment of *O*-methylhydroxylamine with *p*-nitrobenzenediazonium chloride (I) gives MeOH, HCl, and *p*-nitrophenylazide. (I) converts *ON*-dimethylhydroxylamine into N-p-*nitrobenzeneazo*-N-*methoxymethylamine*, m. p. 66°, hydrolysed by conc. HCl at 70° to N_2, *p*-nitrophenol, and *ON*-dimethylhydroxylammonium chloride. N-p-*Nitrobenzeneazo*-N-*ethoxyethylamine*, m. p. 38°, -*methoxy*iso*propylamine*, m. p. 67° (hydrolysed to *O*-methyl-*N*-*iso*propylhydroxylammonium chloride), and -*benzyloxybenzylamine*, m. p. 100°, are obtained from (I) and the requisite *ON*-dialkylhydroxylamines. *N*-Methoxyamylamine and HNO_2 give the N-*nitroso*-derivative, b. p. 83—84°/15 mm., hydrolysed by conc. HCl to diethylcarbinol (3 : 5-*dinitrobenzoate*, m. p. 97°), CH_2O, and N_2, and reduced catalytically (Adams) in AcOH to MeOH and amylamine. The N-*nitroso*-derivatives of *N*-methoxymethylamine and *N*-ethoxyethylamine have b. p. 59—60°/30 mm. and 56—57°/15 mm., respectively; these behave similarly to the above NO-derivative on hydrolysis and reduction. Catalytic reduction (Adams) of these NO-derivatives in EtOH–HCl gives the original *N*-alkoxyalkylamine hydrochloride and NH_4Cl. *O*-Methylhydroxylamine and HNO_2 give MeOH and N_2O; the changes are: $NH_2OMe+HNO_2 \longrightarrow HO{\cdot}N{:}N{\cdot}OMe \longrightarrow MeOH+N_2O$. HOCl converts *N*-ethoxyethylamine and *N*-methoxyamylamine into *O*-ethylacetaldoxime and *O*-methyldiethyl ketoxime, respectively. The p-*nitrophenylhydrazone* of $COEt_2$ has m. p. 144.°
H. Burton.

Catalytic reactions of *cyclo*hexanol at active charcoal. T. Bahr (Ber., 1931, 64, [*B*], 2258—2265).—At 250—300° *cyclo*hexanol is mainly dehydrated by active C (Baeyer) in N_2 to *cyclo*hexene; some dehydrogenation to *cyclo*hexanone and a little to PhOH is observed so that the issuing gas contains H_2. *cyclo*Hexane appears to be due to secondary change, probably union of *cyclo*hexane with nascent H. Slight union of *cyclo*hexene and mol. H_2 is observed at C at 300°. At 350—400° the dehydrogenating effect of active C is more pronounced; production of *cyclo*hexene and *cyclo*hexane is diminished, and the formation of *cyclo*hexanone and PhOH is increased, accompanied by that of a larger proportion of products of higher b. p., including diphenylene oxide and triphenylene. Ph_2O and diphenylene oxide are obtained from PhOH and active C at 300—400°. The results with birch C are similar to those with Baeyer C, but the latter has the greater catalytic activity. $CH_2Ph{\cdot}OH$ and birch C at 300° afford PhCHO, PhMe, and H_2O.
H. Wren.

Hydrogenation of phenol. V. E. Tischtschenko and M. A. Belopolski (J. Appl. Chem., Russia, 1930, 3, 1159—1173).—Liquid-phase hydrogenation of PhOH to *cyclo*hexanol is best effected at 155—160°/10—15 atm., a Ni catalyst obtained by igniting Ni formate being used.
Chemical Abstracts.

Lignin. III. Sulphonation in the hydroaromatic series. Preparation of *cyclo*hexanol-2-sulphonic acid. H. Friese (Ber., 1931, 64, [*B*], 2103—2108).—*cyclo*Hexene does not react with H_2SO_4 (mol. ratio 1 : 1) in cold AcOH but addition of Ac_2O to the mixture causes the production of cyclo*hexanol*-2-*sulphonic acid* (*Ba* and *Na* salts). It is stable towards boiling H_2O, but converted by 25% H_2SO_4 at 150° into an oil of high b. p. derived from primary *cyclo*hexanol (under similar conditions, anisole-*o*-sulphonic acid affords unchanged material, PhOMe, and a little PhOH). The Na salt and KCN yield a nitrile incompletely hydrolysed by 33% HCl to hexahydrosalicylic acid, m. p. 109—111°. *cyclo*Hexene and H_2SO_4 in AcOH at 100° (in absence of Ac_2O) yield *cyclo*hexyl acetate, also derived from the hydrocarbon and AcOH in absence of mineral acid by heating under pressure. *cyclo*Hexene and H_2SO_4 react vigorously to from a dark resin, insol. in H_2O. Sulphonation therefore occurs only in presence of all three components. *cyclo*Hexanol can be sulphonated under similar conditions, but the reaction is complicated by the formation of sulphoacetic acid; since *cyclo*hexene is found as a by-product, it is probable that the primary change is dehydration of the alcohol. *cyclo*Hexene oxide is converted by Ac_2O–AcOH–H_2SO_4 into the monoacetate of *o*-*cyclo*hexane-1 : 2-diol, b. p. 238—241°, hydrolysed to *cis*-*cyclo*hexanediol, m. p. 102—104°; sulphonation of the glycol does not occur.
H. Wren.

Steric transformation of alkoxides. W. Hückel and H. Naab (Ber., 1931, 64, [*B*], 2137—2141).—*cis*-Decahydro-α-naphthol becomes isomerised when heated in the form of its Na derivative in xylene to *trans*-decahydro-α-naphthol, m. p. 63°, the change corresponding with the racemisation of Na amyloxide by heat. The second *trans*-decahydro-α-naphthol, m. p. 49°, is similarly isomerised to the compound, m. p. 63°, whereas the latter remains unchanged. Isomerisation at the point of junction of the rings does not occur when the alcoholic OH is in the β-position to the C atom 9. The Na derivatives of the *cis*-decahydro-β-naphthols, m. p. 105° and 17°, respectively, yield a mixture containing about 80% of the Na derivative of *cis*-decahydro-β-naphthol, m. p. 105°, and about 20% of that of the substance m. p. 17°; *trans*-decahydro-β-naphthol is not produced. In the *trans*-β-series the Na compounds of the isomeric decahydro-β-naphthols, m. p. 75° and 53°, respectively, yield almost exclusively that of the naphthol, m. p. 75°; *cis*-decahydro-β-naphthol is not produced. In the α-series, the transformation is invariably accompanied by the formation of *trans*-α-ketodecahydronaphthalene in amount which varies, since the ketone is further converted into acids and auto-condensation products. In the β-series the secondary changes occur so much more rapidly that the formation of ketone cannot be established; pre-added ketone is destroyed in less time than is necessary for the isomerisation.
H. Wren.

Phenols of coal tar. O. Kruber and A. Schmitt (Ber., 1931, 64, [*B*], 2270—2277).—The initial material is the residue from the technical distillation of crude cresols. Isolation of *p*-ethylphenol is effected by sulphonation at 100° of the fraction of b. p. 215—218°, removal of xylenol, hydrolysis of the sulphonic acid, and treatment of the phenols with NaOH and $CH_2Cl\cdot CO_2H$. The Na *p*-ethylphenoxyacetate is cryst. from H_2O and decomposed with aq. NaOH at 275°/120 atm. *m*-Ethylphenol is isolated after fractional treatment with aq. NaOH of the product of b. p. 215—218°, through *m*-ethylphenoxyacetic acid, m. p. 76—77°. Technical isolation of *m*-ethylphenol is effected through the corresponding K sulphonate. *p*-Ethylphenol is obtained by sulphonation at 103°, fission of the sulphonates with superheated steam, and collection of the product volatile at 110—130°, followed by re-sulphonation and purification of the Na salt of the sulphonic acid.

The residue, b. p. 227—230°, from the xylenol distillation contains 1 : 3 : 5- and 1 : 2 : 4-xylenol, *iso*-ψ-cumenol [2 : 3 : 5-trimethylphenol] and 3-methyl-5-ethylphenol. *iso*-ψ-Cumenol, m. p. 95—96°, b. p. 233°/760 mm., gives a dibromo-compound, m. p. 152°, *benzoate*, m. p. 50°, *phenylurethane*, m. p. 174°, *phenoxyacetate*, $C_{11}H_{14}O_3$, m. p. 128°, and *Me ether*, b. p. 214—216°/755 mm. 3-*Methyl*-5-*ethylphenol* has m. p. 55°, b. p. 232·5—234·5°/760 mm. (*benzoate*, m. p. 40°; *phenylurethane*, m. p. 152°; *phenoxyacetate*, m. p. 95°). The *Me ether*, b. p. 210°/752 mm., is oxidised by $KMnO_4$ to 5-*methoxyiso*p*hthalic acid* ($+H_2O$), m. p. 270°, obtained also from 5-methoxy-*m*-xylene. 2 : 3 : 5 : 6-Tetramethylphenol accompanies indole in the fractions of b. p. above 240°. H. WREN.

Replacement of bromine in bromophenols by the nitro-group. I. 2 : 4 : 6-Tribromo-3-nitro- and -3-chloro-phenol. Some cases of group migration. H. H. HODGSON and E. W. SMITH (J.C.S., 1931, 2268—2272; cf. this vol., 958).—*m*-Nitrophenol by an improved process gives 3 : 4-, and 2 : 5-dinitrophenol, converted by Br respectively into 2 : 4-*dibromo*-3 : 6-*dinitrophenol*, m. p. 137°, and 2 : 6-*dibromo*-3 : 4-*dinitrophenol*, m. p. 142°, the latter being also obtained by the action of HNO_3 on 2 : 4 : 6-tribromo-3-nitrophenol. Action of HNO_3 on 3-chloro-2 : 4 : 6-tribromophenol, or of Br on 3- or on 5-chloro-2-nitrophenol, gives 3-*chloro*-4 : 6-*dibromo*-2-*nitrophenol*, m. p. 90°, converted by reduction and diazotisation into (*a*) 2 : 3-dichloro-4 : 6-dibromophenol (A., 1930, 1033), and (*b*) into 3-*chloro*-4 : 6-*dibromo*-2-*iodophenol*, m. p. 105°, both also obtained by reduction, diazotisation, and bromination of 3-chloro-2-nitrophenol. Similarly 5-chloro-2-nitrophenol yields 3 : 6-*dichloro*-2 : 4-*dibromo*-, m. p. 98°, and 3-*chloro*-2 : 4-*dibromo*-6-*iodophenol*, m. p. 93°. 3-Chloro-2 : 6-dibromo-4-nitrophenol, when reduced to 3-*chloro*-2 : 6-*dibromo*-4-*aminophenol*, m. p. 168°, and diazotised gives 3-*chloro*-2 : 6-*dibromo*-4-*iodophenol*, m. p. 102°, also obtained by reduction, diazotisation, and bromination of 3-chloro-4-nitrophenol. A. A. LEVI.

Antipyretic action of *p*-acetamidophenylurethanes. R. F. B. COX, C. R. ECKLER, and R. L. SHRINER (J. Amer. Chem. Soc., 1931, 53, 3498—3501).—The following alkyl *p*-acetamidophenylcarbamates are prepared from the *p*-NO_2 derivatives (this vol., 709) by catalytic reduction (Adams) in AcOH and subsequent acetylation: *Me*, m. p. 193°; *Et*, m. p. 198°; *Pr*, m. p. 175°; *Pr*$^{\beta}$, m. p. 164°; *Bu*, m. p. 170·5°; *Bu*$^{\beta}$, m. p. 165°; sec.-*Bu*, m. p. 177°; sec.-*amyl*, m. p. 165°; n-*hexyl*, m. p. 158°; n-*heptyl*, m. p. 162°, and sec.-*octyl*, m. p. 197·5°. None of these esters has an antipyretic action as great as that of NHPhAc or aminopyrin, and none of them possesses hypnotic activity. H. BURTON.

Interaction of nitroaminophenols with sulphonyl chlorides. F. BELL (J.C.S., 1931, 2343—2353; cf. this vol., 629).—Picramic acid with *p*-toluenesulphonyl chloride (1 mol.) in pyridine gives the *pyridine* salt of 2 : 4-dinitro-6-*p*-toluenesulphonamidophenol, m. p. 203° (Ac derivative, m. p. 190°), both hydrolysed to 2 : 4-*dinitro*-6-p-*toluenesulphonamidophenol*, m. p. 191° (*Ac acetate*, m. p. 174°), also obtained by nitration of 2-*p*-toluenesulphonamidophenol. Picramic acid in pyridine with *p*-toluenesulphonyl chloride (2 mol.) gives *anhydro*-2 : 4-*dinitro*-6-p-*toluenesulphonamidophenylpyridinium hydroxide*, m. p. 249° (decomp.), purified by decomp. of the *chloride*, m. p. 174°, or *nitrate*, m. p. 161° (decomp.), with boiling NaOAc. 2-*p*-Toluenesulphonamidophenyl *p*-toluenesulphonate by mononitration gives the 5-*nitro*-derivative (I), m. p. 159°, hydrolysed to 5-nitro-2-aminophenol, or its p-*toluenesulphonate*, m. p. 188° (*Ac* derivative, m. p. 189°, also obtained in small yield by nitration of 2-acetamidophenyl *p*-toluenesulphonate, and hydrolysed by acid to the nitroaminophenyl *p*-toluenesulphonate, or by alkali to the nitroaminophenol). The nitroaminophenol is reconverted into a mixture of the *p*-toluenesulphonate and (I) by *p*-toluenesulphonyl chloride in pyridine. 2-*p*-Toluenesulphonamidophenyl *p*-toluenesulphonate by more intense nitration gives the 3 : 5-*dinitro*-derivative, m. p. 188°, hydrolysed to 3 : 5-*dinitro*-2-*aminophenol*, m. p. 218° [p-*toluenesulphonate* (II), m. p. 186°; *Ac* p-*toluenesulphonate* (III), m. p. 205°; *Ac acetate*, m. p. 180°]. The Ac acetate gives 3 : 5-*dinitro*-2-*acetamidophenol*, m. p. 171°, converted by *p*-toluenesulphonyl chloride into (III), or by β-naphthoyl chloride into 3 : 5-*dinitro*-2-β-*naphthamidophenyl* β-*naphthoate*, m. p. 185°, hydrolysed to 3 : 5-*dinitro*-2-β-*naphthamidophenol*, m. p. 200°. 3-Nitro-2-aminophenol gives a p-*toluenesulphonate* (IV), m. p. 136° [*Ac* derivative (V), m. p. 134°]. 3-Nitro-2-acetamidophenol gives (*a*) a *p*-toluenesulphonate, hydrolysed to (IV), and further acetylated to (V), and (*b*) a β-*naphthoate*, m. p. 177°, which with warm NaOH gives 3-*nitro*-2-β-*naphthamidophenol*, m. p. 140°. 4-Nitro-2-aminophenol gives a p-*toluenesulphonyl* p-*toluenesulphonate*, m. p. 132°, nitrated to 3(?) : 4-*dinitro*-2-p-*toluenesulphonamidophenyl* p-*toluenesulphonate*, m. p. 154° (*pyridine* salt, m. p. 124°, hydrolysed to the *dinitro*-2-*aminophenol*, which gives a *mono*-p-*toluenesulphonyl* derivative, m. p. 165°). 5-Nitro-2-acetamidophenol gives a β-*naphthoyl* β-*naphthoate*, m. p. 213°, hydrolysed to a mixture of the original, and 5-*nitro*-2-β-*naphthamidophenol*, m. p. 282° (VI). 5-Nitro-2-acetamidophenol with β-naphthoyl chloride gives a little (VI), and a β-*naphthoate*, m. p. 167°, which is converted into (VI) by treatment with warm NaOH. 2-*p*-Toluenesulphonamidophenyl acetate gives a mixture of (*a*) the 5-*nitro*-derivative, m. p.

178°, hydrolysed to 5-nitro-2-aminophenol, or to 5-*nitro*-2-p-*toluenesulphonamidophenol*, m. p. 188° (β-*naphthoate*, m. p. 188°, hydrolysed to the *p*-toluenesulphonyl derivative), which gives (I) with *p*-toluenesulphonyl chloride; and (*b*) the 3-*nitro*-derivative, m. p. 122°, hydrolysed to 3-nitro-2-aminophenol. 3-*p*-Toluenesulphonamidophenyl *p*-toluenesulphonate is nitrated to the 4 : 6-*dinitro*-derivative, m. p. 158°, hydrolysed to 4 : 6-dinitro-3-aminophenol, m. p. 227°, and converted by pyridine and subsequent treatment of the HCl solution of the product with boiling NaOAc into *anhydro*-4 : 6-*dinitro*-3-p-*toluenesulphonamidophenylpyridinium hydroxide*, m. p. 263°, also obtained as follows. *m*-Chloroaniline and *p*-toluenesulphonyl chloride give p-*toluenesulphon*-3-*chloroanilide*, m. p. 135°, nitrated to a mixture of 1-*chloro*-4-*nitro*-5-p-*toluenesulphonamidobenzene*, m. p. 135° (hydrolysed to 5-chloro-2-nitroaniline, m. p. 124°), and 1-*chloro*-2 : 4-*dinitro*-5-p-*toluenesulphonamidobenzene*, m. p. 158°, hydrolysed to 5-chloro-2 : 4-dinitroaniline, m. p. 174°, and converted by pyridine and boiling NaOAc into the above anhydro-compound. Less energetic nitration of 3-*p*-toluenesulphonamidophenyl *p*-toluenesulphonate gives the 4-*nitro*-derivative, m. p. 114°, hydrolysed to 4-nitro-3-aminophenol. 4-Benzylideneaminophenol on nitration gives a small yield of 2 : 4-dinitro-4-aminophenol, which gives with *p*-toluenesulphonyl chloride in pyridine, and treatment of the product with HCl, 2 : 6-*dinitro*-4-p-*toluenesulphonamidophenylpyridinium chloride*, m. p. 205°, converted by hot NaOAc into *anhydro*-2 : 5-*dinitro*-4-p-*toluenesulphonamidophenylpyridinium hydroxide*, m. p. 243°.

A. A. Levi.

Separation of cresols : properties of pure *m*-cresol. G. Darzens (Compt. rend., 1931, **192**, 1657—1659).—Separation of mixtures of *m*- and *p*-cresol is effected by treatment of the mixture in an org. solvent with anhydrous NaOAc with vigorous stirring, when only the *m*-cresol forms a compound. The complex $2m\text{-}C_6H_4Me\cdot OH,5NaOAc$ is collected and decomposed by H_2O, and the *m*-cresol recovered. *p*-Cresol is separated from the filtrate by treatment with powdered oxalic acid. Further purification of *m*-cresol is effected by fractional crystallisation of the benzoate, followed by hydrolysis. Pure *m*-cresol has m. p. 11·8°, b. p. 200°/752 mm., 98°/17 mm. (benzoate, m. p. 56°; acetate, m. p. 12°); Raschig nitration index 184%.

G. Discombe.

Addition of phenols to the ethylenic linking. II. Action of phenols on allyl alcohol, allyl acetate, vinyl acetate, and allyl ethers. J. B. Niederl, R. A. Smith, and M. E. McGreal (J. Amer. Chem. Soc., 1931, **53**, 3390—3396).—*m*-Cresol and allyl alcohol in presence of conc. H_2SO_4 (cf. this vol., 346) give 4-*iso*propenyl-*m*-cresol, also formed similarly from allyl acetate, Et allyl ether, and diallyl ether, and when m-*tolyl* iso*propenyl ether*, b. p. 188—189° (from K *m*-tolyloxide and *iso*propenyl bromide), is treated with H_2SO_4 in AcOH. *o*-*iso*Propenylphenol is obtained similarly using PhOH and the above allyl compounds, whilst PhOH and vinyl acetate give *o*-vinylphenol. The reactions can be explained by the mechanism previously suggested (*loc. cit.*).

H. Burton.

Alkyl and arylsulphonyl derivatives of *o*-aminophenols. L. C. Raiford and O. Grosz (J. Amer. Chem. Soc., 1931, **53**, 3420—3426).—3-Bromo-5-amino-*p*-cresol yields the same N-*carbethoxy*-O-*benzoyl* derivative, m. p. 142°, no matter in which order the groups are introduced. Diacylation gives isomeric derivatives when 1 of the acyl groups is SO_2R and the other contains CO or CO_2R, depending on the order of introduction. No rearrangements occur during hydrolysis of these isomerides. It is considered that the repulsion energy of atomic kernels (Latimer, A., 1930, 9) cannot be the sole factor in the migration of acyl groups between N and O in *o*-aminophenols.

The following derivatives of 3-bromo-5-amino-*p*-cresol are described : N-*benzenesulphonyl*, m. p. 157°; N-β-*naphthalenesulphonyl*, m. p. 174·5°; N-*carbethoxy*-, m. p. 83°; N-*carbomethoxy*-, m. p. 112—112·5°; ON-*Bz*₂, m. p. 166°; ON-*dibenzenesulphonyl*, m. p. 230°; N-*Bz*-O-*benzenesulphonyl*, m. p. 114°; O-*Bz*-N-*benzenesulphonyl*, m. p. 172°; N-*Ac*-O-*benzenesulphonyl*, m. p. 116—116·5°; O-*Ac*-N-*benzenesulphonyl*, m. p. 156—157°; N-*carbethoxy*-O-*benzenesulphonyl*, m. p. 115—115·5°; O-*carbethoxy*-N-*benzenesulphonyl*, m. p. 144—145°; ON-*di*-β-*naphthalenesulphonyl*, m. p. 141—142°; N-*benzenesulphonyl*-O-β-*naphthalenesulphonyl*, m. p. 123°; O-*benzenesulphonyl*-N-β-*naphthalenesulphonyl*, m. p. 126°; N-*carbomethoxy*-O-2-*chloro*-5-*nitrobenzenesulphonyl*, m. p. 151°; ON-*di*-2-*chloro*-5-*nitrobenzenesulphonyl*, m. p. 221°; ON-*di*-*butanesulphonyl*, m. p. 78·5°; ON-*di*-2-*nitro*-p-*toluenesulphonyl*, m. p. 175—176°; ON-*di*-p-*bromobenzenesulphonyl*, m. p. 130—131°, and ON-*di*-3 : 4-*dichlorobenzenesulphonyl*, m. p. 114°. Et *o*-hydroxyphenylcarbamate gives a *benzenesulphonyl* derivative, m. p. 78·5—79°, whilst *o*-benzenesulphonamidophenol and $ClCO_2Et$ afford an oily product.

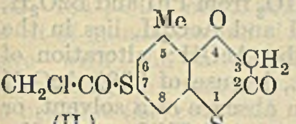
H. Burton.

Stereochemical studies on hydronaphthalene and derivatives. I. Catalytic reduction of β-naphthol under high temperature and pressure. II. Catalytic oxidation-reduction of hydronaphthalenes and sesquiterpenes. S. Kimura (Mem. Coll. Sci. Kyōtō, 1931, A, **14**, 173—193; cf. A., 1928, 285). I. β-Naphthol is reduced by H_2 in presence of Ni at 130—150°/63 atm. to *ac*- (I) (59·3%) and *ar*-tetrahydro-β-naphthol (II) (40·7%); the amount of (II) is thus increased at high pressure (cf. A., 1923, i, 105). At 160°/73 atm., the products are (I) (47·2%), (II) (51·6%), and β-decalol (III) (1·2%), whilst at 190°/57 atm., (I) (41·5%), (II) (43·2%), (III) (8·4%), and hydronaphthalenes (6·9%), are formed. Reduction of (II) at 180°/58 atm. gives a mixture of liquid (*A*) (containing 85% of *cis* and 15% of *trans*) and *cis-cis*-, m. p. 105°, -decahydro-β-naphthols, whilst (I) is reduced more difficultly at 200—270°/65 atm. to hydronaphthalenes (37%) and liquid decahydro-β-naphthol (consisting of 24·2% of *cis* and 75·8% of *trans*). The results suggest that the unsubstituted ring in β-naphthol is the more activated under high pressure and temp. When *A* is kept in presence of H_2 and Ni at 240—260°/100 atm. a mixture of *cis-trans*- and *trans-trans*-decahydro-β-naphthols is obtained together with a little decahydronaphthalene (*cis*+*trans*).

II. When 1 : 2-dihydronaphthalene is passed over palladised asbestos at 250—300° in CO_2, $C_{10}H_8$ and

1 : 2 : 3 : 4-tetrahydronaphthalene (IV) are produced. Similarly *cis*-1 : 2 : 3 : 4 : 5 : 8 : 9 : 10-octahydronaphthalene at 200—220° affords (IV) and *trans*-decahydronaphthalene (formed by rearrangement of the *cis*-form at high temp.). These results indicate that a hydronaphthalene containing one double linking in each ring will yield $C_{10}H_8$ and (IV), whilst (IV) and decahydronaphthalene will be the products when both double linkings are in one ring. The formation of cadalene and decahydrocadalene from the sesquiterpene from Japanese cedar oil, and the conversion of octa- into a mixture of tetra- and deca-hydrocadalenes support the structures previously assigned (J. Chem. Soc. Japan, 1930, **51**, 518) to the sesquiterpene and the octahydrocadalene. H. BURTON.

Hydroxy- and amino-thiophenols. R. POLLAK, E. RIESZ, and J. RIESZ (Monatsh., 1931, **58**, 129—136).—Chloroacetyl-*p*-thiocresol [prepared from *p*-thiocresol, aq. Na_2CO_3, and $CH_2Cl·COCl$ (I)], when heated with conc. aq. NH_3 at 50—55°, gives *glycyl*-p-*thiocresol*, m. p. 117°, and, when heated with chloranil on the water-bath, gives *tetra*-p-*tolylthiolbenzoquinone*, m. p. 203°. 3 : 5-Dimercapto-*o*-cresol, when boiled with (I), gives 5-*methyl-2-keto-7-(chloroacetylmercapto)benzthioxin* (II), m. p. 195°, and with chloranil yields 3-*chloro-9-mercapto-2 : 5-diketo-4-(3′-methyl-4′-hydroxy-5′-mercaptophenyl)-7-methylphenoxthin* (III), decomp. above 250°. *o*-Aminophenol and (I) give, when boiled, o-*chloroacetamidophenylchloroacetate*, m. p. 120°. 2 : 4-Dinitrothiophenol (prepared by reduction of the disulphide with dextrose and NaOH) is reduced by Zn dust and HCl in warm AcOH to the diamino-compound, which, when treated with chloranil in AcOH, yields a *substance*, $C_{42}H_{17}O_8N_6S_3Cl_5$, giving a light yellow vat and dyeing wool grey. Zinc *p*-toluidine-2 : 5-dimercaptide with chloranil in EtOH gives a *substance*, $C_{45}H_{27}O_8N_2S_6$, reddish-violet. Of the two last-mentioned products the former is considered to consist of thiazine and quinone rings joined by NH groups, whilst in the latter the rings are joined by S and the CO groups are replaced by OH. R. S. CAHN.



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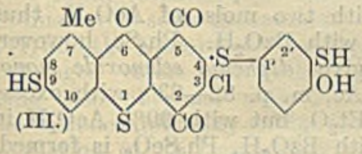


(III.)

Bactericidal properties of monoethers of dihydric phenols. I. Monoethers of resorcinol. E. KLARMANN, L. W. GATYAS, and V. A. SHTERNOV (J. Amer. Chem. Soc., 1931, **53**, 3397—3407).—The following resorcinol mono-alkyl and -aralkyl ethers are prepared from resorcinol and the appropriate bromide in presence of either xylene or alcoholic KOH (the figures in parentheses are the PhOH-coeff. determined by Reddish's method with *B. typhosus* and *Staph. aureus*, respectively): Me (1·3, 1·2); Et (3·6, 3·0); Pr (6·9, 5·4); Bu, b. p. 130°/5 mm. (20, 18); n-*amyl*, b. p. 140°/5 mm. (38, 36); sec.-*amyl*, b. p. 138°/5 mm. (26, 31); n-*hexyl*, b. p. 145°/5 mm. (46, 125); cyclo*hexyl*, b. p. 160°/6 mm. (18, 20); n-*heptyl*, b. p. 160°/5 mm. (21, 330); n-*octyl*, b. p. 170°/5 mm. (2·3, 580); n-*nonyl*, b. p. 171°/4·5 mm. (3·4, 650); *benzyl*, b. p. 200°/5 mm., m. p. 69·2° (21, 16); *p-chlorobenzyl*, b. p. 235°/13 mm., m. p. 76° (61, 38); β-*phenylethyl*, b. p. 202°/6 mm., m. p. 44° (35, 39); γ-*phenylpropyl*, b. p. 202°/5·5 mm. (34, 89). *Resorcinol Ph ether*, b. p. 150°/4·5 mm. (40, 37), is obtained by diazotisation of *m*-aminodiphenyl ether. The activity of the *n*-alkyl ethers towards *B. typhosus* reaches a max. at C_6 and then decreases, but with *S. aureus* it increases with length of the C chain. The *sec.*- have smaller activities than the *n*-alkyl compounds (which are similar to nuclear substituted resorcinols). H. BURTON.

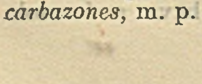
Preparation and bacteriological study of *sym.* organic sulphides. F. DUNNING, B. DUNNING, jun., and W. E. DRAKE (J. Amer. Chem. Soc., 1931, **53**, 3466—3469).—*Sulphides* of the type of 4 : 4′-dihydroxydiphenyl sulphide are prepared (the m. p. are given in parentheses) from the following phenols and SCl_2 in CCl_4 or Et_2O; resorcinol (165—167°); *m*-cresol (142·5°); *p*-chlorophenol (173°); *p*-bromophenol (180°), and thymol (152·5—153·5°). The sulphides (except that from resorcinol) are approx. 10 times as toxic towards *S. aureus* as the phenols from which they are derived. *o*-Substituted phenols and *m*- and *p*-substituted phenols containing a *m*-orienting substituent would not react with SCl_2. H. BURTON.

Lignin. IV. Reaction of phenolic derivatives with acetic anhydride–acetic acid–sulphuric acid. H. FRIESE (Ber., 1931, **64**, [*B*], 2109—2112).—Mono- and di-hydric phenols and their ethers, like PhOEt, are quantitatively converted by $AcOH–Ac_2O–H_2SO_4$ into the corresponding sulphonic acids. Sulphoacetic acid is produced when more H_2SO_4 is present than is necessary for 1 mol. of substance. Phloroglucinol yields triacetyltriketohexamethylene, m. p. 156°. The presence of a CHO group alters the nature of the reaction. Piperonal affords a bluish-violet condensation product, free from S, divisible into different fractions. Vanillin gives a brownish-red compound, insol. in H_2O and containing not more than traces of S. Cinnamaldehyde yields partly a resin free from S and partly sulphonic acids of undetermined structure. Furfuraldehyde or its diacetate affords black, brittle products. H. WREN.

Composition of sitosterol. H. SANDQVIST and E. BENGTSSON (Ber., 1931, **64**, [*B*], 2167—2171).—Quantitative hydrolysis of the acetates of sitosterol and dihydrositosterol from Swedish " tallöl " leads to the formulæ $C_{29}H_{49}·OAc$ and $C_{29}H_{51}·OAc$ and hence to the formulæ $C_{29}H_{49}·OH$ and $C_{29}H_{51}·OH$ for the non-acetylated products, in contrast to the generally accepted compositions, $C_{27}H_{45}·OH$ and $C_{27}H_{47}·OH$. Experiments with cholesteryl acetate establish the validity of the method provided that the requisite time is allowed for complete acetylation and hydrolysis. Since the C_{27} formula for sitosterol appears to be based on analyses and determinations of mol. wt. and also on analogy to cholesterol, a sterol from soya bean, rich in γ-sitosterol and free from stigmasterol, and a technical sterol have been similarly examined. Only the dihydrositosterol (and cholesterol) appear absolutely uniform; of the others, only the γ-sitosterol from soya bean can have a formula simpler than C_{29} but scarcely as low as C_{27}. Natural dihydrositosterol and sitosterol have the formulæ $C_{29}H_{52}O$ and $C_{29}H_{50}O$, respectively. H. Wren.

Stereochemical structure. III. Glycols derived from *d*(−)-mandelic acid. R. Roger and W. B. McKay (J.C.S., 1931, 2229—2238; cf. this vol., 487).—α(+)-Tolylhydrobenzoins differ little in sp. rotation from (+)triphenylethylene glycol. Various criteria indicate that the substances are similar in stereochemical structure, although the tolylhydrobenzoins contain a new asymmetric C atom, which is therefore considered to have a weak rotatory power. *r*-Benzoin with Mg *o*-tolyl bromide gives α-r-o-, m. p. 154—155°, and with Mg *m*-tolyl bromide, α-r-m-*tolylhydrobenzoin*, m. p. 135—137°. *d*(−)-Benzoin with the appropriate Grignard reagent gives α-d(+)-o-, m. p. 113—115° (and *r*-benzoin), α-d(+)-m-, m. p. 106—108°, and α-d(+)-p-*tolylhydrobenzoin*, m. p. 120—121°. Et *r*-mandelate similarly gives *α-phenyl-ββ-di-*m*-tolylethylene glycol*, m. p. 132—134°, whilst Et *d*(−)-mandelate gives d(+)-*α-phenyl-ββ-di-*p*-tolylethylene glycol*, m. p. 149—150°. A. A. Levi.

Condensation of olefinic acids and benzene rings. E. Fourneau and P. M. Baranger (Bull. Soc. chim., 1931 [iv], 49, 1161—1172).—With the object of obtaining esters of therapeutic value in treating leprosy, undecenoic and hydnocarpic acid have been condensed with C_6H_6 and some of its derivatives in presence of $AlCl_3$. None of the substances prepared had any therapeutic value. The esters of olefinic acids afford higher yields than the free acids and the yields increase with the distance between the double linking and the CO_2H group. Derivatives of C_6H_6 containing *p*-directing substituents give better yields than C_6H_6 itself. The following are described: ω-phenylundecoic acid, b. p. 225°/16 mm. (*amide*, m. p. 57°; *Et* ester, b. p. 170—190°/14 mm.), depositing crystals, m. p. 19—20°, when kept at −10°, and ω-l-*phenylundecoic acid*, b. p. 198°/15 mm. (*amide*, m. p. 79°; *Et* ester, b. p. 190—207°/14 mm.); the esters are obtained in 50% yield; ethyl ω-phenylundecoate is also obtained from ethyl ω-bromoundecoate; p-*methoxyphenylundecenoic acid*, b. p. 220°/0·9 mm. (*Et* ester, yield 85% from anisole, b. p. 193°/1·7 mm.), converted by HI (*d* 1·7) and AcOH into p-*hydroxyphenylundecoic acid*, b. p. 220°/1·5 mm., a weak disinfectant; *phenyldihydrohydnocarpic acid*, m. p. 43—44° (*Et* ester, b. p. 195°/1·5 mm.); p-*methoxyphenyldihydrohydnocarpic acid*, b. p. 220°/1·5 mm. (*Et* ester, yield 80% from PhOEt, b. p. 220°/1·7 mm.).

The following dicarboxylic acids are obtained similarly: p-*methoxyphenylbutylmalonic acid*, m. p. 144·5° (*Et* ester, b. p. 209°/20 mm., yield 30% from Et allylmalonate), converted at 160—170° into p-*methoxyphenylvaleric acid*, m. p. 65°; *phenylenediundecoic acid* (*Et*$_2$ ester, b. p. 245°/2 mm.); *Et 4-carboxymethylphenylundecoate*, b. p. 220—230°/2 mm. (yield 18% from phenylacetic acid and ethyl undecenoate in CS_2), the *Th* salt of which on distillation at 300—500°/45 mm. affords the ketones,  $C_6H_4{<}{\scriptsize\begin{matrix}[CH_2]_{10}\\CH_2\end{matrix}}{>}CO$ and  $C_6H_4{<}{\scriptsize\begin{matrix}[CH_2]_{8}\\CH_2\end{matrix}}{>}CO$ (*semicarbazones*, m. p. 226° and 205°, respectively). Stoll, by distillation of the Ce salt at 10 mm., has obtained a ketone, $C_{15}H_{26}O$, b. p. 180—195°/9 mm. (*semicarbazone*, m. p. 199—201°). Et undecenoate and β-phenylpropionic acid in CS_2 in presence of $AlCl_3$ similarly afford *Et* p-β-*carboxyethylphenylundecoate*, b. p. 270°/3 mm. Undecenyl acetate and $CH_2Ph{\cdot}CN$ in presence of $AlCl_3$ yield 4-*cyanomethylphenylundecyl acetate*, m. p. 72°; 4-*cyanomethylphenylundecoic acid*, m. p. 123—124°, is similarly obtained from undecenoic acid. Attempts to hydrolyse the above nitriles failed. *X*-Ray examination indicates that the mols. of the last acid are oriented parallel to one another in reticular planes 10·82 Å. apart, and the mode of packing accounts for its resistance to hydrolysis and cyclisation. R. Brightman.

Oxidation of organic compounds with peracetic and perbenzoic acids. B. A. Arbusov (J. pr. Chem., 1931, [ii], 131, 357—372).—The view of Böeseken and Schneider (this vol., 207) that the mechanisms of oxidation of org. compounds by AcO_2H and BzO_2H are essentially different is criticised, and it is suggested that the divergent results obtained are a consequence of the conditions of reaction. The cause of the formation of $PhIO_2$ from PhI and BzO_2H, and of $PhI(OAc)_2$ from PhI and AcO_2H, lies in the readier acylation of PhIO by AcOH; alteration of the reaction conditions, *e.g.*, by use of 90% AcO_2H in conc. Et_2O solution, or in absence of a solvent, or in dil. aq. solution in presence of $NaHCO_3$, gives rise to $PhIO_2$ with AcO_2H also. On the other hand, oxidation of PhI with BzO_2H in Et_2O saturated with BzOH gives *iodosobenzene dibenzoate*, m. p. 159—160°, which is also formed by action of BzOH on $PhI(OAc)_2$ in Et_2O. $(CH_2Ph)_2S$ gives the sulphoxide with 1 mol., and the sulphone with two mols. of AcO_2H, thus behaving exactly as with BzO_2H. Ph_2Se, however, resembles PhI and gives *diphenyl selenoxide monoacetate*, $Ph_2Se(OH){\cdot}OAc$, m. p. 82—83°, with excess of AcO_2H in much Et_2O, but with 90% AcO_2H in conc. solution, or with BzO_2H, Ph_2SeO_2 is formed. Oxidation of PPh_3 with AcO_2H in Et_2O gives $POPh_3$ in 93·8% yield. H. A. Piggott.

Allylic rearrangement in reaction between cinnamyl chloride and magnesium. H. Gilman and S. A. Harris (J. Amer. Chem. Soc., 1931, 53, 3541—3546).—The Grignard reagent (*A*) from cinnamyl chloride reacts mainly as Mg α-phenylallyl chloride, since treatment with CO_2 gives α-phenyl-Δ^{β}-butenoic acid, m. p. 23—24° (*anilide*, m. p. 97—98°, obtained from *A* and phenylcarbimide). This acid is converted by warming with acid or alkali into methylatropic acid (cf. A., 1927, 875), and is reduced catalytically (Adams) to α-phenylbutyric acid. Methylatropic acid is also formed by hydrolysis of the product from *A* and $ClCO_2Et$. The formation of *A* is presumed to involve transformation of cinnamyl into α-phenylallyl radicals. H. Burton.

Erlenmeyer synthesis of amino-acids. J. Lamb and W. Robson (Biochem. J., 1931, 25, 1231—1236).—Glacial AcOH is substituted for Ac_2O in the reduction stage of the synthesis by HI and red P introduced by Harington and McCartney (A., 1927, 961). A drastic reduction of the amount of HI leads to the reduction of the unsaturated compound without the loss of Bz radical from the NH_2 group; the oxazolone yields the benzamido-acid by this treatment. If HI is present in sufficient quantity the reduction is also accompanied by the removal of the Bz group, with the consequent production of the α-amino-acid and also of other groups if the reaction is prolonged. Oxazolone can also be made to yield the α-NH_2-acid in this way. Good yields have been obtained by this method in the prep. of the following compounds: benzoylphenylalanine, phenylalanine, tyrosine, α-benzamido-*p*-methoxycinnamic acid, benzoyl-*p*-methoxyphenylalanine. S. S. Zilva.

Conversion of ethyl *l*-α-chloroformoxyphenylacetate into lævorotatory and dextrorotatory ethyl phenylchloroacetate. J. Kenyon, A. G. Lipscombe, and H. Phillips (J.C.S., 1931, 2275—2282; cf. this vol., 480).—Pyridine is without influence on the sign of rotation of the product of interaction of Et *l*-mandelate and PCl_5 or PCl_3. Et l-mandelate in quinoline with $COCl_2$ in PhMe gives Et l-α-*chloroformoxyphenylacetate*, (I), b. p. 72—74°/<0·1 mm., and a little l-α-*carbethoxybenzyl carbonate*, b. p. 195—200°/<0·1 mm., the corresponding *dl*-compound, b. p. 182—184°/<0·1 mm., being obtained by interaction of Et *dl*-mandelate and (I). (I) corresponds in structure with the intermediate pyridine compound assumed in the interaction of $SOCl_2$ and Et *l*-mandelate in pyridine (*loc. cit.*), and, with the products obtained from it, has the expected sign of rotation. Et *l*-mandelate with AcCl, BzCl, or *p*-toluenesulphinyl chloride gives *Et* l-α-*acetoxy*-, b. p. 147°/13 mm., *Et* l-α-*benzoyloxy*-, b. p. 134—135°/<0·1 mm., and *Et* l-α-*toluenesulphinoxy-phenylacetate*, b. p. 136—139°/<0·1 mm., respectively. The same substances are obtained with some racemisation from the interaction of (I) and the Na salts of the corresponding acids, some unchanged ester and some di-*p*-tolyldisulphoxide being also obtained with Na *p*-toluenesulphinate. The toluenesulphinoxy-compound also arises from the interaction of Et *l*-mandelate and Et *p*-toluenesulphinate. With pyridine (I) gives Et *d*-phenylchloroacetate, whilst when heated alone it gives the *l*-compound. Et *dl*-phenylchloroacetate and Na *p*-toluenesulphinate give dl-α-*carbethoxybenzyl*-p-*tolylsulphone*, m. p. 112—113°, hydrolysed to *dl*-α-carboxybenzyl-*p*-tolylsulphone, m. p. 169—170° (decomp.), both being converted into benzyl-*p*-tolylsulphone. Et *d*-phenylchloroacetate gives similarly *d*+*dl*-α-carbethoxybenzyl-*p*-tolylsulphone, m. p. 111—112°. Et *l*-mandelate gives a *urethane*, b. p. 165—166°/<0·1 mm. The corresponding *dl*-compound has m. p. 97° (cf. A., 1899, i, 52). A. A. Levi.

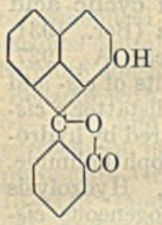
Hydrogen sulphite compounds of naphthalene derivatives. Abnormal reaction between sodium hydrogen sulphite and 2 : 3-hydroxynaphthoic acid derivatives. R. Lantz and G. Mingasson (Compt. rend., 1931, 192, 1664—1666, and Bull. Soc. chim., 1931, [iv], 49, 1172—1180).—1-Nitroso-β-naphthol-3-carboxylic acid and $NaHSO_3$ yield a compound which on acidification yields 1-nitroso-β-naphthol-4-sulphonic acid, eliminating the CO_2H group. In a similar manner, treatment of 1-benzeneazo-β-naphthol-3-carboxylic acid with $NaHSO_3$ causes loss of the carboxyl group. A hydrogen sulphite compound of 1-nitroso-β-naphthol 3-carboxylanilide could not be obtained as described by Battegay and others (A., 1924, i, 722) by the action of $NaHSO_3$ on the Na compound in aq. solution, but by working in EtOH a product was obtained apparently containing 1 mol. of NO-derivative and 1 mol. of SO_2. On acidification this gives the original NO-derivative without loss of the CO·NHPh group. G. Discombe.

Formation and transformation of cyclic acid imides. W. Hückel and H. Müller (Ber., 1931, 64, [*B*], 1981—1990).—Contrary to Sircar (A., 1927, 756) the thermal decomp. of the NH_4 salts of *cis*- and *trans*-hexahydrophthalic acid yields Willstätter's *cis*-hexahydrophthalimide, m. p. 137°, prepared by hydrogenation of phthalimide or tetrahydrophthalimide. The preps. are unchanged by distillation. Hydrolysis with cold alkali hydroxide gives homogeneous *cis*-hexahydrophthalic acid, whereas the *trans*-acid is formed at 100°. The action of Ac_2O or AcCl on *cis*- or *trans*-hexahydrophthalamic acid yields the *cis*-imide and a *substance* $C_{16}H_{20}O_3N_2$, m. p. 167°, possibly identical with Sircar's compound, m. p. 164°, and a small amount of a dye. The compound of m. p. 167° decomposes when distilled in a vac., is hydrolysed by cold and hot alkali hydroxide to *cis*- and *trans*-hexahydrophthalic acid, decolorises $KMnO_4$ and Br, but does not absorb H_2. Dissolution in Na_2CO_3 and precipitation with acid affords the monobasic *acid*, $C_{16}H_{22}O_4N_2$, m. p. 210—212°, cautiously hydrolysed to *cis*-hexahydrophthalic acid. *Me* cis-*hexahydrophthalamate* and *Me* trans-*hexahydrophthalamate* have m. p. 77° and 93—94°, respectively. *cis*-Hexahydrophthalic anhydride is converted by NH_2Ph in C_6H_6 into cis-*hexahydrophthalanilic acid*, m. p. 170—171°, transformed by AcCl into the cis-*anil*, m. p. 134°. trans-*Hexahydrophthalanilic acid*, m. p. 223—224°, and the corresponding trans-*anil*, m. p. 193—194°, are described. Protracted heating caused isomerisation of the *trans*- to the *cis*-anil. Hydrolysis of the *trans*-anil yields the *trans*-anilic acid, whereas the *cis*-anil with aq. $Ba(OH)_2$ at 90° yields a mixture of *cis*- and *trans*-anilic acid, the latter being the sole product with conc. aq. or alcoholic NaOH. *meso*Dimethylsuccinic anhydride and NH_3 in Et_2O give meso*dimethylsuccinamic acid*, m. p. 165—167°, converted by AcCl into a product, m. p. 70—100°, whereas the *imide*, obtained by hydrogenation of dimethylmaleimide has m. p. 66—72°. r-*Dimethylsuccinamic acid*, m. p. 148—149°, and *r*-dimethylsuccinimide, m. p. 105—106°, are described. Cautious hydrolysis of the amic acids or imides gives dicarboxylic acids of the corresponding configuration. The following vals. for the hydrolysis consts. at 0° and 25° are recorded: succinimide 39·4, 248; *r*-dimethylsuccinimide, 30, 204; *cis*-hexahydrophthalimide, 79·9, 322; dimethylmaleimide, 5216, 19,550; tetrahydrophthalimide, 16,300, (38,000). H. Wren.

Synthesis of the *d*- and *l*-3 : 4-dihydroxyphenylalanines. C. R. Harington (Biochem. J., 1931, 25, 1028—1031).—β-3 : 4-Diacetoxyphenyl-α-acetamidoacrylic acid, obtained by condensation of protocatechualdehyde with acetylglycine in presence of Ac_2O and NaOAc, is reduced by $PdCl_4$ and H_2. The brucine salts of the resulting β-3 : 4-diacetoxyphenyl-α-acetamidopropionic acid are then obtained, the l-isomeride by crystallisation from EtOH and the *d*-isomeride from the mother-liquor.

S. S. Zilva.

Condensation of β-naphthol with phthalic anhydride. L. F. Fieser (J. Amer. Chem. Soc., 1931, 53, 3546—3560).—Phthalic anhydride and β-naphthol in presence of $AlCl_3$ at 250° give a yellow *compound* (I) (probably with the annexed structure), $C_{18}H_{10}O_3$, m. p. 198° (*Et ether*, m. p. 163°), and not a hydroxynaphthanthraquinone (G.P., 298,345); the structure assigned to (I) by Rieche and Frühwald (this vol., 1060) does not explain many of the reactions now described. (I) is converted by aq. NaOH into a *Na* salt $C_{18}H_{11}O_4Na$, by PCl_5 and $POCl_3$ into a *chloride* $C_{18}H_9O_2Cl$, m. p. 165°, and by MgPhBr into a *compound* $C_{24}H_{16}O_3$, m. p. 247° (*diacetate*, m. p. 224°). Oxidation of (I) with alkaline $KMnO_4$ affords *benzhydrol*-2 : 3 : 2′-*tricarboxylic acid* 2′-*lactone* (*Me*$_2$ ester, m. p. 149°), which passes at 214° into an *anhydride*, m. p. 205°. The lactone is oxidised further to *benzophenone*-2 : 3 : 2′-*tricarboxylic acid dilactone*, m. p. 230° (*Me* ester, m. p. 186·5°), decarboxylated in presence of 0·5% of Cu powder at 300° to the dilactone of benzophenone-2 : 2′-dicarboxylic acid [Me_2 ester, m. p. 82° (lit. 86°)], which is reduced ultimately to diphenylmethane-2 : 2′-dicarboxylic acid, m. p. 250° (lit. 254·5°).



Phthalic anhydride and β-naphthyl Me ether in presence of $AlCl_3$ and $C_2H_2Cl_4$ at 100° give *o*-2-*hydroxy*-1-*naphthoylbenzoic acid*, m. p. 155° [*Me* ester, m. p. 131°; *Me ether*, m. p. 196° (*Me* ester, m. p. 109°), is the main product when reaction is carried out at room temp.], the *lactone*, m. p. 195°, of which is converted by $AlCl_3$ in hot C_6H_6 into (I). *Phenyl*-2-*hydroxy*-1-*naphthylmethane*-2′-*carboxylic acid* (*lactone*, m. p. 147°; *Me ether*, m. p. 196°) has m. p. 187°. β-Naphthyl Me ether and BzCl in presence of $AlCl_3$ and $C_2H_2Cl_4$ at 25° afford 1-*benzoyl*-β-*naphthol* (53%), m. p. 142°, and its *Me ether* (22%), m. p. 127°; the former is converted by $AlCl_3$ and NaCl at 200° into 4-hydroxybenzanthrone. Me *o*-α-naphthoylbenzoate with $AlCl_3$ and NaCl at 130° yields 10% of the compound, m. p. 177°, described in B., 1930, 706. Phthalic anhydride and leucoquinizarin in presence of $AlCl_3$ at 250° give (probably) 5 : 7 : 12 : 14-*tetrahydroxypentacene*-6 : 13-*quinone* [*tetra-acetate*, m. p. 315° (decomp.)].

H. Burton.

Action of *o*-phthaloyl chloride on phenyl and thiophenyl acetates. W. Knapp (Monatsh., 1931, 58, 176—182).—Attempts to prepare thiophenolphthalein were unsuccessful. *o*-Phthaloyl chloride, PhSAc, and $AlCl_3$ in CS_2 give *as*.-diphenyl dithiophthalate, m. p. 101°; this constitution, previously considered improbable (A., 1927, 970), is favoured by the fact that $KMnO_4$ in warm AcOH gives, not the *s*-disulphone, but two *substances*, m. p. 142—144° and 105—106°, respectively, both decomposed by conc. H_2SO_4, one of which is probably the *as*.-disulphone. *o*-Phthaloyl chloride, PhOAc, and $AlCl_3$ in CS_2 give a little phenolphthalein, *s*-diphenyl phthalate, and a gum. The formation of both *s*- and *as*-derivatives from phthaloyl chloride is difficult to explain.

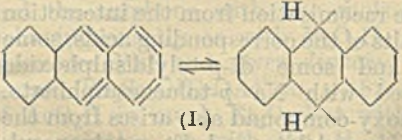
R. S. Cahn.

Synthesis of derivatives of arylacetic and β-arylpropionic acids. J. Hoch (Compt. rend., 1931, 192, 1464—1466).—Arylacetic acids are obtained from benzyl halides through the nitriles, the β-arylpropionic acids through benzylmalonic esters. 2 : 4-Dimethylbenzyl chloride and 2 : 4 : 6-*trimethylbenzyl chloride*, m. p. 37°, b. p. 119°/15 mm., are obtained by the action of $CH_2Cl{\cdot}OEt$ on *m*-xylene or mesitylene in presence of $SnCl_4$, *o*-methylbenzyl bromide by the action of HBr on *o*-methylbenzyl Et ether, and β-p-*tolylethyl bromide* from β-p-*tolylethyl Et ether*, b. p. 105°/14 mm., prepared by the action of $C_2H_4Br{\cdot}OEt$ on Mg *p*-tolyl bromide.

m-4-*Xylylacetonitrile*, b. p. 146°/19 mm., *mesitylacetonitrile*, m. p. 79°, b. p. 150—155°/15 mm., β-2 : 4 : 6-*trimethylphenylpropionic acid*, m. p. 113°; *Et* 2 : 4-*dimethylbenzylmalonate*, b. p. 186—188°/13 mm., *Et* o-*xylylmalonate*, b. p. 180—182°/15 mm., *Et* 2 : 4 : 6-*trimethylbenzylmalonate*, m. p. 36°, b. p. 195—197°/15 mm., and *Et* β-p-*tolylethylmalonate*, b. p. 192—194°/17 mm., are also described.

G. Discombe.

Polynuclear, aromatic hydrocarbons and their derivatives. XI. Constitution of anthracene. E. Clar (Ber., 1931, 64, [*B*], 2193—2200; cf. Diels and Alder, this vol., 848).—Study of the reaction of anthracene and its derivatives with unsaturated acid anhydrides leads to the conclusion that the Armstrong–Hinsberg constitution is inadequate to explain the changes, which can be interpreted by the author's equilibrium formula (I). 9 : 10-*endo*-Anthracene - αβ - succinic anhydride, m. p. 258—259°, from the components in boiling $C_6H_4Me_2$, dissociates into maleic anhydride and anthracene at 260—270°. 9 : 10-endo-2-*Chloroanthracene*-, m. p. (indef.) 213—217°, and -2 : 3 : 6 : 7-*dibenzanthracene*-αβ-*succinic anhydride*, m. p. 298° (slight decomp.), are similarly obtained. In boiling $PhNO_2$, maleic anhydride and the requisite derivative afford 9 : 10 : 1′ : 4′-endo-7 : 7′-*dimethyl*-2′ : 3′-*naphtha*-1 : 2-*anthracenedi*-αβ-*succinic anhydride*, m. p. 308° (decomp.) after darkening at 300°, and 9 : 10-endo-9 : 10-*dichloroanthracene*-αβ-*succinic anhydride*, m. p. 258—259°. The last-named compound is converted by boiling quinoline into 9 : 10-dichloroanthracene. In it the Cl atoms have been rendered so mobile that reaction occurs with $AlCl_3$ and C_6H_6 or *m*-xylene, leading to 9 : 10-diphenylanthracene, m. p. 248°, and 9 : 10-*di*-m-*xylylanthracene*, m. p. 290°. In the former action, a reddish-brown *hydrocarbon*, $C_{26}H_{14}$, m. p. 335° after softening at 330°, is occasionally produced, apparently an iso*rubicene*.



(I.)

H. Wren.

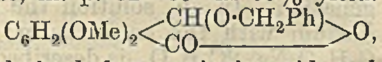
Bicoloured phthaleins. A. Thiel (Z. physikal. Chem., Bodenstein Festband, 1931, 352—356).—The α-naphtholphthaleins and the homologues of phenolphthalein, but not phenolphthalein itself, exhibit two colour changes; the first results in the production of the orange or yellow primary quinonoid anion and the second in that of the deeply coloured meriquinonoid anion. The effect can usually be observed only in EtOH solution, on account of the slight solubility of the phthaleins. The α-naphtholphthaleins prepared according to Schulenburg and Sörensen, respectively, differ in their reactivity with conc. alkali and in their absorption spectra; the former substance is probably an *oo'*- and the latter a *pp'*-compound.

H. F. Gillbe.

Synthesis of 2-hydroxy-4 : 5-dimethoxybenzoic acid. F. S. H. Head and A. Robertson (J.C.S., 1931, 2432—2433; cf. this vol., 841).—2-Hydroxy-4 : 5-dimethoxybenzaldehyde, m. p. 107° (this vol., 73), gives an *acetate*, m. p. 95°, which is oxidised by $KMnO_4$ in $COMe_2$ to 2-*acetoxy*-4 : 5-*dimethoxybenzoic acid*, m. p. 166°, hydrolysed to 2-hydroxy-4 : 5-dimethoxybenzoic acid, m. p. 213—214° (decomp.).

A. A. Levi.

Opianic acid. II. Esterification of opianic acid and internal condensation of certain of its esters. P. Schorigin, V. Issagulanz, and V. Belov (Ber., 1931, **64**, [*B*], 1931—1935).—Anhydrous K opianate is converted by CH_2PhCl in C_6H_6 at 100° into *benzyl α-opianate*, m. p. 82—83° in 60% yield. *Benzyl ψ-opianate*,



$$C_6H_2(OMe)_2{<}\begin{matrix}CH(O{\cdot}CH_2Ph)\\CO\text{————}\end{matrix}{>}O,$$

m. p. 94—95°, is derived from opianic acid and $CH_2Ph{\cdot}OH$ at 100—110°. Analogously, anhydrous K opianate and $CH_2Cl{\cdot}CO_2Et$ in C_6H_6 afford *Et carbethoxymethyl α-opianate*, m. p. 87—88°, transformed by NaOEt into Et ψ-opianate, unaffected by anhyd. oxalic acid or pyridine, but transformed by Na in xylene into 7 : 8-*dimethoxy*iso*coumarin*-3-*carboxylic acid*, m. p. 264—265°, and Et ψ-opianate. Benzyl α-opianate is converted by pyridine at 160—170° into 7 : 8-*dimethoxy*-2-*phenyl*iso*coumarin*, m. p. 132—133°, and a substance, m. p. 235—238°. H. Wren.

Condensation of monochloromethyl ether with ethyl phenylmalonate. M. G. Rao and J. L. Simonsen (Proc. XV Indian Sci. Cong., 1928, 149).—The product $(CO_2Et)_2CPh{\cdot}CH_2{\cdot}OMe$, when treated with 50% KOH, affords atropic acid, or with 10% alcoholic KOH it affords methyltropic acid.

Chemical Abstracts.

Action of sulphuric acid and bromine on ethyl benzylidenediacetoacetate. B. M. Gupta and S. C. Roy (Proc. XV Indian Sci. Cong., 1928, 158).—Et α-bromo-αα'-diacetyl-β-phenylglutarate, m. p. 131°, was obtained. Chemical Abstracts.

Bromination of dehydrodeoxycholic acid. T. Noguchi (Z. physiol. Chem., 1931, **200**, 48—50).—Bromination gives a *bromo*- (+½EtOAc), m. p. 172° (froths at 100—105°), and a *dibromo-dehydrodeoxycholic acid* (+½EtOAc), m. p. 160—165° (decomp.) (froths at 146—147°). The dibromo-acid is debrominated by aq. $Ba(OH)_2$ to hydroxydiketocholenic acid (+½AcOH), m. p. 248° (decomp.).

J. H. Birkinshaw.

Bile acids. XXXI. M. Schenck (Z. physiol. Chem., 1931, **200**, 41—47; cf. this vol., 841).—Oxidation of *iso*bilianic acid oxime lactone with alkaline $KMnO_4$ eliminates the NOH group yielding the ketolactonetricarboxylic acid, decomp. 245°. 90% H_2SO_4 at 100° produces from the oximinoamino-acid an inversion *product*, decomp. 258°, which has lost the NOH group. J. H. Birkinshaw.

Manufacture of substituted salicylic acids. I. G. Farbenind. A.-G.—See B., 1931, 917.

Manufacture of 6-halogeno-3-aminodiphenylmethane-2'-carboxylic acids and substitution products and derivatives. Newport Co.—See B., 1931, 918.

Inhibitory action of anthracene in the autoxidation of benzaldehyde. H. L. J. Bäckström and H. A. Beatty.—See this vol., 1245.

Autoxidation of benzaldehyde. II. Action of catalysts. G. Raymond.—See this vol., 1248.

ε-Phenylpentadienal. V. Alexa (Ber., 1931, **64**, [*B*], 2250—2252).—ε-Phenylpentadienal, conveniently prepared by the fractionation of the residues from the technical production of cinnamaldehyde, is converted into the corresponding azine, m. p. 228°, and into di-ζ-phenylhexatrienyl ketone, m. p. 189—190°. ε-*Pentadienylideneindene*, m. p. 182—183°, and ε-*pentadienylideneindan*-1 : 3-*dione*, m. p. 167—168°, are described. H. Wren.

Acids derived from diphenyl-4-aldehyde. D. H. Hey (J.C.S., 1931, 2476—2479; cf. A., 1921, i, 417).—Diphenyl-4-aldehyde (improved prep.; cf. A., 1906, i, 589) is oxidised by $KMnO_4$ in Na_2CO_3 to diphenyl-4-carboxylic acid, which by prolonged action with NaOAc and Ac_2O gives p-*phenylbenzylidene diacetate*, m. p. 131° (also obtained from the aldehyde with Ac_2O and a little H_2SO_4), and *diphenylyl*-4-*acrylic acid*, m. p. 223—224° (*Et* ester, m. p. 87°), also obtained during the prep. of, and by heating, p-*phenylbenzylidenemalonic acid*, m. p. 215° (decomp.), obtained from diphenyl-4-aldehyde and malonic acid. The above diphenylylacrylic acid gives αβ-*dibromo*-β-4-*diphenylylpropionic acid*, m. p. 196—197° (decomp.), converted by prolonged action of KOH in EtOH into *diphenylyl*-4-*propiolic acid*, m. p. 175—176°.

A. A. Levi.

[Preparation of phenylglyoxal.] M. Henze (Z. physiol. Chem., 1931, **200**, 232).—1 mol. of $CH_2Bz{\cdot}OH$ requires theoretically 2 mols. of $Cu(OAc)_2$ and produces 1 mol. of Cu_2O, not as previously stated (cf. this vol., 843). Heating facilitates the reaction.

J. H. Birkinshaw.

Action of phenylglyoxal on acetoacetic acid. M. Henze and R. Müller (Z. physiol. Chem., 1931, **200**, 101—107; cf. this vol., 843).—Na acetoacetate and phenylglyoxal afford $COPh{\cdot}CH(OH){\cdot}CH_2{\cdot}COMe$ (I), m. p. 59—60°, oxidised by $FeCl_3$ or $Cu(OAc)_2$ to the *triketone* (Cu salt, m. p. 206°), deep red with $FeCl_3$. Oxidation of (I) with alkaline $KMnO_4$ gives pyruvic and glyoxylic (p-*nitrophenylhydrazone*, m. p. 158°) acids. $COMe{\cdot}CH(OH){\cdot}CH_2{\cdot}COMe$ gives the corresponding *triketone* (*Cu* salt, sublimes at 190° and decomposes at 223°). Oxidation of acetylacetone with alkaline $KMnO_4$ at low temp. yields pyruvic acid.

J. H. Birkinshaw.

Wandering of groups during bromination. M. G. S. Rao, C. Srikantia, and M. S. Iyengar (Proc. XV Indian Sci. Cong., 1928, 158—159).—Wandering of the NO_2 group on bromination of 5-nitro-4-methoxy-β-resorcylaldehyde is recorded.

CHEMICAL ABSTRACTS.

3-Acenaphthyl ethyl ketone (3-propionylacenaphthene). K. DZIEWOŃSKI and J. MOSZEW (Bull. Acad. Polonaise, 1931, A, 158—164).—Acenaphthene and propionyl chloride in presence of $AlCl_3$ and CS_2 give a substance, m. p. 122—123° (picrate, m. p. 129°), and 3-*propionylacenaphthene* (I), m. p. 69—70° (*picrate*, m. p. 109°; *phenylhydrazone*, m. p. 107°; 4-*NO_2 derivative*, m. p. 164—165°; *oxime*, m. p. 185—186°, converted by HCl in AcOH and Ac_2O into the *propionyl* derivative, m. p. 150—151°, of 3-aminoacenaphthene). Oxidation of (I) with $Na_2Cr_2O_7$ in AcOH affords 3 : 3′-*dipropionyldiacendione*, $\left[\mathrm{EtCO{\cdot}C_{10}H_5}{<}\begin{matrix}\mathrm{C{:}}\\ \mathrm{CO}\end{matrix}\right]_2$, m. p. 286° (decomp.), and (mainly) 4-*propionylnaphthalic anhydride*, m. p. 152—153° (*bisphenylhydrazone*, m. p. 192—193°). 4-*Propionylnaphthalimide* has m. p. 221—222°.

H. BURTON.

Anthracene derivatives. VII. E. DE B. BARNETT, N. F. GOODWAY, and L. H. W. SAVAGE (Ber., 1931, 64, [*B*], 2185—2194).—2-*Chloro*-10-p-*dimethylaminophenylanthrone*, m. p. 128° according to the rate of heating, and 3-*chloro*-10-p-*dimethylaminophenylanthrone*, m. p. 190—195° (decomp.), are derived from the respective chloro-10-bromoanthrones and $NPhMe_2$. *o*-3′ : 4′-Dichlorobenzoylbenzoic acid is reduced by Zn dust and NH_3 to o-3′ : 4′-*dichlorobenzylbenzoic acid*, m. p. 146°, converted by conc. H_2SO_4 at room temp. into 2 : 3-dichloroanthrone. Unlike 2- and 3-chloro- or 1 : 4- and 1 : 5-dichloro-anthrone, the 2 : 3-compound is converted by aq. KOH and CH_2PhCl into *benzyl* 2 : 3-*dichloro*-10-*benzylanthranyl ether*, m. p. 165°. Br in CS_2 transforms 2 : 3-dichloroanthrone into 2 : 3-*dichloro*-10-*bromoanthrone*, m. p. 165° (decomp.), converted by $NPhMe_2$ into 2 : 3-*dichloro*-10-p-*dimethylaminophenylanthrone*, decomp. about 140°, and by piperidine into 2 : 3 : 2′ : 3′-*tetrachlorodianthraquinone*, m. p. above 300°. Treatment of 2 : 3-dichloro-10-bromoanthrone with $AlCl_3$ in C_6H_6 affords 2 : 3-*dichloro*-10-*phenylanthrone*, m. p. (indef.) 155° (2 : 3-*dichloro*-10-*phenylanthranyl acetate*, m. p. 177°); 1 : 4-*dichloro*-10-*phenylanthrone*, m. p. 188°, and 1 : 4-*dichloro*-10-*phenylanthranyl acetate*, m. p. 187°, are similarly prepared. 1 : 4-*Dichloro*-10-*phenyl*-9-*benzylidene*-9 : 10-*dihydroanthracene* has m. p. 163°. Phthalic anhydride, PhOMe, and $AlCl_3$ afford *o-p′*-methoxybenzoylbenzoic acid reduced by Zn dust and NH_3 to *o-p′*-methoxybenzylbenzoic acid, m. p. 117°, dehydrated by 90% H_2SO_4 at room temp. or by 80% H_2SO_4 at 50° to 2-*methoxyanthrone*, m. p. 100°. 2-*Methoxyanthranyl acetate*, m. p. 157°, 10-*bromo*-2-*methoxyanthrone*, decomp. about 120°, and 2-*methoxy*-10-p-*dimethylaminophenylanthrone*, m. p. (indef.) 123° (decomp.), are described. 2-Methoxyanthraquinone, m. p. 196°, is prepared by oxidising the anthrone with CrO_3 in boiling AcOH. Reduction of 3-methoxyanthraquinone with Cu powder at 40° affords 3-methoxyanthrone, from which 10-*bromo*-3-*methoxyanthrone*, decomp. 107—108°, 3-*methoxy*-10-p-*dimethylaminophenylanthrone*, m. p. 146—148° (decomp.) after blackening at 135°, and 3 : 3′-*dimethoxydianthraquinone*, m. p. 298°, are derived. Phthalic anhydride and veratrole yield *o*-3′ : 4′-dimethoxybenzoylbenzoic acid, whereas prolongation of the action leads to o-4-*hydroxy*-3-*methoxy*- (or, less probably, o-3-*hydroxy*-4-*methoxy*-) -*benzoylbenzoic acid*, m. p. 207°, derived also from the dimethoxybenzoylbenzoic acid and $AlCl_3$ in CS_2. o-3′ : 4′-*Dimethoxybenzylbenzoic acid*, m. p. 119°, is converted by 80% H_2SO_4 at 50° into 2 : 3-dimethoxyanthrone, m. p. 134° (2 : 3-dimethoxyanthranyl acetate, m. p. 172°). o-2′ : 5′-*Dimethoxybenzylbenzoic acid*, m. p. 124·5°, and 80% H_2SO_4 at 55° yield 1 : 4-*dihydroxyanthrone*, decomp. 185—195° (corresponding *triacetate*, m. p. 203°, and *tri*-p-*nitrobenzoate*, decomp. about 285°, but not completely molten below 300°).

H. WREN.

Dihydropyrocatechol or *cyclo*hexane-1 : 2-dione. E. URION (Compt. rend., 1931, **192**, 1662—1664).—Divinyl glycol heated with reduced Cu at 280° yields cyclo*hexane*-1 : 2-*dione* (20% yield), m. p. 104·5°, sublimes at 97°/10 mm. (*dihydrate*, m. p. 78—79°; *dioxime*, m. p. 148—149°; *bisphenylhydrazone*, m. p. 143°; *dibromide*, m. p. 153—154°; *monophenylurethane*, m. p. 135°; *quinoxaline*, m. p. 73—73·5°; *semicarbazone*, m. p. 280°). Its production from divinyl glycol is explained by the intermediate formation of adipaldehyde, followed by ring-closure and dehydrogenation. In aq. solution the diketone is in equilibrium with the enolic form; a *sodio*-derivative, $C_6H_8O_2Na_2,2C_6H_8O_2$, is described. G. DISCOMBE.

Mixed benzoins. VII. Maximal catalytic reduction. J. S. BUCK and W. S. IDE (J. Amer. Chem. Soc., 1931, 53, 3510—3513).—Catalytic reduction (Adams) of benzoin, *o*-chlorobenzanisoin, and *o*-chlorobenzveratroin in EtOH (sometimes containing HCl) at about 70° gives, in each case, αβ-dicyclohexylethane and a *compound* (? αβ-*dicyclohexylethylene glycol*), $C_{14}H_{26}O_2$, m. p. 193—194°, re-solidifying with m. p. 200° (*Ac* derivative, m. p. 133°). Similar reduction of *p*-dimethylaminobenzoin, *p*-dimethylaminobenzanisoin, and *o*-, *m*-, and *p*-chloro-*p′*-dimethylaminobenzoins affords, in each case, 4-*dimethylamino*-αβ-*dicyclohexylethane*, b. p. 170°/9 mm. (*picrate*, m. p. 148—150°). Anisoin, benzanisoin, piperoin, and *o*-chlorobenzpiperoin were reduced similarly to the corresponding hydrobenzoins. H. BURTON.

Oxidation of nitrobenzylamines. G. GALLAS, V. M. VIVALDI, and P. MORENO (Anal. Fís. Quím., 1931, 29, 458—463).—When *p*-nitrobenzylamine is oxidised by H_2O_2 in AcOH and the product distilled in steam, there separates from the residue o-*hydroxy*-p′-*nitrobenzildianil*, m. p. 225°, which is hydrolysed by HCl to give p-*hydroxy*-p′-*nitrobenzil*, m. p. 172° [*quinoxaline*, m. p. 250° (darkens 210°), with *o*-phenylenediamine; *bisphenylhydrazone*, m. p. 198°]. Similarly, *p*-nitrobenzyl-*p*-toluidine yields p-*hydroxy*-p′-*nitrobenzildi*-p-*tolil*, m. p. 232°. R. K. CALLOW.

Haloform reaction. III. Trihalogenoacetyl derivatives of mesitylene, durene, and *iso*durene. A. R. GRAY, J. T. WALKER, and R. C. FUSON (J. Amer. Chem. Soc., 1931, 53, 3494—3498; cf. A., 1930, 1291).—The following are prepared by the action of Na hypohalite on the requisite Ac compound : *di*(*trichloroacetyl*)-, m. p. 95—95·3° (all m. p. are corr.), and *di*(*tribromoacetyl*)-, m. p. 160—161·5°, -*mesitylenes*;

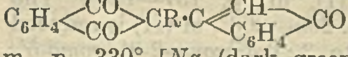
trichloroacetyl- (I), b. p. 158·5—159·5°/7 mm., *tribromoacetyl-*, m. p. 83·8—84·3°, *di(trichloroacetyl)-*, m. p. 134·8—135·2°, and *di(tribromoacetyl)-* m. p. 180·5° (decomp.), -iso*durenes*; *trichloroacetyl-* (II), m. p. 107—107·5°, and *tribromoacetyl-* (III), m. p. 102—102·5°, *-durenes*. These derivatives are generally stable to cold alkali; (I), (II), and (III) are not affected by 40% NaOH at 95—100°. H. BURTON.

Supposed exceptions to the rules for the substitution of benzene derivatives. K. VON AUWERS and E. RISSE (Ber., 1931, 64, [*B*], 2216—2222).—Contrary to Simonis (A., 1927, 154), the product obtained by the action of cinnamyl chloride on resorcinol Et_2 ether is 2 : 4-diethoxychalkone, m. p. 90·5°, identical with the substance derived from 2 : 4-diethoxyacetophenone and PhCHO. It is hydrolysed by $AlCl_3$ to 2-hydroxy-4-ethoxychalkone, m. p. 104°, and oxidised by $KMnO_4$ in alkaline solution to 2 : 4-diethoxybenzoic acid, m. p. 99°. Similarly, Simonis' 2 : 6- is 2 : 4-dimethoxychalkone, m. p. 78—79°, identical with that derived from 2 : 4-dimethoxyacetophenone and PhCHO and converted by $AlCl_3$ into 2-hydroxy-4-methoxychalkone, m. p. 107—107·5°. The product from *as-o*-xylenyl Me ether and cinnamyl chloride is identified as *2-methoxy-4 : 5-dimethylchalkone*, m. p. 78°, since it is oxidised to *2-methoxy-4 : 5-dimethylbenzoic acid*, m. p. 142·5—143·5° (hydrolysed by $AlCl_3$ to 4 : 5-dimethylsalicylic acid, m. p. about 199°), and is also obtained from 2-methoxy-4 : 5-dimethylacetophenone and PhCHO. The condensation of resorcinol Me_2 ether with phenylpropiolyl chloride affords small amounts of a product, m. p. 135—136°, which, in agreement with Simonis, is not identical with 7-methoxyflavone and does not give typical flavone reactions.

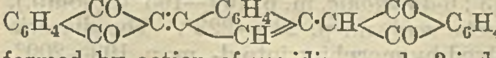
Isomerisation of *m*-tolyl propionate by $AlCl_3$ at 130° affords 2-hydroxy-4-methylpropiophenone, m. p. 41·5—42·5° (*p-nitrophenylhydrazone*, m. p. 204—205°). H. WREN.

Photochemistry of tetrabenzoylethylene. II. H. VON HALBAN and K. RAST (Z. physikal. Chem., Bodenstein Festband, 1931, 303—308).—The behaviour of tetrabenzoylethylene when exposed to light is much more complex than was postulated by Andres (Diss., Strassburg, 1911). The yellow compound *B* produced by the action of light yields on further exposure a colourless, very sparingly sol. *compound D*, m. p. 300° (decomp.), which yields a fluorescent solution and contains 1 atom of O more than *B*. In acid solution, in the dark, *B* is converted into a colourless *monohydrate C*, but in neutral solution a faintly yellow *compound E*, m. p. 155°, probably isomeric with *C*, is formed. Treatment of *C* with NaOEt yields two *compounds*; one is isomeric with *C* and the other is very similar to *D*, but has m. p. 230·5°, whilst its solution in pyridine is extremely light-sensitive. When tetrabenzoylethylene is covered with CS_2 the greater part dissolves, but within a few min. the solution sets to a jelly; if the solvent is removed by suction a soft white substance remains which is completely unchanged by sunlight, but appears to be otherwise identical with the original compound (mixed m. p.). On heating at 140°, or recrystallising from any solvent other than CS_2, the original compound is obtained. The solubility relationships indicate a transition temp. between 20° and 78°. H. F. GILLBE.

Isomeride of anhydrobisdiketohydrindene (di-indone). W. M. FISCHER and G. WANAG (Annalen, 1931, 489, 97—106).—iso*Di-indone*,



$C_6H_4<\overset{CO}{\underset{CO}{}}>CR\cdot C\overset{CH-}{\underset{C_6H_4}{\ll}}>CO$ (I; R=H), yellow, m. p. 330° [*Na* (dark green), and *Ag* salts; *Br*- (+$CHCl_3$), m. p. 285°, and *Br_3*- (unstable), m. p. 287° (decomp.), derivatives], is found among the products of the self-condensation of 1 : 3-indandione by alkali (even of glass), and of the decomp. by acid of Et 1 : 3-indandione-2-carboxylate. It is best obtained by heating 1 : 3-indandione with pyridine at 120°, or from the Na salt of the -2-carboxylate and AcOH, or, better, AcOH+Ac_2O. It is converted into di-indone by dil. aq. alkalis at the b. p. Interaction of its Na salt with MeI in MeOH gives a *Me* derivative, m. p. 252°, which, on account of its greenish-yellow colour and stability to alkaline hydrolysis, is regarded as a *C*-Me compound (I; R=Me). The Ag salt gives with cold 2*N*-HNO_3 or -H_2SO_4 an orange-yellow substance, m. p. 281°. A *substance*, $C_{27}H_{14}O_4$, m. p. 337°, probably



$C_6H_4<\overset{CO}{\underset{CO}{}}>C{:}C<\overset{C_6H_4}{\underset{-CH}{}}\gg C\cdot CH<\overset{CO}{\underset{CO}{}}>C_6H_4$, is also formed by action of pyridine on 1 : 3-indandione at 120° (cf. A., 1927, 669). H. A. PIGGOTT.

Organic sulphur–nitrogen linking. VII. R. POLLAK, E. RIESZ, and J. RIESZ (Monatsh., 1931, 58, 170—175; cf. this vol., 1284).—The quinonoid formula for the unimol. oxidation products of arylthiolarylamines is confirmed by synthesis of two typical examples. 4-Chloro-2-nitrothiolbenzene (I), quinonechloroimide, and Na_2CO_3 in cold aq. EtOH afford *N*-4-chloro-2-nitrophenylthiolbenzoquinoneimine. *p*-Thioltoluene and β-thiolnaphthalene give similarly the corresponding *p*-tolyl- and *β-naphthylthiolbenzoquinoneimine*, respectively, the latter (red) having m. p. 128°. The first two imines were identical with oxidation products. A similar experiment with quinonedichlorodi-imine gave the disulphide, which was also obtained on treating (I) with NaOCl. *N*-1-Anthraquinonylthiolaniline (II), when oxidised with $Na_2Cr_2O_7$ in AcOH, gives a black bimol. *substance*, $C_{40}H_{24}O_4N_2S_2$, giving a non-oxidisable vat. (II) itself gives a similar vat. 1-Bromothiolanthracene and *as*-dimethyl-*p*-phenylenediamine in cold C_6H_6 give p-N-1-*anthraquinonylthiolaminodimethylaniline*, brown, m. p. 196°, which with HNO_3 in AcOH gives N-1-*anthraquinonylthiol*-N′-*methylbenzoquinonedi-imine methonitrate*, red, m. p. 177°, which dyes wool and cotton mordanted with tannin bright red, but is destroyed by vatting. R. S. CAHN.

Stereochemistry of phenylquinones. Preparation and resolution of 2-3′-bromo-2′ : 4′ : 6′-trimethylphenyl-5-methyl-*p*-benzoquinone-3 : 6-diacetic acid. XVIII. D. W. HILL and R. ADAMS (J. Amer. Chem. Soc., 1931, 53, 3453—3461).—Mesitylene and *p*-toluquinone in presence of $AlCl_3$ below 5° give 2-2′ : 4′ : 6′-*trimethylphenyl-5-methylquinol* (I), m. p. 134—135° (all m. p. are corr.) (*diacetate*, m. p. 138—139°), oxidised by *p*-benzoquinone in 95% EtOH to 2-2′ : 4′ : 6′-*trimethylphenyl*-5-*methyl*-p-*benzoquinone*, m. p. 129°. (I) and Br in CCl_4 afford 3 : 6-*dibromo*-2-3′-*bromo*-2′ : 4′ : 6′-*trimethylphenyl*-5-*methylquinol*, m. p. 148—149° (*diacetate*, m. p. 137—138°), oxidised as above to 3 : 6-*dibromo* - 2 - 3′ - *bromo* - 2′ : 4′ : 6′ - *trimethylphenyl* - 5 - *methyl*-p-*benzoquinone* (II), m. p. 137—138°. The 5′-*nitro*-derivative, m. p. 205—206°, of (II) is reduced catalytically (Adams) to 3 : 6-*dibromo*-2-3′-*bromo*-5′-*nitro*-2′ : 4′ : 6′-*trimethylphenyl*-5-*methylquinol*, m. p. 178—179°, which is converted by successive reduction (Sn+HCl) and oxidation (as above) into 3 : 6-*dibromo*-2 - 3′ - *bromo* - 5′ - *amino* - 2′ : 4′ : 6′ - *trimethylphenyl* - 5 - *methyl-quinol*, m. p. 223°, and -p-*benzoquinone*, decomp. 135—140°. Stable salts could not be prepared from this aminoquinone and optically active acids. (II) is converted by NaOH in aq. MeOH into 3 : 6 - *dihydroxy* - 2 - 3′- *bromo* - 2′ : 4′ : 6′- *trimethyl*-*phenyl*-5-*methyl*-p-*benzoquinone*, m. p. 282° (decomp.) [*brucine*, m. p. 185—190° (decomp.), and *strychnine*, m. p. 194—200° (decomp.), salts], which could not be resolved. Et sodiocyanoacetate and (II) give *Et* 2-3′-*bromo*-2′ : 4′ : 6′-*trimethylphenyl* - 5 - *methyl* - p - *benzoquinone*-3 : 6-*dicyanoacetate*, m. p. 205—206°, which on alkaline hydrolysis affords either the corresponding 3 : 6-*dimalonic*, m. p. 160—165° (decomp.), or 3 : 6-*diacetic acid*, m. p. 220—223°. The diacetic acid is resolved by morphine into d-, m. p. 198—200°, $[\alpha]_D^{20}$ +34·7° in MeOH, and l-*forms*, m. p. 205—207°, $[\alpha]_D^{20}$ −18·8° in MeOH. This resolution is in accordance with the prediction of *X*-ray data (cf. A., 1930, 1588). 2-3′-*Bromo*-2′ : 4′ : 6′-*trimethylphenyl*-5-*methylquinol*-3 : 6-*diacetic acid* has m. p. 242—245° (decomp.).

H. BURTON.

Action of aldehydes on naphthaquinones. H. RAUDNITZ and G. PULUJ (Ber., 1931, **64**, [*B*], 2212—2216).—Treatment of α-naphthaquinone with *iso*valeraldehyde and other aldehydes and HCl in AcOH at 100° (cf. J.C.S., 1896, **69**, 1356, 1363) yields small amounts of intensely coloured substances containing Cl and sol. in alkali carbonate. The hypothesis that their production is due to reduction by the aldehyde of the quinone to the quinol and subsequent condensation is established by the observation that they are formed in good yield from 1 : 4-dihydroxynaphthalene. The products are tetrahydroxydinaphthylalphyl- (or -aryl-)methyl chlorides, the colour of which is explained on the basis of Pfeiffer's theory. They dissolve in alkali hydroxide to intensely bluish-violet solutions, the colour of which gradually fades; acidification with dil. H_2SO_4 ppts. the quinone hydrate. The following *compounds* are derived from 1 : 4-dihydroxynaphthalene: with *iso*valeraldehyde, $C_{25}H_{23}O_4Cl$; with heptaldehyde, $C_{27}H_{27}O_4Cl$; with *n*-butaldehyde, $C_{24}H_{21}O_4Cl$; with propaldehyde, $C_{23}H_{19}O_4Cl$; with crotonaldehyde, $C_{24}H_{19}O_4Cl$; with PhCHO, $C_{27}H_{19}O_4Cl$; with salicylaldehyde, $C_{27}H_{19}O_5Cl$. β-Naphthaquinone is reduced by *iso*valer- or hept-aldehyde to β-dinaphthaquinol, isolated as the tetra-acetate, m. p. 185—187°. 2-Hydroxy-α-naphthaquinone and *iso*valeraldehyde afford *iso*-β-lapachol (cf. *loc. cit.*).

H. WREN.

Anthraquinonesulphonic acids. H. E. FIERZ-DAVID (J. pr. Chem., 1931, [ii], **131**, 373—374).—A criticism of Lauer (B., 1931, 751). 1 : 6- and 1 : 7-Disulphonic acids are formed as by-products during β-monosulphonation (cf. Krebser, Diss., Zürich, 1925, 9). The conversion of anthraquinonedisulphonic acids into the corresponding dichloroanthraquinones by Ullmann's method is quant. only at high dilutions.

H. A. PIGGOTT.

Anthraquinonesulphonic acids. K. LAUER (J. pr. Chem., 1931, [ii], **131**, 375).—A reply to Fierz-David (preceding abstract) reaffirming the results already published.

H. A. PIGGOTT.

1-Methylanthraquinone series. F. MAYER and O. STARK (Ber., 1931, **64**, [*B*], 2003—2010).—The prep. is described of 3-methylphthalic acid from *o*-toluidine through *o*-oximinoacetotoluidide, 7-methylisatin, 2-amino-*m*-toluic acid and its *Me* ester, b. p. 151°/18 mm., and *Me* 2-*cyano*-m-*toluate*, b. p. 284°, m. p. 68—70°. With C_6H_6 and $AlCl_3$, 3-methylphthalic anhydride yields a mixture of 6- and 3-methyl-*o*-benzoylbenzoic acids, transformed by conc. H_2SO_4 at 100° into 1-methylanthraquinone, m. p. 171°. Similarly, with PhMe the anhydride gives a mixture of 6- and 3-methyl-*o*-*p*′-toluylbenzoic acids, converted into a non-separable mixture of 1 : 6- and 1 : 7-dimethylanthraquinone. 3- and 6-Methyl-*o*-2′ : 5′-dimethylbenzoylbenzoic acid and 1 : 5 : 8-*trimethylanthraquinone*, m. p. 146—147° (reduced by Zn dust and NH_3 to the corresponding *anthrone*, m. p. 125° after softening at 80°), are described. 3-Methylphthalic anhydride and quinol in presence of $AlCl_3$ and NaCl at 160—190° give 5 : 8-*dihydroxy*-1-*methylanthraquinone*, m. p. 238—238·5° (*diacetate*, m. p. 224°); shortened heating leads to 3- or 6-*methyl*-o-2′ : 5′-*dihydroxybenzoylbenzoic acid*, m. p. 230—231°. The anthraquinone derivative is converted by $Na_2S_2O_3$ and NH_3 at 135—140° into 5 : 8-*diamino*-1-*methylanthraquinone*, m. p. 205°. 5 : 8-*Ditoluidino*-1-*methylanthraquinone* has m. p. 219—220°. The following substances are obtained from 3-methylphthalic anhydride and the requisite phenol: 5 : 8-*dihydroxy*-1 : 7(or 1 : 6)-*dimethylanthraquinone*, m. p. 171—172° (*diacetate*, m. p. 234°); 5 : 6 : 8(or 5 : 7 : 8)-*trihydroxy*-1-*methylanthraquinone*, m. p. 272—274° (*triacetate*, m. p. 182—184°), also derived from 5 : 8-dihydroxy-1-methylanthraquinone and $Pb(OAc)_4$ in AcOH and conversion of the diquinone into the triacetate; 5 : 7-*dihydroxy*-1-*methylanthraquinone*, m. p. 285—286° (*diacetate*, m. p. 165—166°); 5 : 6(or 7 : 8)-*dihydroxy*-1-*methylanthraquinone*, m. p. above 310° and m. p. 206—207°. 4-Methylphthalic anhydride and *p*-xylene yield 4-(or 5)-*methyl*-o-2′ : 5′-*dimethylbenzoylbenzoic acid*, m. p. 151°, whence 1 : 4 : 6-*trimethylanthraquinone*, m. p. 143°. Oxidation of 6-diethylacetyl-2 : 5-dimethylbenzoic acid with hypochlorite gives a *product*, $C_{16}H_6O_3Cl_2$, m. p. 215°, oxidised by HNO_3 to 4 : 5-*dichloro*-3 : 6-*dimethylphthalic acid*, m. p. 207°, which with quinol affords 6 : 7-*dichloro*-1 : 4-*dihydroxy*-5 : 8-*dimethylanthraquinone*, m. p. 209—210° (*diacetate*, m. p. 221—222°). 3 : 6-Dimethylphthalic acid and PhMe give successively 2 : 5-*dimethyl*-6-p′-*toluylbenzoic acid*, m. p. 180°, and 1 : 4 : 6-trimethylanthraquinone, m. p. 143°. 2 : 5-Dimethylbenzoic acid is converted through its chloride by condensation with *p*-xylene into di-*p*-xylyl ketone,

b. p. 197°/19 mm., which passes by loss of H_2O into 1 : 4 : 6-trimethylanthracene, m. p. 227°; on oxidation, the hydrocarbon gives a 1 : 4 : 6-trimethylanthraquinone, m. p. 227° (Elbs, m. p. 184°). One of the above methods of prep. is therefore accompanied by wandering of a Me group. 4-Methylphthalic anhydride and *m*-xylene give a mixture of 3- and 5-methyl-*o*-2′ : 4′-dimethylbenzoylbenzoic acid, transformed into 1 : 3 : 7-*trimethylanthraquinone*, m. p. 128—129°, and 1 : 3 : 6-trimethylanthraquinone, m. p. 192°. The following compounds are derived from 3 : 6-dimethylphthalic anhydride and the requisite phenol : 5 : 8-*dihydroxy*-1 : 4-*dimethylanthraquinone*, m. p. 252—253° (*diacetate*, m. p. 181—182°); 5 : 8-*dihydroxy*-1 : 4 : 7-*trimethylanthraquinone*, m. p. 218° (*diacetate*, m. p. 196—198°); 5 : 7 : 8-*trihydroxy*-1 : 4-*dimethylanthraquinone*, m. p. 227—228° (*diacetate*, m. p. 192°); 5 : 6 : 7-*trihydroxy*-1 : 4-*dimethylanthraquinone*, m. p. 243° (*diacetate*, m. p. 203°).

H. Wren.

Retene. I. Synthesis of retene derivatives. M. T. Bogert and T. Hasselström (J. Amer. Chem. Soc., 1931, **53**, 3462—3466).—Retene and AcCl in presence of $AlCl_3$ and CS_2 give *acetylretene* (I), m. p. 99—99·5° (all m. p. are corr.) (*picrate*, m. p. 142—143°; *oxime*, m. p. 167—168°; *phenylhydrazone*, m. p. 202°; *dinitro*-derivative, m. p. 215—216°), oxidised by CrO_3 in AcOH to *acetylretenequinone*, m. p. 213—214° (decomp.) (*quinoxaline*, m. p. 196—197°, from *o*-phenylenediamine). (I) condenses with benzaldehyde and *p*-nitrobenzaldehyde in alcoholic NaOEt, forming *cinnamoyl*-, m. p. 154·5—155·5°, and p-*nitrocinnamoyl*-, m. p. 188—189°, -*retene*, respectively. *Acetylretenesemicarbazone*, m. p. 248·5—249·5° (decomp.), and NaOEt at 190—200° give *ethylretene*, m. p. 54—55° (*picrate*, m. p. 145—146°), oxidised to *ethylretenequinone*, m. p. 205·5—206·5°. H. Burton.

Manufacture of 4-halogeno-1-amino-9-anthrones and substitution products and derivatives. Newport Co.—See B., 1931, 918.

Manufacture of *o*-aminocarboxylic esters of the anthraquinone series. I. G. Farbenind. A.-G. —See B., 1931, 918.

Manufacture of 1-hydroxy- and 1-alkoxyanthraquinone-3-carboxylic acids and derivatives. I. G. Farbenind. A.-G.—See B., 1931, 918.

Cantharidin from *Mylabris pustalata*. B. H. Iyer and P. C. Guha.—See B., 1931, 993.

Pinabietic acid in Canada balsam. J. Ranedo and M. L. Navarro (Anal. Fís. Quím., 1931, **29**, 425—430).—The distillate from Canada balsam collected at 250—300°/55 mm. yields an acid, m. p. 177—178°, in 0·6% yield. It is not identical with any of the substances described by Tschirch and Brüning (A., 1900, i, 679), but resembles pinabietic acid (Aschan, A., 1921, i, 669). It absorbs $2H_2$ on catalytic hydrogenation, yielding a *compound*, m. p. 161—162°.

R. K. Callow.

Physodalic acid. G. Koller and K. Locker (Monatsh., 1931, **58**, 209—212).—Physodalic acid from *Parmelia physodes* is identical with capraric acid (cf. A., 1899, i, 381), since it has the same formula, crystal form, and constituent groups, gives an Ac derivative and an anilide, decomp. 260°, and when heated with Zn dust and NaOH at 100° yields orcinol and 3 : 5-dihydroxy-*p*-tolualdehyde. R. S. Cahn.

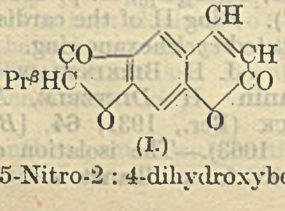
Strophanthin. XXII. Correlation of strophanthidin and periplogenin with digitoxigenin and gitoxigenin. W. A. Jacobs and R. C. Elderfield. **XXIII. Ring II of strophanthidin and of related aglucones.** W. A. Jacobs and E. L. Gustus (J. Biol. Chem., 1931, **92**, 313—321, 323—344; cf. this vol., 827).—XXII. Heating Me *iso*periplogonate with MeOH containing HCl gives *Me anhydro*iso*periplogonate*, m. p. 225—226°, which on catalytic hydrogenation yields two isomeric *Me deoxy*iso*periplogonates*: I (less sol.), m. p. 251—252°, $[\alpha]_D^{24}$ −44°, and II (more sol.), m. p. 192—193·5°, $[\alpha]_D^{25}$ −40·5° (free *acid*, m. p. 206—208°). The free acid with aq. HCl affords *γ-deoxy*iso*periplogonic acid*, m. p. 225—226°, $[\alpha]_D^{25}$ +70±2° (*Me* ester, m. p. 180—181°). These derivatives of periplogenin are identical with those obtained from digitoxigenin.

XXIII. An improved yield of Me_2 undephanthontriacidate (I) from Me_2 anhydro*iso*strophanthonate was obtained by oxidation with O_3. A better yield of duodephanthondiacid (II) was obtained by substituting piperidine for 0·1*N*-NaOH in its prep. The Me_2 ester of (II) when treated with N_2H_4 yields the *ketazine*, m. p. 184°. Catalytic reduction of (II) gives the *hydroxy-acid*, $C_{21}H_{30}O_7$, m. p. 234°, or the *dilactone*, $C_{21}H_{28}O_6$, m. p. 253°. Reduction of the Me_2 ester of (II) gives the *dilactone monomethyl* ester, m. p. 240°. (II) when heated with Ac_2O and AcCl gives the unsaturated *lactone anhydride* (III), $C_{21}H_{24}O_5$, m. p. 242°. Hydrogenation of (III) affords a saturated *deoxy-acid anhydride* (IV), $C_{21}H_{30}O_5$, m. p. 173°. (IV) gives a saturated *triacid*, softens above 120° (*Me_3* ester, m. p. 62°). Heating (I) with Ac_2O and AcCl at 80° gives an unsaturated *lactone*, $C_{24}H_{30}O_8$, m. p. 199°. Oxidation of Me anhydro*iso*periplogonate with O_3 yields *Me undeplogondiacidate* (V), m. p. 182—184°, which with Ac_2O and AcCl at 80° affords the unsaturated *lactone*, $C_{23}H_{30}O_6$, m. p. 235—236°. Saponification of the saturated lactone Me_2 ester, $C_{25}H_{36}O_7$ (previously described), with pyridine and aq. NaOH gives the saturated *triacid*, $C_{23}H_{34}O_8$ (VI), effervesces at 225° ($+\frac{1}{2}H_2O$) [*Me_3* ester (VII), m. p. 199°], hydrolysis with aq. NaOH+EtOH, giving the dibasic *lactone acid*, froths at 258°. Oxidation of (VII) with CrO_3 in AcOH affords the *keto-ester*, m. p. 220° (*oxime*, m. p. 210°). Me_2 β-*iso*strophanthate forms *Me_2* β-iso*strophanthonate* (VIII), m. p. 248—250° (*oxime* froths at 190°, remelts at 215—217°). (VIII) forms an anhydro-compound identical with that from the α-ester. The chief product of hydrogenation of Me_2 anhydro-α-*iso*strophanthonate is the sparingly sol. Me_2 deoxy*iso*strophanthonate, revised $[\alpha]_D$ +8°. The other isomeride is oxidised by CrO_3 in AcOH to the dibasic *acid*, $C_{25}H_{34}O_{10}$, m. p. 191—193° (anhydride, m. p. 256°). Ring II of the cardiac aglucones must be a substituted *cyclo*hexane ring.

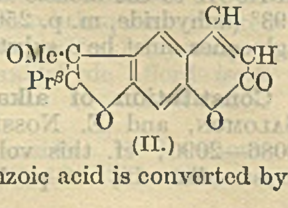
J. H. Birkinshaw.

Constitution of alkannin. H. Dieterle, A. Salomon, and E. Nosseck (Ber., 1931, **64**, [*B*], 2086—2090; cf. this vol., 1063).—The isolation of cryst. alkannin, m. p. 120°, from alkanet root is described. The composition $C_{15}H_{14}O_4$ is confirmed by the analysis of a *diacetate*, $C_{15}H_{12}O_4Ac_2$, m. p. 147°, and of *dihydroalkannin tetra-acetate*, $C_{15}H_{12}O_4Ac_4$, m. p. 120°. Distillation of alkannin with Zn dust yields 2-methylanthracene. Ozonisation in $CHCl_3$ yields a *compound*, $C_{13}H_8O_8$, m. p. 138—139°, regarded as a dihydroxynaphthoquinonedicarboxylic acid (*diacetate*, m. p. above 360°), which loses CO_2 when heated above its m. p. Further ozonisation gives an aldehyde, $C_{11}H_6O_5$, characterised by a *phenylhydrazone*, m. p. 168—169°, whilst subsequent ozonisation affords oxalic acid. The behaviour of alkannin towards O_3 differs from that of 5 : 8-*dihydroxy*-1-*methyl*-1 : 2 : 3 : 4-*tetrahydroanthraquinone*, m. p. 118° (prepared through the *diacetate*, m. p. 120—122°, derived from diacetylnaphthazarin and piperylene at 100°), which gives an *acid*, $C_{13}H_8O_8$, m. p. 211° (decomp.), and 5 : 8-*dihydroxy*-2-*methyl*-1 : 2 : 3 : 4-*tetrahydroanthraquinone*, m. p. 150° (from diacetylnaphthazarin and isoprene). Sublimation of the 1-Me compound yields a *substance*, $C_{13}H_8O_3$, m. p. 240°, whereas alkannin affords 5 : 8-dihydroxy-1-methylanthraquinone, m. p. 237°, and a *substance*, $C_{12}H_{10}O_3$, m. p. 140°. Treatment of alkannin in AcOH with H_2 in presence of Pd–C gives a tetrahydro-derivative from which 2H is removed by atm. oxidation giving *dihydroalkannin*, m. p. 130°. Alkannin is considered to be a 5 : 8-dihydroxy-1-α-methyl-Δ^{β}-butenyl-1 : 4-naphthaquinone. H. Wren.

Constitution of peucedanine and oreoselone. E. Späth, K. Klager, and C. Schlösser (Ber., 1931, 64, [*B*], 2203—2211).—Peucedanine, $C_{15}H_{14}O_4$, is converted by HCl in EtOH–H_2O into oreoselone, $C_{14}H_{12}O_4$, m. p. 177—178°; both are optically inactive. In alkaline solution in presence of Pd–C oreoselone absorbs 2H giving *dihydro-oreoselonic acid* $C_{14}H_{16}O_5$, m. p. 173—174°, transformed at 200—220°/0·04 mm. into *dihydro-oreoselone*, $C_{14}H_{14}O_4$, m. p. 170—171°. *Me dihydro-oreoselonate*, m. p. 95—97°, is derived from the acid and diazomethane. Peucedanine suspended in MeOH absorbs 4H in presence of Pd–C yielding a product which foams when distilled in vac., giving a substance, $C_{14}H_{14}O_3$, m. p. 126°, free from OMe. Oreoselone is not dehydrogenated by Pd at 180°. Dihydro-oreoselonic acid is oxidised in faintly alkaline solution by $KMnO_4$ at room temp. to much oxalic and succinic acid. Succinic acid is also obtained by oxidation with HNO_3, whereas styphnic acid, readily derived from oreoselone and HNO_3, is not derived from the dihydro-acid. Oreoselone is oxidised by $KMnO_4$ in alkaline solution to α-hydroxy*iso*butyric acid, whereas when a smaller proportion of the oxidising agent is used the product is 4 : 6-*dihydroxybenzene*-1 : 3-*dicarboxylic acid*, identified as *Me* 4 : 6-*dimethoxybenzene*-1 : 3-*dicarboxylate*, m. p. 149—150°. To oreoselone and peucedanine the constitutions (I) and (II) are respectively assigned.



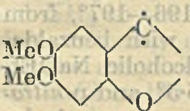
(I.)



(II.)

5-Nitro-2 : 4-dihydroxybenzoic acid is converted by diazomethane in MeOH into *Me* 5-*nitro*-2 : 4-*dimethoxybenzoate*, m. p. 147°, reduced by $Na_2S_2O_4$ to *Me* 5-*amino*-2 : 4-*dimethoxybenzoate*, m. p. 84°. This is diazotised and transformed into *Me* 5-*cyano*-2 : 4-*dimethoxybenzoate*, m. p. 116—117°, hydrolysed to 4 : 6-*dimethoxybenzene*-1 : 3-*dicarboxylic acid*, m. p. 272° (decomp.) (*Me* ester, m. p. 147—148°). Assuming that nitration of β-resorcylic acid actually occurs in the 5-position (cf. von Hemmelmayr, A., 1904, i, 319) it follows that the 2 : 4-dihydroxybenzene-1 : 3-dicarboxylic acid of Waitz (A., 1911, i, 541) is the 4 : 6-dihydroxy-acid. This is shown to be the case; von Hemmelmayr's acid is decarboxylated to 4-nitroresorcinol, which is converted successively into its Me_2 ether, 4-aminoresorcinol Me_2 ether, and 4-*cyano*-1 : 3-*dimethoxybenzene*, m. p. 95—96°, hydrolysed to 2 : 4-dimethoxybenzoic acid, m. p. 106°. Oxidation of the dibenzylidene derivative of 2 : 4-dimethoxy-1 : 5-diacetylbenzene (Eykman and others, A., 1905, i, 359) with $KMnO_4$ affords 4 : 6-dimethoxybenzene-1 : 3-dicarboxylic acid (Me ester, m. p. 150°). H. Wren.

Deguelin. III. Orientation of the methoxy-groups in deguelin, tephrosin, and rotenone. E. P. Clark (J. Amer. Chem. Soc., 1931, 53, 3431—3436).—The hydroxydimethoxybenzoic acid previously obtained (this vol., 841) by oxidising dehydrodeguelin is the 2-hydroxy-4 : 5-dimethoxy-acid, since when heated with NH_2Ph it gives 3 : 4-*dimethoxyphenol*, m. p. 79—80° (3 : 5-*dinitrobenzoate*, m. p. 158°), also prepared from 4-aminoveratrole. Since deguelin, tephrosin, and rotenone are inter-related (this vol., 491, 1065), the annexed grouping occurs in all these compounds. H. Burton.



Rotenone. XIV. Relation of optical activity of rotenone derivatives to the structure of tubaic acid. H. L. Haller and F. B. La Forge (J. Amer. Chem. Soc., 1931, 53, 3426—3431).—Of the two asymmetric centres in rotenone, one disappears during the prep. of dehydro-derivatives, whilst the other is lost during isomerisation to *iso*-derivatives. The formation of deoxy-acids (A., 1928, 1017) by fission of a lactone group during catalytic reduction also involves the disappearance of an asymmetric centre, which, however, does not occur during hydrolytic fission. The above (and other evidence) supports the view that the structure proposed by Takei *et al.* (this vol., 847) for tubaic acid is incorrect and that the tubaic acid structure does not occur in rotenone.

When rotenonic acid, m. p. 206°, $[\alpha]_D^{20}$ +45° (all rotations are in $CHCl_3$), is heated with EtOH–KOH, racemisation occurs. dl-*Rotenonic acid*, m. p. 184°, is reduced catalytically (Adams) in AcOEt to the dihydro-derivative, m. p. 194° (also formed from dihydrorotenonic acid, $[\alpha]_D^{20}$ +67°, and EtOH–KOH), is oxidised by alkaline H_2O_2 to hydroxyrotenonic acid, and isomerised by acid to dl-β-*dihydrorotenone*, m. p. 171°. The last-named is oxidised by alkaline $K_3Fe(CN)_6$ to dehydro-β-dihydrorotenone. Clemmensen reduction of rotenone and *iso*rotenone gives *deoxyiso*rotenone, $C_{23}H_{24}O_5$, m. p. 165—166°, $[\alpha]_D^{20}$ −113·2°. The following vals. of $[\alpha]_D^{20}$ are also recorded: rotenol, −77·3°; dehydrodihydrorotenol,

−8·05°; dihydroderritol Me ether, −32·8°, and dihydrorotenone, −123·2°. Dihydrorotenolic, dehydrodihydrorotenolic, methylderritolic, and dehydrodihydrorotenonic acids, β-dihydrorotenolone, and *iso*derritol are optically inactive. H. BURTON.

Resins and resin substances. VIII. β-Amyrin from Manila elemi resin. V. A. ROLLETT (Monatsh., 1931, 58, 113—117; cf. B., 1930, 623).—β-Amyrin (I) is probably unsaturated, because ozonolysis of it and its benzoate (II) yields substances which appear to be stable molozonides. Ozonolysis of (I) in $CHCl_3$ at room temp. gives amorphous substances of progressively increasing O content. (II) gives similarly an amorphous *substance* (III), $C_{37}H_{54}O_6$, m. p. 196—215° (decomp.), and a cryst. *substance*. In AcOH (II) gives unchanged material, together with a cryst. *substance*, $C_{37}H_{54}O_6$, m. p. 225—235° after decomp. from 140—160° [regarded as identical with (III)], which on hydrolysis gives much (I). R. S. CAHN.

Phytosterols and abietic acid as parents of the optically active components of petroleum. N. D. ZELINSKI and N. S. KOSLOV (Ber., 1931, 64, [*B*], 2130—2135).—Betulin heated with $AlCl_3$ yields about 66% of a liquid condensate partly volatile with steam. The fractions of lower b. p. from the volatile portion appear to be saturated and free from aromatic hydrocarbons, whereas hydrogenation of the fractions of higher b. p. in presence of Pt–C at 200—220° indicates the presence of unsaturated and aromatic hydrocarbons. The product not volatile with steam gives a dextrorotatory hydrocarbon fraction when distilled under diminished pressure. Similarly, abietic acid is converted by heating with $AlCl_3$ into hydrocarbons fractions of which are markedly dextrorotatory, the activity appearing to be due to an unsaturated hydrocarbon. The products appear rich in aromatic hydrocarbons of varying b. p. American colophony and $AlCl_3$ also yield hydrocarbons.

H. WREN.

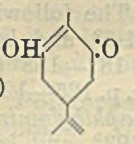
Plant colouring matters. XXXV. Constitution of β-carotene and β-dihydrocarotene. P. KARRER and R. MORF (Helv. Chim. Acta, 1931, 14, 1033—1036).—Comparison of the amounts of geronic acid obtained by ozonolysis of β-carotene (I) and β-dihydrocarotene with the quantity obtained from β-ionone under similar conditions indicates that each of the former compounds contains two β-ionone groups per mol. and supports the sym. formula (A., 1930, 1422) for (I). The sp. rotation of α-carotene in C_6H_6 varies considerably with the wave-length.

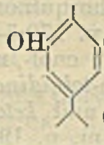
H. BURTON.

Taraxanthin, a new xanthophyll with 4 oxygen atoms. R. KUHN and E. LEDERER (Z. physiol. Chem., 1931, 200, 108—114).—Dandelion (*Taraxacum officinale*) blossoms yield a mixture of xanthophylls from which by fractional adsorption on $CaCO_3$ there was isolated *taraxanthin*, $C_{40}H_{56}O_4$, m. p. 184·5—185·5° (corr.), $[\alpha]^{22}_{6439}$ +204°, adsorption max. 501, 468·5 mμ. J. H. BIRKINSHAW.

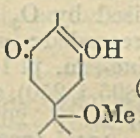
Autoxidation of αβ-unsaturated ketones. II. W. TREIBS (Ber., 1931, 64, [*B*], 2178—2184; cf. this vol., 94).—The hydroxy-acid $C_{10}H_{18}O_3$, m. p. 112—114°, obtained by the autoxidation of piperitone (*loc. cit.*) is prepared in approx. the same yield by the action of H_2O_2 in presence of KOH and MeOH. Carvone is transformed by H_2O_2 into a diketone, $C_{10}H_{14}O_2$, sol. in alkali hydroxide, and insol. products (see below). The diketone behaves as a monobasic acid and is not precipitated from alkaline solution by CO_2. With Ac_2O in presence and absence of catalysts it affords a *monoacetate*, $C_{12}H_{16}O_3$, b. p. 154—156°/16 mm. Benzoylation or methylation could not be effected. It yields a monosemicarbazone. It is transformed by $FeCl_3$, $ZnCl_2$, or H_2SO_4 into an isomeric *substance*, $C_{10}H_{14}O_2$, m. p. 130—132° (*dibenzoate*, m. p. 80°; *Me₂ ether*, b. p. 142°/20 mm.). Mild oxidising agents give a yellow ppt. with its aq. solutions and it is very readily autoxidised, particularly in alkaline solution. The relationships of diketone (I) and dihydroxy-isomeride (II) are shown. Particularly when the oxidation of carvone is effected slowly, the formation of the diketone is accompanied by that of (1) a viscous *liquid*, $C_{11}H_{18}O_3$, b. p. 150—160°/17 mm., d_{15}^{20} 1·067, which yields MeI and resin under the action of HI and immediately decolorises $KMnO_4$ and hence probably has the constitution (III) and (2) a cryst. *substance*, $(C_{10}H_{13}O)_2O$ or $(C_{10}H_{14}O)_2O$, m. p. 154°, the yield of which increases as that of the diketone decreases; it is therefore regarded as a secondary product from carvone and the diketone, although it could not be produced by condensation of these substances. Since it gives a *monoacetate*, a *monosemicarbazone*, m. p. 220° (decomp.), is unsaturated towards $KMnO_4$, and resinified by HI, it probably has the constitution (IV). H. WREN.

(I.)

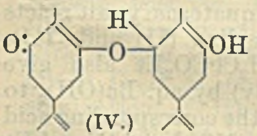




(II.)



(III.)

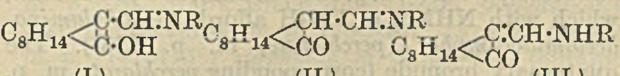


(IV.)

Isomerisation of linalool to camphor under the action of aluminium. J. V. VINOGRADOVA (Ber., 1931, 64, [*B*], 1991—1997).—The action of Al powder in the presence of a trace of $HgCl_2$ on linalool at 160—200° gives a mixture of dipentene (30%), traces of myrcene or linaloolene, camphor (about 2%), borneol (0·8%), dimyrcene (22%), resin (15%), and H_2O (8·5%). The products are optically inactive or of activity opposite to that of the initial material. Under similar conditions, geraniol affords dipentene and camphorene, but not camphor or borneol.

H. WREN.

Mechanism of mutarotation of primary amino-derivatives of *d*-methylenecamphor. T. HAYASHI (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, 16, 200—203; cf. J.C.S., 1909, 95, 171).—The mutarotation of derivatives of aminomethylenecamphor (obtained from the amine and hydroxymethylenecamphor) is ascribed to the process: I (enol) ⟶ II ⟶ III (keto). In two cases the rotation passes through a max., whilst in others it reaches a lower



$$C_8H_{14}{<}\begin{matrix}C\cdot CH{:}NR\\ \|\\ C\cdot OH\end{matrix} \qquad C_8H_{14}{<}\begin{matrix}CH\cdot CH{:}NR\\ |\\ CO\end{matrix} \qquad C_8H_{14}{<}\begin{matrix}C{:}CH\cdot NHR\\ |\\ CO\end{matrix}$$

(I.) (II.) (III.)

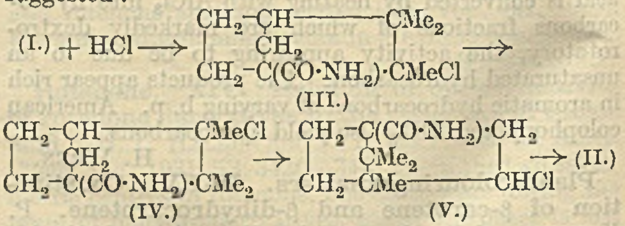
const. val. through two stages. Fractionation of the solute after mutarotation gives forms corresponding with (I) and (III), the enolic form giving by ozonolysis a peroxide, which yields camphoric anhydride when heated, whilst the ketonic forms give oximes, and are oxidised by O_3 to camphorquinone. The following are recorded : enol-, m. p. 170·5—171·5°, and *keto-anilino-*, m. p. 108—110° ; enol-, m. p. 187—188° (cf. A., 1895, i, 250), and *keto-*p-*toluidino-*, m. p. 125—126° ; *enol-*, m. p. 202—203°, and *keto-*β-*naphthylamino-*, m. p. 171—173° ; *enol-*, m. p. 192—193°, and *keto-*p-*nitroanilino-*, m. p. 151—152° ; and *enol-*, m. p. 186—187°, and *keto-carbazolacridonylamino-methylene-camphor*, m. p. 235—236°, and >295° (geometrical isomerides). Et *p*-aminobenzoate and NHPhMe condensed with hydroxymethylenecamphor give a di-(carbethoxyanilino)-, m. p. 187—188°, and a di-(methylanilino)-derivative, m. p. 124° (cf. *loc. cit.*), respectively. A. A. Levi.

Camphor betaines. I. H. Rupe and W. Flatt (Helv. Chim. Acta, 1931, 14, 1007—1033).—Dimethylaminocamphor (I) (convenient method of prep. given) (*perchlorate*, m. p. 229—230°) heated with $CH_2Cl·CO_2Et$ gives camphoryltrimethylammonium chloride (II) [corresponding *perchlorate*, m. p. 233°, prepared from $HClO_4$ and (II) or the quaternary salts from (I) and MeI or Me_2SO_4] and *Et* N-*camphoryl-*N-*methylaminoacetate* (III), b. p. 163·5°/10 mm. (*hydrochloride*, m. p. 159°) ; the initial quaternary salt reacts with a further mol. of (I) yielding (II) and (III). Methylaminocamphor and $CH_2Cl·CO_2Et$ also give (III), hydrolysed (in 1 case only) by aq. $Ba(OH)_2$ to the *Ba* salt, m. p. 233—235°, of the corresponding acid and converted by HNO_2 into the NO-derivative of Et *N*-camphorylaminoacetate (A., 1903, i, 44). MeBr and (III) at 100° afford camphoryltrimethylammonium bromide and $CH_2Br·CO_2Et$. *Me* N-*camphoryl-*N-*methylaminoacetate*, b. p. 159°/11 mm. (*hydrochloride*, m. p. 155°), is prepared from $CH_2Cl·CO_2Me$ and (I) or methylaminocamphor. (I) and $CH_2Br·CO_2Et$ at room temp. give *camphoryldimethylcarbethoxymethylammonium bromide* (corresponding *perchlorate*, m. p. 74°), converted by moist Ag_2O into the *betaine*, $C_{10}H_{15}O·\overset{+}{N}Me_2·CH_2·\overset{-}{C}O_2$, m. p. 198° (*perchlorate*, m. p. 232°). (I) and $CH_2Br·CH_2·OH$ at 100° afford *camphoryldimethyl-*β-*hydroxyethylammonium bromide*, converted by AgOH into the corresponding *hydroxide* (*chloroaurate*, m. p. 117—118°) and by successive treatment with conc. HCl and $HClO_4$ into *camphoryldimethylvinylammonium perchlorate*, m. p. 237—238° (corresponding *chloroaurate*, m. p. 213—218°) (also formed by the action of AgOH on camphoryldimethyl-β-bromoethylammonium bromide and subsequent treatment with $HClO_4$), and a trace of a substance (*perchlorate*, m. p. 130°). Aminocamphor and $CH_2Cl·COCl$ in C_6H_6 and pyridine give *chloroacetamidocamphor* (IV), b. p. 194°/13 mm., 114°/0·007 mm., which with $NHMe_2$ in EtOH affords *dimethylaminoacetamidocamphor* (*perchlorate*, m. p. 228°). The quaternary bromide (corresponding *perchlorate*, m. p. 135°) from this and $CH_2Br·CO_2Et$ is converted by AgOH into the *betaine*,

$C_{10}H_{15}O·NH·CO·CH_2·\overset{+}{N}Me_2·CH_2·\overset{-}{C}O_2$, m. p. 248° (crystallographic data given) (*perchlorate*, m. p. 217°). (IV) and NMe_3 in EtOH afford the *chloride*, $C_{10}H_{15}O·NH·CO·CH_2·NMe_3Cl$, m. p. 224° (corresponding *perchlorate*, m. p. 110°, and *chloroaurate*, m. p. 175°), converted by AgOH into the corresponding hydroxide.

The sp. rotations and dispersion of many of the above compounds are discussed. H. Burton.

Camphor and terpenes. VII. Replacement of the 2 : 6-rearrangement in the camphor series, [and interpretation of] racemisation of optically active camphene derivatives and conversion of *d*- into *l*-camphor derivatives by the camphene rearrangement of type 2. J. Houben and E. Pfankuch (Annalen, 1931, 489, 193—224).—The action of HCl on *d*-camphene-1-carboxylamide (I) (cf. this vol., 558) gives 2-*chlorocamphane-*4-*carboxylamide*, $[\alpha]_D^{20}$ +36° in EtOH (V), converted by aq. K_2CO_3 into *camphene-*4-*carboxylamide* (II), m. p. 164—165° [previously " camphene-2-carboxylamide " (A., 1926, 1252) ; the corresponding *acid*, m. p. 158—159°, $[\alpha]_D^{18}$ −83·3°, is obtained from " *d*-6-hydroxycamphane-2-carboxylic acid " (now 2-hydroxycamphane-4-carboxylic acid) through the corresponding *chloro*-derivative, m. p. 147—148° ; a number of related substances previously described need correspondingly altered numeration]. Addition of HCl to (I) is quant. (this vol., 558), yet 2-chlorocamphane-2-carboxylamide cannot be isolated, and does not itself undergo rearrangement in cresol to (V), but slowly loses HCl and gives camphene-1-carboxylamide. The Meerwein 2 : 6- change of the Cl atom is therefore excluded, and the following mechanism is suggested :

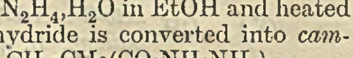


The change of (III) into (IV) is a normal pinacone rearrangement without ring isomerisation (type 2) and is postulated to occur without change of optical structure, although it may be accompanied by a change of sign. It is responsible for the racemisation of *iso*bornyl chloride (*e.g.*, in *m*-cresol) in which the equivalence of the 1 : 4-positions masks the structural change involved. The constitution of (II) is proved by conversion of the corresponding dihydro-acid (A., 1926, 1251) into its *chloride*, m. p. 40°, b. p. 110—112°/19 mm., which is not acted on by PCl_5 at 140°, and therefore lacks an α-H atom. It is confirmed by reduction of (V) with H_2 and $Pd–BaSO_4$ to the *dihydro*-derivative, m. p. 126—130°, which is degraded by NaOMe and Br in MeOH to the (*methyl*)*urethane*, m. p. 74—75°, of 4-*aminodihydrocamphene* (*hydrochloride*) (hydrolysis with KOH in MeOH) ; the NH_2 compound gives with HNO_2 4-*hydroxydihydrocamphene*, m. p. 133—134°, b. p. 105°/30 mm. (*acetate*, b. p. 104—105°/12 mm.), the tertiary nature of which is proved by its stability to oxidation by $CrO_3–AcOH$. 4-*Aminocamphene*, m. p. 135°, $[\alpha]_D^{19}$ −90° in EtOH [*hydrochloride*, m. p. above 290° ; *methylurethane*,

m. p. 73—74°; *Ac* derivative, m. p. 141° (*H_2* derivative, m. p. 153—154°)], is similarly prepared, but is not readily reduced. Its urethane and AcH_2 derivatives are hydrolysed by acids to *d*-camphor.

An example of the optical inversion that may accompany this rearrangement is the successive conversion of *l*-camphor-4-carboxylic acid, m. p. 238—240° (best purified by means of its *amide*, m. p. 207—208°), into l-4-*aminocamphor*, m. p. 230—232° (*CO_2Me*, m. p. 117°, and *Ac*, m. p. 122—123°, derivatives), l-4-*hydroxycamphor*, m. p. 250° (*oxime*, m. p. 212°; *semicarbazone*, m. p. 236—238°; *Ac* derivative, b. p. 132°/11 mm.) [with an unsaturated *acid*, $C_{10}H_{16}O_2$, m. p. 155—158° (*lactone*, m. p. 142°)], and l-4-(*hydroxycamphene*-1-*carboxylamide* (oxime and HNO_2), m. p. 201—203° (decomp.) (*H_2* derivative, m. p. 138—140°), which when evaporated with conc. HCl gives *d*-camphor-4-carboxylic acid. Further, the rearrangement of camphor dichloride (A., 1924, i, 188) gives, not 2 : 6-, but 2 : 4-dichlorocamphane, for the (4-)chlorocamphene obtained by elimination of HCl from the product gives with $CCl_3·CO_2H$ at 60—70° dl-4-*chloro*iso*borneol*, m. p. 235—236°, oxidised by CrO_3–AcOH to dl-4-*chlorocamphor*, m. p. 198—199° [*oxime*, m. p. 158—160°; *semicarbazone*, m. p. 260—264° (decomp.)], identified by its prep. from 4-aminocamphor, and also by conversion into its 3-*oximino*-derivative, m. p. 174—175° (decomposed by PCl_5 in $CHCl_3$ with formation of HCN), and dl-4-*chlorocamphorquinone*, m. p. 219—220°, which with H_2O_2 in AcOH gives 3-chlorocamphoric anhydride. *d*-2-*Hydroxycamphane-4-carboxylic acid*, $[\alpha]_D^{20}$ +15·7°, is obtained by not too prolonged heating of *d*-camphene-1-carboxylic acid with $CCl_3·CO_2H$ at 60—70°. The $·CO_2Me$ derivative, b. p. 136—137°/16 mm. (*hydrochloride*), of camphorimine is readily decomposed to camphor by acids. H. A. PIGGOTT.

Action of hydrazine hydrate on camphoric anhydride. V. ALEXA and G. GHEORGHIU (Bull. Soc. chim., 1931, [iv], 49, 1112—1119).—When treated with 2 mols. of N_2H_4,H_2O in EtOH and heated at 120° camphoric anhydride is converted into *camphoric dihydrazide*,



$$\left.\begin{matrix}CH_2·CMe(CO·NH·NH_2)\\CH_2—CH(CO·NH·NH_2)\end{matrix}\right>CMe_2$$

[$+H_2O$, lost at 100°, m. p. 126° (sinters at 118°); anhyd., m. p. 158—160°], yielding the corresponding dihydrazone, m. p. 273°, with PhCHO and converted by heating at 150° into N-*aminocamphorimide*, m. p. 156° [*picrate*, $+H_2O$, m. p. 128° (anhyd., m. p. 112—115°); hydrochloride; picrolonate], which with PhCHO and 3 : 4-dihydroxybenzaldehyde yields *benzylidene*-N-*aminocamphorimide*, m. p. 106°, and 3 : 4-*dihydroxybenzylidene*-N-*aminocamphorimide*, m. p. 195—197°. The basic properties of the aminocamphorimides in contrast to the acidic hydrazides, ·CO·NH·NH·CO·, and the absence of analogy with the dihydroxyphthalazines in the absorption spectra of *N*-aminocamphorimide, establish the constitution of phthalhydrazide and its derivatives.

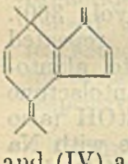
R. BRIGHTMAN.

Silver camphorcarboxylate. Silver organosols. M. PICON (Compt. rend., 1931, 192, 1660—1662, and J. Pharm. Chim., 1931, [vii], 14, 273—281).—Ag camphorcarboxylate, precipitated in H_2O (Na salt and $AgNO_3$) and dried over P_2O_5, is sol. in C_6H_6, $CHCl_3$, and CS_2, from which another form separates. This retains solvent tenaciously, and is sol. only in $CHCl_3$, from which, by evaporation, a solid similar to the H_2O ppt. is obtained. The aq. solution is converted into a colloidal solution by the action of traces of H_2S in impure H_2, the latter always containing small quantities of O_2 or S. G. DISCOMBE.

Polyterpenes and polyterpenoids. LV. Alantolactone. L. RUZICKA and P. PIETH (Helv. Chim. Acta, 1931, 14, 1090—1103; cf. this vol., 734).—The so-called *iso*alantolamide is an additive *compound* (I), m. p. 233°, of NH_3 (1 mol.) and *iso*alantolactone (2 mols.). Thermal decomp. of (I) regenerates only a small amount of the lactone (cf. this vol., 360). Technical "helenin" is separable by repeated fractional crystallisation from EtOH into alantolactone, *iso*alantolactone, and dihydro*iso*alantolactone (II), m. p. 167·5—168°, $[\alpha]_D^{22}$ +72° in EtOH (also obtained by reduction of Na *iso*alantolate with Na and EtOH). Hydrolysis of the ozonide of (II) gives the keto-lactone (III), $C_{14}H_{20}O_3$, m. p. 198—199°, previously described (*loc. cit.*, where the m. p. is given as 203—205°), reduced (Clemmensen) to a *monocarboxylic acid*, $C_{14}H_{24}O_2$, b. p. 130—133°/0·1 mm., and (mainly) 9-methyl-3-ethyl-*cis*-decahydronaphthalene, $[\alpha]_D^{21}$ −2·64° (cf. this vol. 1303) [dehydrogenated by Se at 380° to 2-ethylnaphthalene (cf. Hansen, this vol., 1065)]. Treatment of the glycol (IV) obtained by reduction of tetrahydroalantolactone with Na and EtOH or by catalytic reduction of the glycol, $C_{15}H_{26}O_2$ (*loc. cit.*), with 33% HBr in AcOH, elimination of HBr from the resulting dibromide with $NPhMe_2$ at 190°, and catalytic reduction of the unsaturated hydrocarbon (freed from traces of Br by Na and K at 150°) gives a product, b. p. about 135°/12 mm., dehydrogenated by Se at 295—330° to a hydrocarbon, $C_{15}H_{18}$ [a dimethyl*iso*propylnaphthalene (?)] (*picrate*, m. p. 114°, not identical with cadalene picrate). The same hydrocarbon is obtained when (IV) is reduced with red P and HI and then dehydrogenated. Alternative formulæ for the above lactones are discussed (cf. *loc. cit.*; Hansen, *loc. cit.*).

[With (in part) J. A. VAN MELSEN.] Hydrolysis of the ozonide of an incompletely hydrogenated impure alantolactone and oxidation of the product with $KMnO_4$ in $COMe_2$ gives mainly a *monocarboxylic acid*, $C_{15}H_{22}O_5$ (*Me* ester, b. p. 190—200°/0·4 mm.), and a little (III). H. BURTON.

Polyterpenes and polyterpenoids. LVI. Azulene. LVII. Guaiol. L. RUZICKA and A. J. HAAGEN-SMIT (Helv. Chim. Acta, 1931, 14, 1104—1122, 1122—1132).—LVI. Dehydrogenation of guaiene with S at 180—240° (cf. A., 1926, 299) gives an azulene (designated S-*guaiazulene*) (I), blue, b. p. 167—168°/12 mm. (*picrate*, m. p. 121—122°; *styphnate*, m. p. 105—106°), which differs from Se-*guaiazulene* (II), bluish-violet, b. p. 170—171°/13 mm. (*picrate*, m. p. 114—115°; *styphnate*, m. p. 98—99°) (obtained by dehydrogenation of guaiene with Se). Catalytic reduction (Adams) of (I), which is identical with kessazulene (A., 1928, 616), gives *decahydro*-S-*guaiazulene*, colourless, b. p. 132—134°/12 mm., dehydrogenated by Se to (II), whilst *decahydro*-Se-*guaiazulene*, b. p. 130—131°/13 mm., is dehydrogenated by S to a mixture of products containing a little (II). Elemazulene (III), violet-blue (*picrate*, m. p. 110°; *styphnate*, m. p. about 87°), is obtained in 1% yield by dehydrogenating elemene with Se. *Decahydrochamazulene* has b. p. 119—120°/12 mm. The above decahydroazulenes have approx. the same values for d_4^{15} and n_D^{15}, indicating that they possess similar ring systems. (I), (II), (III), and chamazulene (IV), when oxidised with 4% $KMnO_4$ at room temp., consume 17—19 O per mol. and all give AcOH and oxalic acid; $COMe_2$ and *iso*butyric acid are produced from (I), (II), and (III). When the oxidation is carried out at 100° (bath), (I), (II), and (III) consume 26—27 O per mol. Ozonolysis of (I) gives $COMe_2$, AcOH, HCO_2H, and *iso*butyric acid. The annexed structure is suggested as a possible azulene formula. The absorption spectra of (I) and (IV) are not identical.



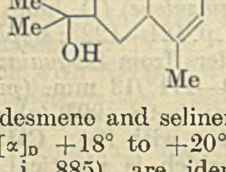
[With H. A. Boekenoogen and H. W. Huyser.] The parachors of (I), (II), (III), and (IV) are practically identical (495·3±1·3).

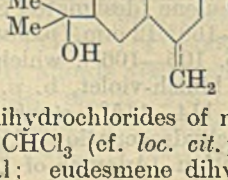
LVII. The (*a*) neutral and (*b*) acidic hydrolysis products of the ozonide of guaiol contain (*a*) a doubly-unsaturated oxide (V), $C_{15}H_{22}O$, b. p. 140—141°/15 mm., a *compound* (VI), $C_{15}H_{26}O_3$, m. p. 218°, $[\alpha]_D$ +7·16° in AcOH (also obtained when guaiol is oxidised with $KMnO_4$ in aq. $COMe_2$), and lactonic products, and (*b*) lactonic and acidic products corresponding with $C_{15}H_{24}O_3$ and $C_{15}H_{26}O_4$, respectively. (VI) contains 2 *tert.*-OH groups and when treated with boiling EtOH–NaOH or with Zn dust and AcOH at 60—70° gives (V). Catalytic reduction (Pt-black) of (V) in AcOEt affords an *oxide*, $C_{15}H_{26}O$, b. p. 138—139°/12 mm. Guaiene is reduced catalytically (Adams) in *cyclo*hexane to *tetrahydroguaiene*, b. p. 126—128°/12 mm., whilst guaiol yields similarly *dihydroguaiol*, m. p. 79—80°, and a mixture of hydrogenated sesquiterpene and sesquiterpene alcohol.

H. Burton.

Polyterpenes and polyterpenoids. LVIII. Relation between eudesmol and selinene. LXI. Proof of identity of machilol with eudesmol. L. Ruzicka, D. R. Koolhaas, and A. H. Wind (Helv. Chim. Acta, 1931, 14, 1132—1151, 1178—1186).—LVIII. Eudesmol (*A*), m. p. 82—83°, $[\alpha]_D$ +31·3° in $CHCl_3$ (impure benzoate), is shown to consist of a mixture of α- (I) and β-eudesmol [to which formula (II) is now assigned (cf. A., 1927, 569)]. Selinenol (Semmler and Risse, A., 1913, i, 66) is (I), since dihydroselinenol and dihydroeudesmol are identical.

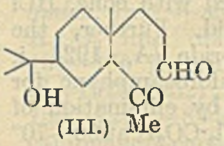
(I.)



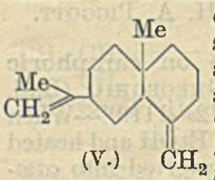


(II.)

Eudesmene and selinene dihydrochlorides of m. p. 74°, $[\alpha]_D$ +18° to +20° in $CHCl_3$ (cf. *loc. cit.*; A., 1913, i, 885), are identical; eudesmene dihydrochloride, m. p. 79—80°, is considered to be a structural isomeride. A new *selinene dihydrochloride*, m. p. 52°, $[\alpha]_D$ −70° in $CHCl_3$, is now described. The alcohol, m. p. 78—79°, $[\alpha]_D$ +38° in $CHCl_3$, obtained from this and aq. $Ca(OH)_2$ does not depress the m. p. of *A* [the variation in physical data is ascribed to the different ratios of (I) to (II) in the alcohols], and is reduced catalytically (as is *A*) to dihydroeudesmol, m. p. 85—86°, $[\alpha]_D$ +17° in $CHCl_3$. Contrary to a previous statement (A., 1927, 569), a dihydrochloride could not be obtained from the hydrocarbon prepared from eudesmol (m. p. 79—80°) and conc. H_2SO_4 in EtOH. The neutral hydrolysis products from the ozonide of *A* contain a hydroxyketoaldehyde, $C_{15}H_{26}O_3$ (probably III) (*semicarbazone*, m. p. about 145°), which is derived from (I), and 5-*keto*-9-*methyl*-3-β-*hydroxy*iso*propyldecahydronaphthalene*, m. p. 119—120°, which arises from (II), whilst the acidic products contain an acid (III, where $CHO=CO_2H$) (*Et* ester, b. p. about 167°/0·15 mm.), dehydrated by hot HCO_2H to the corresponding *iso*propylidene derivative (*Et* ester, b. p. about 125°/0·08 mm.). Ozonolysis of 3 dihydroeudesmenes obtained (*a*) from dihydroeudesmol and MgPhBr, (*b*) from dihydroeudesmyl chloride and MeOH–KOH, and (*c*) from dihydroeudesmyl chloride and NH_2Ph gives 3-*acetyl*-5 : 9-*dimethyldecahydronaphthalene* (IV), b. p. 145—147°/12 mm., $[\alpha]_D$ +5·2° (*semicarbazone*, m. p. 206—208°; *picrate* of aminoguanidine compound, m. p. 175—176°), in each case; 3-keto-5 : 9-dimethyldecahydronaphthalene (*semicarbazone*, m. p. 215—217°; *picrate* of aminoguanidine compound, m. p. 207—209°) is obtained from (*c*) (and from "dihydroselinene" prepared by method *c* from dihydroselinenyl chloride), whilst the acidic products consist of a mixture of ketomonocarboxylic and dicarboxylic acids. The results show that the dihydroeudesmenes are mixtures of isomerides. (IV) and MgMeI give dihydroeudesmol. Ozonolysis of selinene (V) gives 5-*keto*-3-*acetyl*-9-*methyldecahydronaphthalene*, b. p. 123—125°/0·2 mm. (*disemicarbazone*, m. p. 222°), the *benzylidene* derivative, m. p. 170°, of which is oxidised by successive treatment with O_3 and CrO_3 in AcOH to 5-keto-9-methyldecahydronaphthalene-3-carboxylic acid (*Me* ester, b. p. 153—155°/0·25 mm.).



(III.)

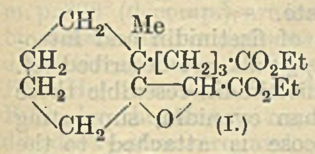


(V.)

LXI. Machilol (A., 1921, i, 732) is shown by ozonolysis experiments to consist mainly of β-eudesmol; machilol and eudesmol give the same derivatives.

H. Burton.

Polyterpenes and polyterpenoids. LIX. Synthesis of alkylated *trans*-decahydronaphthalenes in connexion with the stereochemistry of sesquiterpenes. LX. Spatial configuration of the decahydronaphthalene ring in sesquiterpenes. L. Ruzicka, D. R. Koolhaas, and A. H. Wind (Helv. Chim. Acta, 1931, 14, 1151—1171, 1171—1178).—LIX. 2-Methyl*cyclo*hexanone and Et β-iodopropionate in presence of $NaNH_2$ and Et_2O give a mixture of products which, after condensation with Et oxalate in presence of Na and light petroleum, affords some *Et* 2-*methyl*-2-*carbethoxyethyl*cyclo*hexanone*-6-*carboxylate*, b. p. 153—157°/0·3 mm. Hydrolysis of this (whereby the 6-CO_2H group is eliminated) and subsequent esterification gives *Et 2-methyl*cyclo*hexanone-2-β-propionate*, b. p. about 150°/15 mm., which with $CH_2Br·CO_2Et$ and Zn yields *Et 2-methyl-2-carbethoxyethyl*cyclo*hexylideneacetate*, b. p. 130—132°/0·3 mm. 2-Methyl*cyclo*hexanone and γ-iodobutyronitrile in presence of $NaNH_2$ and Et_2O afford a mixture of products which after hydrolysis, esterification, condensation with Et oxalate, further hydrolysis, re-esterification, and final condensation with $CH_2Cl·CO_2Et$ in NaOEt affords the *ester* (I), b. p. 148—150°/0·1 mm.


(I.)

Various *trans*-decahydronaphthalenes are prepared by the Clemmensen reduction of their diketo-derivatives, which are obtained usually by the method of Kon and Qudrat-i-Khuda (A., 1927, 150).

[With H. A. Boekenoogen, J. van der Kamp, and P. Nebbeling.] Liquid (*a*) and solid (*b*) Et 1 : 3-diketodecahydronaphthalene-4-carboxylates are obtained from *cyclo*hexenyl Me ketone and Et sodiomalonate (cf. *loc. cit.*). These are hydrolysed by 15% HCl to mixtures of products containing a considerable amount of a keto-acid, $C_{10}H_{16}O_3$ (*semicarbazone*, m. p. 179°). Reduction of these hydrolysis products and purification of the resultant hydrocarbons by heating with K and subsequent treatment with $KMnO_4$, gives *trans*-decahydronaphthalene (from *b*) and a mixture of *cis*- and *trans*-decahydronaphthalenes (from *a*).

[With T. Ausems, A. Baart, and H. J. Wigman.] The product from 2-methyl-Δ¹-*cyclo*hexenyl Me ketone and Et sodiomalonate is hydrolysed, the acidic products [oxidised by NaOBr to 1-methyl-1-carboxymethyl*cyclo*hexane-2-carboxylic acid (*Me_2* ester, b. p. about 140°/12 mm.)] reduced, and the resulting trans-9-*methyldecahydronaphthalene*, b. p. 70—71°/12 mm., purified as above.

[With H. J. Edelmann.] The *carbinol*, b. p. 112—113°/12 mm., from MgMeBr and *trans*-β-ketodecahydronaphthalene is dehydrated with 95% HCO_2H and the resulting product reduced catalytically (Adams) in *cyclo*hexane to trans-2-*methyldecahydronaphthalene*, b. p. 76°/12 mm.

[In part with H. Goedhart.] Et 2-methyl*cyclo*hexanone-6-carboxylate, prepared from 2-methyl*cyclo*hexanone and Et oxalate in NaOEt, is methylated by MeBr and NaOMe to *Et* 2 : 6-*dimethyl*cyclo*hexanone*-6-*carboxylate*, b. p. 112—118°/12 mm., hydrolysed by mineral acids to 2 : 6-dimethyl*cyclo*hexanone, b. p. 62°/12 mm. (*semicarbazone*, m. p. 176°). This is reduced by Na and moist Et_2O to 2 : 6-*dimethyl*cyclo*hexanol*, b. p. 172°/750 mm., 73°/16 mm., dehydrated by $KHSO_4$ at 180—190° to 1 : 3-*dimethyl*-Δ¹-cyclo*hexene* (II), b. p. 124—126°, oxidised by 3% $KMnO_4$ (=3O) to an *acid*, $C_8H_{14}O_3$, b. p. 150—155°/12 mm. Oxidation of (II) with 1% $KMnO_4$ at 0° gives a glycol (not characterised), converted by hot 20% H_2SO_4 into a stereoisomeric 2 : 6-dimethyl*cyclo*hexanone (*semicarbazone*, m. p. 196°). AcCl and (II) in presence of $SnCl_4$ and CS_2 afford (after treatment of the intermediate product with $NPhEt_2$) 2 : 6-*dimethyl*-Δ¹-cyclo*hexenyl Me ketone*, b. p. 90—95°/14 mm. (*semicarbazone*, m. p. 215°), which after condensation with Et sodiomalonate and subsequent hydrolysis gives trans-5 : 7-*diketo*-4 : 9-*dimethyldecahydronaphthalene*, m. p. 166°. This is reduced to trans-4 : 9-*dimethyldecahydronaphthalene*, b. p. 77—78°/12 mm.

[With J. H. van der Hulst.] 2-Methyl-Δ¹-*cyclo*hexenyl Pr ketone (from 1-methyl-Δ¹-*cyclo*hexene and butyryl chloride in presence of $SnCl_4$ and CS_2) is converted by the general method into trans-9-*methyl*-3-*ethyldecahydronaphthalene*, b. p. 97—98°/12 mm.

[With J. de Liver.] trans-5 : 9-*Dimethyl*-3-*ethyldecahydronaphthalene*, b. p. 112—113°/14 mm., is prepared from 2 : 6-dimethyl-Δ¹-*cyclo*hexenyl Pr ketone.

LX. Clemmensen reduction of the various ketodecahydronaphthalenes obtained from eudesmol and its derivatives (this vol., 1302) gives *cis*-decahydronaphthalenes; the *cis*- and *trans*-configurations (above) are assigned from physical data. cis-4 : 9-*Dimethyl*-, b. p. about 85°/12 mm., cis-5 : 9-*dimethyl*-3-*ethyl*-, b. p. about 115—116°/12 mm., and cis-9-*methyl*-3-*ethyl*-, b. p. about 102—103°/12 mm., -*decahydronaphthalenes* are thereby obtained from 3-keto-5 : 9-dimethyl-, 3-acetyl-5 : 9-dimethyl-, and 5-keto-3-acetyl-9-methyl-decahydronaphthalene (III), respectively. The ketones are, therefore, all *cis*-derivatives. The glycol from (III) and MgMeI is dehydrated to a *hydrocarbon*, $C_{15}H_{24}$, b. p. 128—131°/13 mm., reduced catalytically (Adams) to its *tetrahydro*-derivative ("synthetic tetrahydroselinene"), b. p. about 128—130°/12 mm., which, like tetrahydroselinene, is also a *cis*-derivative. The viscosities of the *cis*-decahydronaphthalenes are invariably higher than those of the isomeric *trans*-compounds.

H. Burton.

Sesquiterpenes. I. Sesquiterpenes and sesquiterpene alcohol from Japanese camphor oil. S. Komatsu, H. Fujimoto, and S. Tanaka.—See B., 1931, 993.

Hydroxy-carbonyl derivatives. IV. Preparation of coumarins and 1 : 4-pyrones from phenol, *p*-cresol, quinol, and α-naphthol. A. Robertson, W. Sandrock, and (in part) C. B. Hendry (J.C.S., 1931, 2426—2432; cf. this vol., 962).—The substances obtained when *o*-hydroxy- (I), 2-hydroxy-5-methyl- (II), and 2 : 5-dihydroxy-propiophenone (III) are treated with Ac_2O and NaOAc are identical with the condensation products of Et α-methylacetoacetate with phenol, *p*-cresol, and quinol, respectively; they are, therefore, 1 : 4-pyrones (cf. A., 1914, i, 424). This confirms the generalisation (this vol., 963) that ω-substituted *o*-hydroxyacetophenones yield 1 : 4-pyrones on vigorous acetylation. However, the Simonis reaction, when applied to α-naphthol (IV), gives the naphthacoumarin. *o*-Methoxybenzoyl chloride and Et sodio-α-methylacetoacetate in Et_2O, or *o*-methoxybenzonitrile and MgMeI in Et_2O, give *o*-methoxypropiophenone (*semicarbazone*, m. p. 154°), which with $AlCl_3$ in boiling C_6H_6 yields (I) (*semicarbazone*, m. p. 213°); this, when heated with Ac_2O and NaOAc at 170—180°, affords 2 : 3-dimethyl-1 : 4-benzopyrone. (II) (modified prep.) when heated with Ac_2O and NaOAc at 180—190° yields

2 : 3 : 6-trimethyl-1 : 4-benzopyrone. *p*-Cresol, Et methylacetoacetate, and cold 80% H_2SO_4 give 3 : 4 : 6-*trimethylcoumarin* (non-fluorescent), m. p. 165°. The *Ac* derivative of 6-hydroxy-3 : 4-dimethylcoumarin (modified prep.) has m. p. 159—161°. Quinol, EtCOCl, and pyridine give (III), obtained only in traces by the Nencki reaction. (III), when heated with Ac_2O and NaOAc at 170—180°, yields 6-*acetoxy*-2 : 3-*dimethyl*-1 : 4-*pyrone*, m. p. 139°, hydrolysed by KOH in cold MeOH to the corresponding hydroxypyrone, m. p. 247° after sintering at 241° (lit. 242°). 4-Methyl-α-naphthacoumarin is obtained from (IV) and Et acetoacetate with either cold 84% H_2SO_4, or P_2O_5 at 100° (cf. A., 1910, i, 405); with Et α-methylacetoacetate 3 : 4-*dimethyl*-α-*naphthacoumarin*, m. p. 203—204°, is obtained by both methods. 2-Propionyl-α-naphthol, Ac_2O, and NaOAc, when heated at 180—190° give 2 : 3-*dimethyl*-1 : 4-α-*naphthapyrone*, m. p. 143—144° (green fluorescence in conc. H_2SO_4). R. S. Cahn.

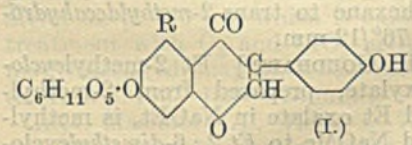
Synthesis of coumarins from phenols and β-ketonic esters using phosphorus pentoxide. II. Coumarins from polyhydric phenols and α-naphthol. D. Chakravarti (J. Indian Chem. Soc., 1931, 8, 407—411; cf. this vol., 962).—Coumarins are prepared from phenols and the requisite Et acylacetates and α-chloroacylacetates in presence of P_2O_5 or conc. H_2SO_4. The following are described: (*a*) from orcinol: 5-hydroxy-4 : 7-dimethyl- (*Ac* derivative, m. p. 195°); 3-chloro-5-hydroxy-4 : 7-dimethyl- (*Ac* derivative, m. p. 160°); 5-*hydroxy*-3 : 4 : 7-*trimethyl*-, m. p. 250° (*Ac* derivative, m. p. 135°), and 5-*hydroxy*-4 : 7-*dimethyl*-3-*ethyl*-, m. p. 206°, -*coumarins*; (*b*) from pyrogallol: 7 : 8-dihydroxy-4-methyl-; 3-chloro-7 : 8-dihydroxy-4-methyl- (*Ac* derivative, m. p. 197°); 7 : 8-*dihydroxy*-3 : 4-*dimethyl*-, m. p. 270°, and 7 : 8-*dihydroxy*-4-*methyl*-3-*ethyl*-, m. p. 218°, -*coumarins*; (*c*) from phloroglucinol: 3-chloro-5 : 7-dihydroxy-4-methylcoumarin; (*d*) from α-naphthol: 4-methyl-, 3-chloro-4-methyl-, 3 : 4-*dimethyl*-, m. p. 197—199°, 4-*methyl*-3-*propyl*-, m. p. 118°, and 4-*methyl*-3-iso*propyl*-, m. p. 165°, -1 : 2-α-*naphthapyrones*. H. Burton.

Reduction of quercetin. T. Malkin and M. Nierenstein (Ber., 1931, 64, [*B*], 1976; cf. A., 1930, 1189).—The investigations of Asahina and Inubuse (this vol., 940) emphasise the distinction between cyanidin chloride and 3 : 5 : 7 : 3′ : 4′-pentahydroxyflavylium chloride. H. Wren.

Synthesis of pyrylium salts of anthocyanidin type. Fisetinidin and luteolinidin chlorides. R. Robinson and A. León (Anal. Fís. Quím., 1931, 29, 415—425; cf. A., 1925, i, 825).—2 : 4-Dihydroxybenzaldehyde yields with BzCl and aq. KOH 2-*hydroxy*-4-*benzoyloxybenzaldehyde*, m. p. 103°, converted by MeI into the 2-*OMe*-derivative, m. p. 85—86°, which yields 4-hydroxy-2-methoxybenzaldehyde on hydrolysis. 2 : 4-Dihydroxybenzaldehyde condenses with ω-3 : 4-triacetoxyacetophenone in dry EtOAc under the action of HCl to give fisetinidin chloride. Catalytic reduction of fisetinidin chloride yields an amorphous material (*Pb* compound) with the colour reactions of catechins. ω-Chloro-3 : 4-dihydroxyacetophenone is prepared by heating pyrocatechol, $CH_2Cl{\cdot}CO_2H$, and $POCl_3$ in PhMe. The Ac_2 derivative is reduced in EtOH solution by Fe and H_2SO_4, with NaI as catalyst, to 3 : 4-dihydroxyacetophenone. Condensation of 3 : 4-diacetoxyacetophenone with the Bz derivative of phloroglucinolaldehyde yields the 5-Bz derivative of luteolinidin chloride, decomp. 182°, which is hydrolysed and converted into luteolinidin chloride by way of the picrate.

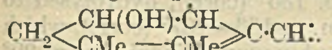
The colours of solutions of fisetinidin and luteolinidin chlorides at various p_H vals. are described (cf. A., 1929, 477). Those of fisetinidin resemble those given by cyanin rather than cyanidin, supporting the assumption that glucose is attached to the 5-OH group in cyanin. R. K. Callow.

iso*Flavone and saponin glucosides in *Soja hispida*.* E. Walz (Annalen, 1931, 489, 118—155).—The glucosides described were isolated from the soya bean after removal of the outer skin, and are found in the fraction sol. both in 90% MeOH and in $COMe_2$. *Genistin*, m. p. 254—256°, $[\alpha]_D^{21}$ −27·7° [Ac_6, m. p. 188°, and Bz_6, m. p. 132°, derivatives; Me_3 *ether* (MeI and K_2CO_3 in MeOH), m. p. 200—205° (decomp.)], is hydrolysed by HCl in aq. MeOH to dextrose and genistein (5 : 7 : 4′-trihydroxy*iso*flavone; cf. A., 1925, i, 1299; 1926, 1253), m. p. 296—298° (decomp.) [Ac_3, m. p. 200—202°, and Bz_3, m. p. 239°, derivatives; *Me*, m. p. 189—191° (5 : 7-*dihydroxy*-4′-*methoxy*iso*flavone* ?), and Me_2, m. p. 139—140°, ethers], identified by fission with boiling 30% aq. KOH to HCO_2H, *p*-hydroxyphenylacetic acid, and phloroglucinol; with 5% KOH the intermediate 2 : 4 : 6-trihydroxyphenyl *p*-hydroxybenzyl ketone can be isolated. Acid hydrolysis of genistin Me_3 ether gives a new *dimethylgenistein*, m. p. 290—293° (7-*hydroxy*-5 : 4′-*dimethoxy*iso*flavone*), which does not give a coloration with $FeCl_3$ and is therefore methylated in position 5, and is hydrolysed by boiling 30% KOH to HCO_2H and 2 : 4-*dihydroxy*-6-*methoxyphenyl* p-*methoxybenzyl ketone* (*oxime*, m. p. 178°); the last-named is stable to alkalis, but is oxidised by alkaline $KMnO_4$ to anisic acid. The glucose residue therefore occupies the 7-position in genistin (I; R=OH). *Daidzin*, m. p. 235°, $[\alpha]_D^{20}$ −36·4° (Ac_5, m. p. 203°, Bz_5, m. p. 145—150°, derivatives; *Me ether*, m. p. 206°), is separated from genistin by virtue of its greater solubility in aq. EtOH and hot H_2O. It is hydrolysed to dextrose and *daidzein*, m. p. 315—320° (Ac_2 derivative, m. p. 182°; Me_2, m. p. 154°, and *Me*, m. p. 251°, *ethers*); the latter is a dihydroxy-compound, and on fission with KOH gives HCO_2H and 2 : 4-*dihydroxyphenyl* p-*hydroxybenzyl ketone*, m. p. 192° (*oxime*, m. p. 202—203°). Similarly, methyldaidzein gives 2 : 4-*dihydroxyphenyl* p-*methoxybenzyl ketone*, m. p. 158° (*oxime*, m. p. 220°). The two ketones were identified by synthesis from *p*-hydroxy- and *p*-methoxy-phenylacetonitrile, respectively, by condensation with resorcinol and HCl in Et_2O, and hydrolysis of the iminochlorides. Daidzin is therefore represented by formula I (R=H). Three *saponin-glucosides*, *C*, m. p. 272° (*aglucone*, m. p. 235—236°),

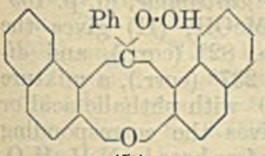

(I.)

C_1, m. p. 225° (*aglucone*, m. p. 243—245°), and C_2, m. p. 280°, are isolated from the crude genistin by extraction with H_2O; they appear to contain both glucose and pentose residues, and the first is strongly hæmolytic. They are accompanied by alkali-sol. flavone derivatives from which, by acid hydrolysis, *aglucone D*, $C_{15}H_9O_4{\cdot}OMe$, m. p. 310°, and *aglucone E*, m. p. 306° (decomp.), are isolated; these are converted by alkali into *substances* (probably $PhCO{\cdot}CH_2Ph$ derivatives), m. p. 159° and 188°, respectively, and HCO_2H; the formation of a green coloration with $FeCl_3$ by the first is regarded as indicating an *o*-dihydroxy-structure, and consequently aglucone *D* is probably a hydroxymethoxy-derivative of 8-hydroxy-*iso*flavone. H. A. Piggott.

Plant colouring matters. XXXVI. Violaxanthin. P. Karrer and R. Morf (Helv. Chim. Acta, 1931, 14, 1044—1046).—Violaxanthin (I), m. p. 207—208° (corr.) (cf. this vol., 491), and its perhydro-derivative both contain 3 and not 4 OH groups (Zerevitinov). Oxidation of (I) with alkaline $KMnO_4$ in presence of C_6H_6 gives *as*-dimethylsuccinic acid, indicating the presence of the grouping


$CH_2{<}{\begin{matrix}CH(OH){\cdot}\dot{C}H\\CMe_2{-}{-}CMe\end{matrix}}{\gtrdot}C{\cdot}CH{:}$. H. Burton.

Pyrenium salts. XIV. Oxidation of pyrenium salts. F. Quint and W. Dilthey (Ber., 1931, 64, [*B*], 2082—2086).—*Phenylxanthenium perchlorate* suspended in AcOH is oxidised by H_2O_2 to 2-*o*-*hydroxyphenoxybenzophenone*, m. p. 104°, transformed by distillation with Zn dust into 9-phenylxanthen and a little PhOH. It is converted by KOH and Me_2SO_4 into 2-*o*-*methoxyphenoxybenzophenone*, m. p. 128—129°, obtained also from *o*-hydroxybenzophenone, *o*-bromoanisole, and Cu powder. Similar oxidation of phenyldibenzoxanthenium perchlorate affords the expected *H peroxide* (I), m. p. 167—168° (decomp.) (also $+ 1C_6H_6$, m. p. 167—168°; $+ 1COMe_2$, m. p. 167—168°; $+ 1C_5H_5N$, m. p. about 127°), reconverted by $HClO_4$ in AcOH into phenyldibenzoxanthenium perchlorate. H. Wren.

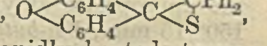
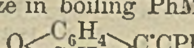
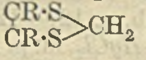
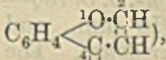
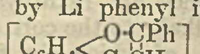
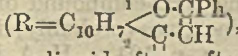


(I.)

Synthetical experiments in the chromone group. III. Diflavones. K. C. Gulati and K. Venkataraman (J.C.S., 1931, 2376—2381; cf. this vol., 963).—Resorcinol diacetate, when heated with anhyd. $FeCl_3$ in an atm. of CO_2, gives a poor yield of 4 : 6-diacetylresorcinol (I). With $FeCl_3$ in AcOH, however, it yields *resacetophenone 2-monoacetate*, m. p. 119—120°, also obtained under certain conditions with $AlCl_3$, and transformed by $FeCl_3$ at 180° into (I); under other conditions use of $AlCl_3$ led to a *substance*, m. p. 83—84°, whilst with $ZnCl_2$ at 130° resacetophenone was obtained. (I), Bz_2O, and NaOBz at 180—185° give diflavone and 7-*hydroxy*-6-*acetylflavone*, m. p. 123°. Anisic anhydride and Na anisate yield similarly 4′ : 4″-*dimethoxydiflavone*, yellow, m. p. 192°, and 7-*hydroxy*-4′-*methoxy*-6-*acetylflavone*, m. p. 160—161°; the former flavone with Ac_2O and HI gives 4′ : 4″-*dihydrodiflavone*, m. p. 317° (Ac_2 derivative, m. p. 204—205°). Under similar conditions, however, trimethylgallic anhydride (modified prep.) and Na trimethylgallate give very little 3′ : 4′ : 5′ : 3″ : 4″ : 5″-*hexamethoxydiflavone*, m. p. 134—136° (decomp.), and mostly 7-*hydroxy*-3′ : 4′ : 5′-*trimethoxy*-6-*acetylflavone*, m. p. 224—225° (*Ac* derivative, m. p. 156—157°), whilst in the veratryl series only 7-*hydroxy*-3′ : 4′-*dimethoxy*-6-*acetylflavone*, m. p. 182° (*Ac* derivative, m. p. 141°), was obtained. (I), NaOAc, and boiling Ac_2O give 3 : 3′-*diacetyl*-2 : 2′-*dimethyldichromone*, m. p. 261—264°, and 7-*hydroxy*-6-*acetyl*-2-*methylchromone*, m. p. 134—135°. Colour reactions are described for the above substances. R. S. Cahn.

1 : 3-Benzdioxin. F. D. Chattaway and H. Irving (J.C.S., 1931, 2492—2494).—6-*Acetamido*-1 : 3-*benzdioxin*, prepared from the NO_2-derivative, Na, and Ac_2O at 100°, or from the NH_2-derivative, Ac_2O, and a drop of H_2SO_4, has m. p. 224° (decomp.). 1 : 3-Benzdioxin (modified prep.), m. p. 12·5°, b. p. 210—211°/754 mm., 100·5—101·5°/20 mm., with HNO_3 (*d* 1·5) and a little carbamide gives 6 : 8-*dinitro*-1 : 3-*benzdioxin* (I), m. p. 135—136°.

[With M. Goepp.] (I) with CrO_3 in hot AcOH yields 6 : 8-*dinitro*-4-*keto*-1 : 3-*benzdioxin*, m. p. 196·5—197·5°, which with boiling 10% NaOH affords CH_2O and 3 : 5-dinitrosalicylic acid, thus proving the constitution of (I). R. S. Cahn.

Dichromylenes and the valency tautomerism of unsaturated systems. A. Schönberg and S. Nickel (Ber., 1931, 64, [*B*], 2323—2327).—In the search for analogues of dixanthylene (A., 1928, 526), it has been observed that tetraphenyl-, tetra-*p*-anisyl-, and octamethyltetra-*p*-aminotetraphenyl-ethylene are not thermochromic and do not suffer fission at the central ethylenic linking when heated with S. The action of xanthion on diphenyldiazomethane yields oo′-*oxidotetraphenylethylene sulphide*,  $O{<}{\begin{matrix}C_6H_4\\C_6H_4\end{matrix}}{>}C{<}{\begin{matrix}CPh_2\\S\end{matrix}}$, m. p. indef. 185—190° when rapidly heated, transformed by Cu-bronze in boiling PhMe into oo′-*oxidotetraphenylethylene*,  $O{<}{\begin{matrix}C_6H_4\\C_6H_4\end{matrix}}{>}C{:}CPh_2$, m. p. 195—196°, a colourless substance which is reddish-yellow when molten and yields hot, reddish-yellow solutions. 4-Thio-2-phenylchromone is converted by diazomethane in $Et_2O{-}C_6H_6$ into *di*-γ-2 : 2′-*diphenylchromenyl*-4 : 4′-*dithiolmethylene ether*,  $\begin{matrix}CR{\cdot}S\\CR{\cdot}S\end{matrix}{>}CH_2$ (I; R=  $C_6H_4{<}{\begin{matrix}{}^1O{\cdot}\overset{2}{C}H\\{}^4C{\cdot}\underset{3}{C}H\end{matrix}}$), m. p. about 182—183° (decomp.) after softening, transformed by Li phenyl into 2 : 2′-*diphenylchromylene* (II),  $\left[C_6H_4{<}{\begin{matrix}O{\cdot}CPh\\C{\cdot}CH\end{matrix}}\right]_2$, m. p. 224°, yellow crystals which become red when warmed or compressed and melt to a blood-red liquid which becomes yellow when cooled. α-Naphthaflavone is transformed by P_2S_5 into α-*naphtha*-4-*thioflavone*, m. p. 171—172°, converted by diazomethane into the *compound* (I) (R=  $C_{10}H_7{<}{\begin{matrix}{}^1O{\cdot}CPh\\{}^2C{\cdot}CH\end{matrix}}$), m. p. 165°, to a reddish-brown liquid after softening at 164°. H. Wren.

Action of aliphatic diazo-compounds on pyrrole and its homologues. C. D. Nenitzescu and E. Solomonica (Ber., 1931, **64**, [*B*], 1924—1931). —The products of the action of aliphatic diazo-compounds and ketens on pyrroles appear to be invariably *C* derivatives. Pyrrole, Cu powder, and Et diazoacetate at 100° afford *Et pyrrole-2-acetate*, b. p. 129°/15 mm., hydrolysed to *pyrrole-2-acetic acid*, decomp. 83—84°, which is decarboxylated to 2-methylpyrrole. Similarly, *Et* 2 : 4-*dimethylpyrrole-5-acetate*, b. p. 134°/12 mm., yields successively non-cryst. 2 : 4-dimethylpyrrole-5-acetic acid and 2 : 4 : 5-trimethylpyrrole. 2 : 3 : 4 : 5-Tetramethylpyrrole is derived from Et diazoacetate and 2 : 4 : 5-trimethylpyrrole. Benzoylphenyldiazomethane and pyrrole at 50—60° yield 2 : 5-*bisdiphenylacetylpyrrole*, m. p. 225°. 5-*Diphenylacetyl*-2 : 4-*dimethylpyrrole*, m. p. 169°, also prepared from $CPh_2{:}CO$ and 2 : 4-dimethylpyrrole, is oxidised by CrO_3 in AcOH to benzophenone; it is also obtained by the successive addition of dimethylpyrrole and diphenylacetyl chloride to MgEtBr in Et_2O. 2 : 4-Dimethylpyrrole and Et diazoacetoacetate give 5-α-*carbethoxypropionyl*-2 : 4-*dimethylpyrrole*, m. p. 109°, transformed into 5-*propionyl*-2 : 4-*dimethylpyrrole*, m. p. 134°, also prepared from 2 : 4-dimethylpyrrole, EtCOCl, and MgEtBr in Et_2O. *Et* 1-*methylpyrrole-2-acetate*, b. p. 137°/26 mm., and 1-*methylpyrrole-2-acetic acid*, m. p. 112°, are described. With a larger proportion of Et diazoacetate, 1-methylpyrrole gives 1-*methylpyrrole*-2 : 5-*diacetic acid*, decomp. above 150° (*Me* ester, m. p. 56°). H. Wren.

Pyridine derivatives. XV. Hydrogenation of [2-]pyridone and its *N*-alkyl derivatives. C. Räth (Annalen, 1931, **489**, 107—118).—2-Pyridone and its *N*-alkyl derivatives are readily hydrogenated at 180—220°/40 atm. in presence of Ni, Cu, or, best, Ni–Cu, to the corresponding tetrahydro-compounds. By interaction of *K* 2-*pyridone*, m. p. 274—276°, with the appropriate alkyl iodide 1-iso*propyl*-, b. p. 145—150°/15 mm., 1-n-*butyl*-, b. p. 148°/10 mm., and 1-n-*octyl*-, b. p. 189°/12 mm., -2-*pyridones* are obtained. The following are obtained by reduction : 2-piperidone [hydrochloride, m. p. 182—183° (lit. 155—160°); $C_5H_9ON,HgCl_2,H_2O$, m. p. 187° (decomp.)]; *N*-methyl- [*hydrochloride*, m. p. 104°; $+HgCl_2,H_2O$, m. p. 119—120°]; N-*ethyl*-, b. p. 109°/12 mm. (*hydrochloride*, m. p. 108°; $+HgCl_2,H_2O$, m. p. 113°); N-*propyl*-, b. p. 121°/14 mm. (*hydrochloride*, m. p. 112°); N-iso*propyl*-, b. p. 127—128°/15 mm. (*hydrochloride*, m. p. 118°; $+HgCl_2$, m. p. 140—141°); N-*butyl*-, b. p. 130—131°/11 mm.; N-n-*octyl*-, b. p. 172°/10 mm., and N-*benzyl*-, b. p. 193°/8 mm., -2-*piperidones*. The alkylpiperidones are hydrolysed by acids or (very readily) by alkalis to the corresponding δ-alkylaminovaleric acids, of which the following appear to be new : δ-*ethyl*-, m. p. 115°; δ-*propyl*-, m. p. 118—119°; δ-iso*propyl*-, m. p. 123—124°; δ-*butyl*-, m. p. 124°; δ-n-*octyl*-, m. p. 139—140°, and δ-*benzyl*-, m. p. 120°, -*aminovaleric acid hydrochlorides*. Hydrogenation of 2-chloro-5-nitropyridine at 150—200°/30 atm. gives the corresponding NH_2-compound only, and of 2-chloro-5-cyanopyridine gives (probably) *di*-(2-*chloro*-5-*pyridylmethyl*)*amine*, m. p. 104°. H. A. Piggott.

Stereochemistry of *N*-phenylpyrroles. XIX. L. H. Bock and R. Adams (J. Amer. Chem. Soc., 1931, **53**, 3519—3522; cf. this vol., 362).—Et acetonylacetoacetate (I) and *p*-aminobenzoic acid in EtOH give, after alkaline hydrolysis, N-p-*carboxyphenyl*-2 : 5-*dimethylpyrrole*-3-*carboxylic acid*, m. p. 277—280° (corr.) (*brucine H* and *strychnine H* salts). N-m-*Carboxyphenyl*-, m. p. 229—233° (corr.) (*brucine H* and *strychnine H* salts), N-o-*tolyl*-, m. p. 184·5—185·5° (corr.), and N-3-*methoxy*-o-*tolyl*-, m. p. 198—199° (corr.), -2 : 5-*dimethylpyrrole*-3-*carboxylic acids* are prepared similarly from (I) and *m*-aminobenzoic acid, *o*-toluidine, and 3-methoxy-*o*-toluidine, respectively. Anthranilic acid and Et αα′-diacetylsuccinate afford N-o-*carboxyphenyl*-2 : 5-*dimethylpyrrole*-3 : 4-*dicarboxylic acid*, m. p. 237—238° (*strychnine* H_2 and *cinchonine* H_2 salts). None of the above pyrroles could be resolved. Optical isomerism in *N*-phenylpyrroles probably resembles that in the Ph_2 series. H. Burton.

Synthesis of indole derivatives. R. H. F. Manske (Canad. J. Res., 1931, **4**, 591—595).—Et α-acetyl-δ-phenoxyvalerate (I) treated in aq. EtOH alkaline solution with PhN_2Cl gives Et α-anilinoimino-δ-phenoxyvalerate, converted by application of the Fischer indole synthesis into *Et* 3-β-*phenoxyethylindole-2-carboxylate*, m. p. 135° (corr.), hydrolysed to the corresponding *acid*, m. p. 166—167° (corr.), which is decarboxylated to 3-β-*phenoxyethylindole*, m. p. 99° (corr.). Hydrolysis of (I), followed by treatment with PhN_2Cl in alkaline solution, leads to the γ-phenylhydrazone of η-phenoxy-βγ-diketohexane, m. p. 110° (corr.). *Et* 2-*carbethoxy*-7-*methoxy*-β-(3-*indolyl*)-*propionate* (from Et *cyclo*pentanone carboxylate and diazotised *o*-anisidine), m. p. 95—96° (corr.), is hydrolysed to the corresponding dibasic *acid*, m. p. 232° (loss of CO_2), decarboxylated to 7-*methoxy*-β-(3-*indolyl*)*propionic acid*, m. p. 146° (corr.). The azide of indolylpropionic acid (II) is decomposed by hot H_2O, giving *di*-β-(3-*indolylethyl*)*carbamide*, m. p. 159° (corr.). When boiled with MeOH, (II) gives the corresponding *urethane*, m. p. 82° (corr.), and *di-indolylpropionhydrazide*, m. p. 237° (corr.), a mixture of which (crude) heated at 230° with phthalic acid or anhydride (A., 1929, 698) gives the corresponding phthalimide, converted into the free base by N_2H_4,H_2O. By heating the monophenylhydrazone of 1 : 2-diketo*cyclo*pentane with EtOH and HCl, 2-*ketodihydropentindole*, m. p. 248—249° (corr.), is formed. J. D. A. Johnson.

Hydroxyquinoline derivatives obtained by the action of sodium hydrogen sulphite. J. M. Kogan (Ber., 1931, **64**, [*B*], 2150—2156; cf. A., 1930, 1445).—6-Hydroxyquinoline is coupled with diazotised sulphanilic acid to Na 6-hydroxyquinolinebenzeneazo-*p*-sulphonate, which, with $NaHSO_3$ at $\ngtr$ 60—70°, affords the *substance* $C_{15}H_{10}O_4N_3SNa,NaHSO_3$, readily decomposed by NaOH, Na_2CO_3, or $NaHCO_3$. Treatment of 6-hydroxyquinoline hydrochloride with $NaNO_2$ yields 5-nitroso-6-hydroxyquinoline, which with $NaHSO_3$ gives the *compound* $C_9H_6O_2N_2,NaHSO_3$, transformed by aq. H_2SO_4 into 5-*amino*-6-*hydroxyquinoline*-8-*sulphonic acid*; the last-named substance is converted by conc. HCl into the *product* $C_9H_8O_4N_2S,HCl$. H. Wren.

Quinoline derivatives. XXVII. Derivatives of 2-phenyl-3-methylquinoline-4-carboxylic acid.

XXVIII. 4-Amino- and 4-chloro-2-phenyl-3-methylquinoline. XXIX. 4-Amino-2-*p*-tolylquinoline and 4-amino-2-phenylquinoline-4-carboxylic acid. XXX. Derivatives of 2-phenylquinoline-3-carboxylic acid. H. John [with H. Ottawa] (J. pr. Chem., 1931, [ii], **131**, 301—308, 309—313, 314—322, 323—330).—XXVII. 2-Phenyl-3-methylquinoline-4-carboxylic acid (this vol., 1167) is converted through its acid chloride into *Me*, m. p. 76°; *Et*, m. p. 51°; β-*chloroethyl*, m. p. 81°; Pr^{α} (*picrate*, m. p. 163°); and β-*diethylaminoethyl* (*picrate*, m. p. 185°), esters: *diethylamide*, m. p. 127° (*hydrochloride*; *sulphate*; *nitrate*; *picrate*); *hydrazide*, m. p. 141° (*hydrochloride*; *sulphate*; *nitrate*; *picrate*, m. p. 215°), converted into iso*propylidene*, m. p. 151°, and p-*amino*-α-*methylbenzylidene*, m. p. 241°, derivatives, and by HNO_2 into the *azide*. This with boiling H_2O affords s-*bis*-(2-*phenyl*-4-*quinolyl*-3-*methyl*)*carbamide*, m. p. 279° (*hydrochloride*, m. p. above 300°; *picrate*).

XXVIII. NH_3 converts the above acid chloride into the *amide*, m. p. 286° (*hydrochloride*; *sulphate*; *nitrate*; *picrate*), which, with KOBr, yields 4-*amino*-2-*phenyl*-3-*methylquinoline*, m. p. 118° (*Ac* derivative, m. p. 162°; *hydrochloride*, m. p. above 300°; *sulphate*; *nitrate*; *chloroplatinate*), converted by HCl and KNO_2 into 4-*chloro*-, m. p. 97° [*hydrochloride*, m. p. 280° (decomp.); *sulphate*; *nitrate*; *picrate*], together with a little 4-*hydroxy*-, m. p. 267°, -2-*phenyl*-3-*methylquinoline*.

XXIX. Similarly, 2-p-tolylquinoline-4-carboxylic acid gives the acid chloride (*hydrochloride*, m. p. 188°), *Et*, m. p. 54°; β-*chloroethyl*, m. p. 79°; and Pr^{α}, m. p. 32°, esters; *amide*, m. p. 208° (*hydrochloride*; *sulphate*; *nitrate*, *picrate*), and *hydrazide*, m. p. 232—233° (*hydrochloride*; *sulphate*, *nitrate*; and *picrate*, m. p. above 300°), converted by $CH_2Ac\cdot CO_2Et$ into (2-p-*tolyl*-4-*quinolyl*)-3-*methyl*-5-*pyrazolone*, m. p. 305°, and by HNO_2 into the *azide*, decomp. 180°. The last-named is converted by heating in dry C_6H_6 into 2-p-*tolyl*-4-*quinolylcarbimide*, m. p. 206° (decomp.) (hydrolysed by KOH in EtOH to 4-amino-2-*p*-tolylquinoline), by boiling H_2O into s-*bis*-(2-p-*tolyl*-4-*quinolyl*)*carbamide*, m. p. 163° (*hydrochloride*; *sulphate*; *nitrate*; *picrate*), and by hot EtOH into 2-p-*tolyl*-4-*quinolylurethane*, m. p. 98°, hydrolysed by hot HCl (*d* 1·19) to 4-*amino*-2-p-*tolylquinoline*, m. p. 159° (*Ac* derivative, m. p. 195—196°; *hydrochloride*; *sulphate*; *nitrate*; *picrate*, m. p. 255°). Oxidation of 4-amino-2-*p*-tolylquinoline with MnO_2 or CrO_3 and H_2SO_4 affords p-(4-*amino*-2-*quinolyl*)*benzoic acid*, m. p. above 300° (many *salts*).

XXX. By similar methods the acid chloride [*hydrochloride*, m. p. 220° (decomp.)] of 2-phenylquinoline-3-carboxylic acid is converted into its β-*chloroethyl*, m. p. 55°, $CEtMe_2$, m. p. 210°, β-*diethylaminoethyl* (*hydrochloride*, m. p. 102—103°), and CH_2Ph, m. p. 137°, esters; *amide*, m. p. 216° (*hydrochloride*; *sulphate*; *nitrate*; *picrate*); *ethylamide*, m. p. 185° (*hydrochloride*; *sulphate*; *nitrate*; *picrate*); *diethylamide*, m. p. 114° (*hydrochloride*; *sulphate*; *nitrate*; *picrate*); iso*amylamide*, m. p. 86° (*hydrochloride*; *sulphate*; *nitrate*; *picrate*); β-*hydroxyethylamide*, m. p. 150° (*hydrochloride*; *sulphate*; *nitrate*; *picrate*); and β-*benzyloxyethylamide*, m. p. 107°; *urethane*, m. p. 135° (*hydrochloride*; *sulphate*; *nitrate*; *picrate*); 2-*phenyl*-3-*quinolyl*-, m. p. 86° (*hydrochloride*; *sulphate*; *nitrate*; *picrate*), and s-*bis*-(2-*phenyl*-3-*quinolyl*)-, m. p. 236° (*hydrochloride*; *sulphate*; *nitrate*; *picrate*), -*carbamide*; and NN′-(2-*phenyl*-3-*quinolyl*)*ethylenediamine*, m. p. 300° (*hydrochloride*; *sulphate*; *nitrate*; *picrate*).

J. W. Baker.

Quinoline derivatives. XXXI. 3-Amino-2-phenylquinoline. XXXII. 3-Halogeno-2-phenylquinolines. H. John (J. pr. Chem., 1931, [ii], **131**, 346—353, 354—356).—XXXI [with H. Ottawa]. 2-*Phenylquinoline*-3-*carboxyhydrazide*, m. p. 212°, prepared either from the corresponding Me ester or acid chloride, condenses with $CH_2Ac\cdot CO_2Et$ with formation of 1-(2′-*phenyl*-3′-*quinolyl*)-3-*methyl*-5-*pyrazolone*, m. p. 237°, and is converted by HNO_2 into 2-*phenylquinoline*-3-*carboxyazide*. The azide is decomposed in boiling C_6H_6 to 3-*carbimido*-2-*phenylquinoline*, m. p. 262° (decomp.), and on hydrolysis, and alcoholysis, respectively, gives s-*di*-(2-*phenyl*-3-*quinolyl*)*carbamide*, m. p. 268°, and 2-*phenyl*-3-*quinolylurethane*, m. p. 115°. 3-Amino-2-phenylquinoline [*methiodide*, m. p. 238°; *ethiodide*, m. p. 212°; *Ac*, m. p. 124°, and Ac_2, m. p. 173° (cf. A., 1923, i, 481), derivatives] is obtained by hydrolysis of the urethane with conc. aq. HCl, or of the carbimide with 30% KOH in EtOH, or by the action of NaOBr on the carboxylamide.

XXXII. 3-Amino- is converted into 3-hydroxy- (63%) and 3-*chloro*-, m. p. 92°, (37%) -2-phenylquinoline by diazotisation in conc. HCl at −14° to −10°, and subsequent heating. 3-*Bromo*-2-*phenylquinoline*, m. p. 86°, is prepared by the Gattermann reaction. Numerous salts are described.

H. A. Piggott.

Syntheses in the carbazole series. Alleged synthesis of 3-nitro-*N*-ethylcarbazole. F. R. Storrie and S. H. Tucker (J.C.S., 1931, 2255—2263).—Reduction of 2 : 4-dinitro-*N*-ethyldiphenylamine (I) by $(NH_4)_2S$ or Na trisulphide gives 2-nitro-4-amino-*N*-ethyldiphenylamine (II) [*hydrochloride*, m. p. 183—185° (decomp.)], and not the 4-nitro-2-amino-compound (cf. A., 1904, i, 270). Hence the substance, m. p. 108°, obtained from this amine (*loc. cit.*), is not 3-nitro-*N*-ethylcarbazole (cf. J.C.S., 1923, **123**, 2143). The constitution of (II) is proved by conversion into 4-*chloro*-2-*nitro*-N-*ethyldiphenylamine* (III), which has been synthesised by independent methods. Other reduction products of (I) are described. Reduction affects the 4-NO_2-group also of the *N*-Me homologue. The anomalous behaviour of these substances is possibly due to the tert. nature of the N atom. Syntheses of *N*-methyl- and *N*-ethylcarbazole are recorded.

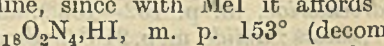
(I) and Na_2S in aq. EtOH give 2-*nitro*-4-*azoxy*-N-*ethyldiphenylamine* (?), m. p. 152—153°, or *aminoazo*-N-*ethyldiphenylamine* (?), m. p. 194°, according to the experimental conditions. The constitution of the former product is rendered probable by its formation from (I), benzoin, and NaOEt in hot EtOH, but Nisbet's formulation (A., 1927, 1063) of this reaction is criticised. The diazonium sulphate of (II) with Cu-bronze gives no identifiable substance, but the diazonium chloride with Cu-bronze or CuCl gives (III), red, m. p. 81—82°, also obtained (i) from 1 : 4-dichloro-2-nitrobenzene, NHPhEt, and K_2CO_3 at 205—215°, and (ii) by adding Et_2SO_4 to 4-chloro-2-nitrodiphenylamine, and KOH in boiling $COMe_2$. 2-Nitro-4-amino-*N*-methyldiphenylamine [*hydrochloride*, m. p. 177—178° (decomp.)] and 4-*chloro*-2-*nitro*-N-*methyldiphenylamine*, orange-red, m. p. 71—72°, were prepared in the same way as the *N*-Et homologues. *o*-Nitrodiphenylamine, KOH, and Me_2SO_4 in $COMe_2$ yield o-*nitro*-N-*methyldiphenylamine*, b. p. 205°/15 mm. (and under certain conditions a yellow *substance*, m. p. 172°), which with Sn and HCl in EtOH gives o-*amino*-N-*methyldiphenylamine*, b. p. 182—184°/15 mm. (*Ac* derivative, m. p. 87—89°; long heating with Ac_2O gives a *substance*, m. p. 118°); this, when diazotised and subsequently heated with aq. NaOH, affords *N*-methylcarbazole. *N*-Ethylcarbazole was similarly prepared from the corresponding *N*-Et compounds. Nitro - 4 - carboxy - 4′ - methyldiphenylamine, when heated with aq. KOH, gives *p*-toluidine and 3-nitro-4-hydroxybenzoic acid. R. S. Cahn.

Phenanthridine series. I. Synthesis of phenanthridine homologues and derivatives. G. T. Morgan and L. P. Walls (J.C.S., 1931, 2447—2456).—Dehydration of acyl-*o*-xenylamines by $POCl_3$ affords smoothly alkyl-, chloroalkyl-, phenyl-, and nitrophenyl-phenanthridines, but fails with formyl-*o*-xenylamine. The nitrophenylphenanthridines are sol. in fairly conc. acids. The corresponding NH_2-compounds (which are diazotisable) give no colour in conc. or dil. AcOH; the *o*- and *p*-, but not the *m*-, compounds give orange-red solutions in dil. mineral acids, owing to tautomerisation to an imino-quinonoid structure; addition of more acid destroys the colour, addition of a proton to the :NH group suppressing the tautomerisation. Acetyl-*o*-xenylamine (2-acetamidodiphenyl), m. p. 120° [prepared from *o*-xenylamine (I) and warm Ac_2O (cf. A., 1927, 236)], when gently boiled with $POCl_3$ for 1 hr., affords 9-methylphenanthridine in 70% yield. Propionyl-*o*-xenylamine gives similarly 9-ethylphenanthridine. (I) and $CH_2Cl\cdot COCl$ in Et_2O give *chloroacetyl*-o-*xenylamine*, m. p. 98·5°, which with $POCl_3$ yields 9-ω-*chloromethylphenanthridine*, m. p. 134°. Benzoyl-*o*-xenylamine (prepared by the Schotten–Baumann method) gives 9-phenylphenanthridine. (I) with *o*-, *m*-, and *p*-nitrobenzoyl chloride and pyridine at 100° gives o-, m-, and p-*nitrobenzoyl*-o-*xenylamine*, m. p. 129—131°, 134°, and 158·5°, respectively, which, when boiled with $POCl_3$ for 2—3 hr., afford 9-o-, -m-, and -p-*nitrophenylphenanthridine*, m. p. 122·5°, 172°, and 192°, respectively. These, when reduced with Fe filings in acidified dil. EtOH, give 9-o-, -m-, and -p-*aminophenylphenanthridine*, yellow, m. p. 168·5°, 159—161°, and 197—199° [*Ac* derivatives, $(+0{\cdot}5C_6H_6)$ m. p. anhyd. 185°, 237·5°, (+ ?EtOH) m. p. anhyd. 219°], respectively. The NHAc-derivatives, when treated with Me_2SO_4 in hot $PhNO_2$, give the *methosulphates*, o-, m. p. about 225° (decomp.) after sintering and decomp., m-, m. p. about 209° (decomp.) after becoming yellow at 170°, and p-, $+PhNO_2$, which is lost on recrystallisation from EtOH, decomp. anhyd. 228° after darkening at 170°, respectively; when these are boiled for 1 hr. with 5*N*-HCl and the p_H is subsequently brought to 5 by addition of aq. NH_3, 9-o-, -m-, and -p-*aminophenyl* 10-*methylpyridinium chloride*, m. p. 226° (decomp.) after decomp. from 170°, 222° (decomp.) after decomp. from 160°, and 247° (decomp.) after sintering, respectively, are obtained. R. S. Cahn.

E. Fischer's tetramethylureidine. H. Biltz and P. Nachtwey (Ber., 1931, 64, [*B*], 1974—1976).—Unsuccessful attempts were made to repeat Fischer's prep. of tetramethylureidine from tetramethyluric acid (cf. Gatewood, A., 1925, i, 1189). It is concluded that the compound does not exist and that Fischer's product was somewhat impure dimethylhydantoylmethylamide. H. Wren.

Reactions of some barbituric acid derivatives. J. Bougault and J. Guillon (Compt. rend., 1931, 193, 463—466).—The action of I and Br on unsaturated derivatives of barbituric acid in aq. $NaHCO_3$ is described. The former causes the addition of HOI followed by elimination of H_2O, giving iodinated lactones. Using Br, allyl derivatives behave similarly, but with other substituted barbituric acids compounds analogous to chloroamides are obtained. E. H. Sharples.

Changes in ultra-violet absorption spectrum of uracil and related compounds under the influence of radiations. F. F. Heyroth and J. R. Loofbourow (J. Amer. Chem. Soc., 1931, 53, 3441—3453).—Ultra-violet absorption spectra are given for uracil, adenine sulphate, thymus nucleic acid, and 2 : 5-dichloro-4-methylpyrimidine in H_2O. The spectra of these compounds during ultra-violet irradiation show that first of all increased absorption occurs in the low regions adjacent to the absorption band, and then selective absorption gradually disappears. The first change indicates an alteration in constitution (which may be due to some type of intramolecular rearrangement producing an unstable ring), whilst the latter shows that the compounds are either decomposed or polymerised. H. Burton.

Methylcaffeidine. H. Biltz and H. Rakett (Ber., 1931, 64, [*B*], 1970—1974).—Methylation of caffeidine with Me_2SO_4 occurs slowly and incompletely (cf. A., 1928, 906), whereas the compound is readily transformed by MeI into methylcaffeidine, m. p. 98—99°, and *caffeidide hydriodide*, m. p. 247—249° (decomp.); methylcaffeidine perchlorate, m. p. 173°, *chloroaurate*, and the complex *salt*, $[Ag(C_8H_{14}ON_4)]NO_3$, are described. *Caffeidine chloroplatinate*, *chloroaurate*, *fluoborate*, m. p. 219° (decomp.), and *thiocyanate*, m. p. 197° [passing at 160—170° into 2-thiotheobromine, m. p. 298° (decomp.)], have been prepared. The constitution  $\left.\begin{array}{l}\text{C(CO·NHMe)·NMe}\\ \text{C(NMe}_2\text{)———N}\end{array}\right\rangle\text{CH}$ is assigned to methylcaffeidine, since with MeI it affords the *hydriodide*, $C_9H_{18}O_2N_4,HI$, m. p. 153° (decomp.). Caffeidine is transformed by methyl- or ethyl-carbamide into theobromine, by *s*-dimethylcarbamide into caffeine, and by *s*-diethylcarbamide into 1-ethyltheobromine. H. Wren.

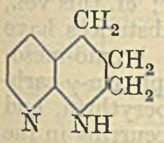
Colour of complex diazoles. III. G. C. Chakravarti (Proc. XV Indian Sci. Cong., 1928, 158).—Since all known coloured condensed pyrrole- and

pyridine-glyoxaline derivatives may be represented as containing a double quinonoid pyrrole or pyridine nucleus, this structure is regarded as the chromophore.
CHEMICAL ABSTRACTS.

Thio-orotic acid. M. BACHSTEZ (Gazzetta, 1931, 61, 520—527; cf. A., 1930, 781).—Condensation of thiocarbamide with Et oxalacetate gives an unstable *ester* which on rapid saponification yields thio-orotic acid [blackens without melting at 322° (corr.); decomp. 339° (corr.)] (*Na*, *K*, NH_4, *Ag*, Ag_2, Ag_3, and *Pb* salts). Thio-orotic acid in MeOH with gaseous HCl gives the O-*Me* derivative, m. p. 261° (corr., decomp.). MeI and the Ag salt give instead of the *N*-Me derivative of thio-orotic acid the *O*-Me derivative of orotic acid. The S atom is not attacked by chloroacetic acid or by HCl. E. E. J. MARLER.

Synthesis of a pyridazine derivative. R. E. MEYER (Helv. Chim. Acta, 1931, 14, 1187—1189).—Et *s*-di(benzeneazo)acetonedicarboxylate, m. p. 125°, prepared from Et acetonedicarboxylate and an excess of benzenediazonium chloride, when heated with EtOH passes (by loss of EtOH from the hydrazone form) into *Et 5-benzeneazo-4 : 6-diketo-1-phenyl-1 : 4 : 5 : 6-tetrahydropyridazine-3-carboxylate*, m. p. 164—165° (free *acid*, m. p. 260°). H. BURTON.

Decahydro-1 : 8-naphthyridine and other naphthyridine derivatives. G. KOLLER and E. KANDLER (Monatsh., 1931, 58, 213—237).—Reduction of 2 : 4-dichloro-1 : 8-naphthyridine with an excess of Na and abs. EtOH gives a poor yield of decahydro-1 : 8-naphthyridine (I), m. p. 119—121°, subliming from 68°/16 mm. (*NO*- and *Bz* derivatives, oils; mixed products obtained by treatment with MeI, oils), together with a substance, probably a partly reduced hydroxy- or methoxy-naphthyridine, which on repeated reduction yields more (I). The structure assigned to (I), in preference to that of 2-amino-3-*n*-propyltetrahydropyridine, is proved because the base cannot be reduced, and because dehydrogenation by Pd affords a base, $C_8H_{10}N_2$, containing a sec. and a tert. N atom, which must be (II). Methylation of (I) gives two methiodides, both of which on degradation yield $NHMe_2$ and a base $C_{10}H_{17}N$; this last base yields NMe_3 on degradation by Emde's method, and must, therefore, be



(II.)

$CHMe{:}C({:}CH_2){\cdot}CH{:}CH{\cdot}CH_2{\cdot}NMe_2$ (III),
$CH_2{:}CH{\cdot}CH{:}C(CH_2{\cdot}NMe_2){\cdot}CH{:}CHMe$ (IV), or
$CH_2{:}CH{\cdot}CH{:}C(CH_2{\cdot}NMe_2){\cdot}CH_2{\cdot}CH{:}CH_2$ (V);

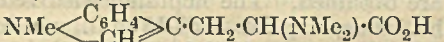
alternative structures containing the grouping $C{:}CH{\cdot}NMe_2$ are impossible, because of the stability of the base to acids. On catalytic reduction this base absorbs 3 mols. of H_2, and the saturated base thus obtained is shown by synthesis to be β-*n*-*propyl*-*n*-*amylamine* (VI). The unsaturated base must, therefore, be (IV) or (V). Methylation of (I), even in the cold, leads to the liberation of NMe_3 and $NHMe_2$; possible mechanisms for this degradation are discussed and considered to favour formula (V) rather than (IV).

(I) and finely-divided Pd at 220° give NH_3 (isolated as *m*-nitrobenzamide), *tetrahydro*-1 : 8-*naphthyridine* (II), m. p. 68—70°, b. p. 140—145°/12 mm. (*picrate*, m. p. 231°; *NO*-derivative, m. p. 79—81°), a little oil, b. p. approx. 80°/12 mm., and an oily residue. (I) gives a *chloroaurate*, m. p. 135°, passing in warm HCl into the monoacidic *salt*, m. p. 166—167°. (I) with MeI and K_2CO_3 in MeOH at room temp. give the *dimethiodide*, m. p. 218°, of a methylated compound derived from (I) by ring fission, and a syrupy *dimethiodide* (?); these salts, singly or mixed, when treated in H_2O with Ag_2O and distilled, yield the *base* (V) [or (IV)], b. p. 82—83°/11 mm. (*picrate*, an oil) (which reduces $AuCl_3$ and resinifies on keeping), together with NMe_3 [chloroaurate, m. p. 257° (decomp.), not as hitherto] and $NHMe_2$. The amorphous *methiodide* of this base, on treatment in H_2O with Ag_2O or Na–Hg, affords NMe_3 and an unsaturated hydrocarbon (resembling acraldehyde in odour), which yields no cryst. derivatives. (V) [or (IV)] in AcOH in presence of PtO_2 absorbs 3 mols. of H_2 to give (VI), b. p. 77—80°/27 mm. (*chloroaurate*, m. p. 158—160°; *methiodide*, decomp. 212°). β-Methyl-*n*-amyl alcohol (prepared by reduction and hydrolysis of Et methyl-*n*-propylacetoacetate with Na and EtOH) with red P and I, first cold and then at 100°, affords the *iodide*, b. p. 53—55°/12 mm., which with Et sodioacetoacetate gives *Et α-acetyl-γ-methyl*-n-*heptoate*, b. p. 120—124°/12 mm. On reducing and hydrolysing this with Na and abs. EtOH, δ-*methyl*-n-*heptanol*, b. p. 188—193°, and a lower-boiling fraction (possibly hydrocarbons) are obtained. The heptanol with red P and I gives the *iodide*, b. p. 92—95°/13 mm., which with $NHMe_2$ in EtOH at 130—135° forms *dimethyl*-δ-*methyl*-n-*heptylamine*, b. p. 75°/29 mm. [*chloroaurate*, m. p. 47—49°; *methiodide*, m. p. 185° (decomp.), depressed by the methiodide of (VI)]. $Pr^{\alpha}Br$ (prepared by distilling $Pr^{\alpha}OH$ with H_2SO_4 and KBr), b. p. 71°, condenses with Et_2 disodiomalonate to give Et_2 di-*n*-propylmalonate, b. p. 248—249°, which on hydrolysis and loss of CO_2 gives α-*n*-propyl-*n*-valeric acid, b. p. 218°, the Et_2 ester of which, when reduced with Na and abs. EtOH at 100°, affords β-n-*propyl*-n-*amyl alcohol*, b. p. 179°, having an odour of peppermint. This alcohol with red P and I gives the corresponding *iodide*, b. p. 90°/14 mm., which with $NHMe_2$ in abs. EtOH at 130° yields (VI) [*chloroaurate*, m. p. 160—161°; *methiodide*, decomp. 215°; neither m. p. is depressed by admixture with the derivatives of (VI) obtained from the base (V)].

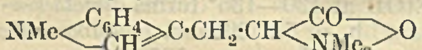
When the *methiodide*, m. p. 212°, of 2 : 4-dimethoxy-1 : 8-naphthyridine is treated with aq. KOH and $K_3Fe(CN)_6$, 2 : 4-*dimethoxy*-8-*methyl*-1 : 8-*naphthyridone*, m. p. 137—138°, distilling at 12 mm., is obtained.
R. S. CAHN.

Formation of semiquinones as intermediary reduction products from pyocyanine and some other dyes. L. MICHAELIS (J. Biol. Chem., 1931, 92, 211—232).—The titration of pyocyanine (this vol., 684) has been applied to α-hydroxyphenazine and rosinduline. In acid solution (below p_H 4 and 2, respectively) reduction of these dyes proceeds in two separate stages, in each of which one H atom is added. The colour changes are red–green–yellow for α-hydroxyphenazine, and red–violet–yellow for rosinduline, the intermediate colour corresponding with the formation of semiquinones. The latter are not mol. compounds of the oxidised and reduced states, but true reduction products, resembling free radicals in constitution. A. COHEN.

Basic components of the secretion of the skin of the toad. H. WIELAND, G. HESSE, and H. MITTASCH (Ber., 1931, 64, [*B*], 2099—2103).—The secretion of *Bufo vulgaris* is freed from neutral and acidic substances, after which extraction of the faintly alkaline solution with Et_2O yields a non-cryst. base isolated as yellow and red *picrates*, m. p. 178°. At about 140° the red passes into the yellow form. In solution the picrates have their individual colours, so that they are not dimorphous, but the colours gradually become identical, showing that an equilibrium has been attained. Analyses of the picrate and *methiodide*, m. p. 209°, indicate the formula $C_{14}H_{18}O_2N_2$ for *bufotenin*. The quaternary NH_4 base, prepared by $Tl(OH)_2$ instead of Ag_2O on account of its strong reducing properties, evolves NMe_3 when heated, leaving an acidic residue; its picrate is identical with the salt of a base isolated by Mittasch from Chinese *Senso*, and now named *bufotenidine*. The latter substance is isolated from this source as the flavianate, decomp. 200°, and is also present in the aq. extracts from *Bufo vulgaris* from which bufotenin has been removed; it gives a *picrate*, m. p. 198°. Bufotenin contains 2 Me groups attached to a tert. N atom. The analogy of bufotenin with hypaphorin (J.C.S., 1911, 99, 2068) leads to the conclusion that the constitutions



$NMe{<}{\substack{C_6H_4\\ CH}}{\geqslant}C{\cdot}CH_2{\cdot}CH(NMe_2){\cdot}CO_2H$ and



$NMe{<}{\substack{C_6H_4\\ CH}}{\geqslant}C{\cdot}CH_2{\cdot}CH{<}{\substack{CO\\ NMe_3}}{>}O$ are possessed by bufotenin and bufotenidine, respectively. In the red picrate, the acid is attached to the indole-N, whereas in the yellow compound it is united to the tert.-N of the NH_2-acid. H. WREN.

Complex salts of 1 : 2 : 4-triazole. M. BAJ and I. DE PAOLINI (Gazzetta, 1931, 61, 557—560).—The following complex salts of the type $[M(C_2H_2ArN_3)_2(H_2O)_2]SO_4$ are described: the *Cu*, *Ni*, and *Co* salts of 1-phenyl-1 : 2 : 4-triazole, the *Cu* salt of 1-tolyl-1 : 2 : 4-triazole, and the Cu salt of 1 : 2 : 4-triazole. E. E. J. MARLER.

Condensation of unsaturated compounds with diazomethane. III. R. ROTTER and E. SCHAUDY (Monatsh., 1931, 58, 245—248; cf. A., 1927, 247).—Carbodi-α-naphthylimide (modified prep.) with diazomethane in Et_2O at 0° during 5—6 days forms 1-α-*naphthyl*-5-α-*naphthylaminotriazole*, m. p. 184°; carbodi-β-naphthylimide, m. p. 144°, and not 145—146° (A., 1886, 1035), with diazomethane in dioxan and C_6H_6 gave, after a few hr., 1-β-*naphthyl*-5-β-*naphthylaminotriazole*, m. p. 199°. R. S. CAHN.

3-Quinolyl methyl ketone. G. KOLLER and H. RUPPERSBERG (Monatsh., 1931, 58, 238—244).—The constitution previously assigned to 3-acetylquinoline (I) (A., 1929, 937) is correct, because this substance yields an *oximino*-derivative, decomp. 172°, and with *o*-aminobenzaldehyde and KOH in abs. EtOH forms 2 : 3-diquinolyl. When (I) is heated with PhCHO and $ZnCl_2$ in a vac. at 130—140° for 2 hr., it yields 3-*quinolyl styryl ketone*, red, m. p. 123°, which is oxidised by $KMnO_4$ to BzOH and quinoline-3-carboxylic acid. The colourless compound, previously (*loc. cit.*) given this structure, must have another constitution. When treated with MgMeI, (I) yields 3-*quinolyldimethylcarbinol*, m. p. 120—121·5° (*picrate*, m. p. 191°), which can be distilled at 12 mm., and is stable to $KMnO_4$ in $COMe_2$. The *phenylhydrazone*, m. p. 167° (decomp.), of Et 3-acetylquinoline-2-carboxylate, when heated at 180—200° in CO_2, loses EtOH to form 4-*keto*-3-*phenyl*-1-*methyl*-3 : 4-*dihydro*-2 : 3 : 5-*naphthtriazine*, yellow, m. p. 244°. The compound $C_{18}H_{17}O_6N$, obtained from Et_2 acetonedioxalate and *o*-aminobenzaldehyde (*loc. cit.*), must be *Et* γ-(2-*carbethoxy*-3-*quinolyl*)-αγ-*diketobutyrate*, since on hydrolysis with KOH it yields 3-acetylquinoline-2-carboxylic acid, which passes into (I) by loss of CO_2 when sublimed in vac. R. S. CAHN.

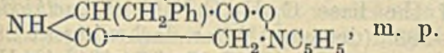
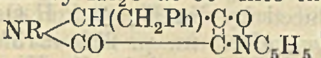
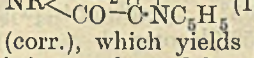
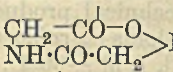
Chlorophyll series. VII. Structure from measurements of absorption spectra. J. B. CONANT and S. E. KAMERLING (J. Amer. Chem. Soc., 1931, 53, 3522—3529).—Absorption spectra of 7 porphyrins, 14 chlorophyll derivatives, and 9 coloured compounds have been determined at the temp. of liquid air by the method previously described (A., 1930, 1341); microphotometric curves of several of the spectra are given. The characteristic phenomenon of a series of narrow sharp bands shown by the porphyrins is not found for the other substances. The chlorins occupy an intermediate position between the porphyrins and coloured substances, being analogous to *cyclo*hexadiene in comparison with C_6H_6 and butadiene; this is considered to support the chlorin formula previously proposed (this vol., 1075). The changes in the spectra of the porphyrins associated with changes in substituents are discussed. H. BURTON.

Constitution and spectra of the porphyrins. II. Spectral properties of porphyrins with substituents in the porphin ring. H. HELLSTRÖM (Z. physikal. Chem., 1931, B, 14, 9—17; cf. this vol., 784).—The spectra of the following substances have been examined: tetrachloro- and bromo-meso-porphyrin, phylloporphyrin, rhodoporphyrin-γ-carboxylic acid, chloroporphyrin e_6, phylloerythrin, and phæoporphyrin a_5. The ring closure occurring in the last two compounds causes a considerable change in the frequency interval and intensity of the bands. The CO_2H group produces a small shift towards the violet. J. W. SMITH.

Atmospheric dealkylation of aqueous solutions of cresol-blue. W. C. HOLMES and A. R. PETERSON (Stain Tech., 1931, 6, 79—82).—In slightly alkaline solutions (*e.g.*, at p_H 7·68) some dealkylation occurs at room temp. in a few weeks. At p_H 9 the change is detectable after 1 day. H. W. DUDLEY.

Action of hydroxylamine on mustard oils; formation of dianilino-1 : 2 : 5-oxadiazole. P. C. GUHA and M. N. CHAKLADAR (Proc. XV Indian Sci. Cong., 1928, 157).—Unstable hydroxythiocarbamide derivatives, NHR·CS·NH·OH are decomposed even at room temp., affording 1 : 2 : 5-oxadiazoles with separation of S and H_2O. CHEMICAL ABSTRACTS.

Compounds resembling peptides. XXXIII. Dehydration of amino-acids and a transition to

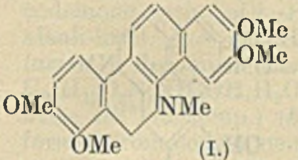
the pyrrole series. M. Bergmann, L. Zervas, and F. Lebrecht (Ber., 1931, **64**, [*B*], 2315—2322).—Chloroacetylphenylalanine is converted by pyridine at 100° into the *hydrochloride* of the *betaine* (I)  $NH<\begin{matrix}CH(CH_2Ph)\cdot CO\cdot O\\ CO\text{————}CH_2\cdot NC_5H_5\end{matrix}$, m. p. 205—206° (corr.), transformed by Ac_2O at 80° into the *pyrrole* derivative (II),  $NR<\begin{matrix}CH(CH_2Ph)\cdot C\cdot O\\ CO\text{————}C\cdot NC_5H_5\end{matrix}$ (R=Ac), m. p. 159—160° (corr.), from which the Ac group is removed by *N*-NaOH, yielding the *compound*, (II; R=H), m. p. 183—183·5° (corr.) after softening at 177° (*hydrochloride*). Treatment of the hydrochloride of the betaine (I) or of chloroacetylphenylalanine with Ac_2O and pyridine at room temp. yields the azlactone of α-acetamidocinnamic acid, m. p. 152—153°. Chloroacetyl-*l*-tyrosine under similar conditions gives the azlactone of *p*-hydroxyacetyl-α-acetamidocinnamic acid, m. p. 137° (corr.). Chloroacetylglycine is converted by Ac_2O and pyridine into the *pyrrole* derivative  $NR<\begin{matrix}CH_2\cdot C\cdot O\\ CO-C\cdot NC_5H_5\end{matrix}$ (III) (R=Ac), m. p. 239—240° (corr.), which yields pyridine when heated at 300°; it is transformed by conc. HCl at 100° into the free *base* (III) (R=H), m. p. 200—201° (corr., slight decomp.) [*hydrochloride*, m. p. 243—244° (corr.)]. With pyridine at 100° chloroacetylglycine gives the *betaine*,  $\begin{matrix}CH_2-CO-O\\ NH\cdot CO\cdot CH_2\end{matrix}>NC_5H_5,HCl$, m. p. 211—212° (corr.), transformed by Ac_2O at 90° into (III) (R=H). Oxidation of the base (III) (R=H) with H_2O_2 in presence of NH_3 yields *NH_4 oxalylaminoacetate*, m. p. 196—197° (corr.) after softening at 193° (corresponding Ag salt), hydrolysed to $H_2C_2O_4$ and glycine.

The *compounds* $C_{11}H_{10}O_3N_2$, m. p. 255—256° (corr.) after softening at 243° and partial decomp. at 249°, from chloroacetylglycine, pyridine, and Ac_2O, and $C_{12}H_{12}O_5N_2$, m. p. 180—181° (corr.), from α-bromopropionylglycine, Ac_2O, and pyridine, are incidentally described. H. Wren.

Synthesis of substituted thiazines. S. Krishna and M. S. Jain (Proc. XV Indian Sci. Cong., 1928, 153—154).—6-Chloro-3-nitrobenzenesulphonic acid condenses with aniline to give 4-nitroacetanilide-2-sulphonic acid. If the blue solution in H_2SO_4 is immediately diluted with H_2O, 3-nitrophenothiazine *S*-oxide is precipitated, but if dilution is delayed for 30 min., 3-nitrophenothiazine is obtained and SO_2 is evolved. 3-Nitrophenothiazine is readily reduced to the 3-NH_2-compound, from which, via the diazo-compound, phenothiazine is obtained. Chemical Abstracts.

Volatility of nicotine. V. L. Nagy (Biochem. Z., 1931, **239**, 324—328).—Nicotine evaporates appreciably when exposed to air at room temp. and is volatile in the vapours of Et_2O, light petroleum, a mixture thereof, or EtOH (96%). W. McCartney.

Chelerythrine and sanguinarine. E. Späth and F. Kuffner (Ber., 1931, **64**, [*B*], 2034—2038; cf. this vol., 854).—Chelerythrine is reduced by Zn dust and dil. HCl to dihydrochelerythrine, m. p. 166—167°, converted by phloroglucinol and H_2SO_4 and subsequently with diazomethane into *tetramethoxy*-N-*methyldihydro-α-naphthaphenanthridine* (I), m. p. (vac.) 182—183°. The same product is derived from *hydrosanguinarine*, m. p. (vac.) 188—189°, obtained by reducing sanguinarine nitrate with Zn and HCl. The formation of the same product from chelerythrine and sanguinarine is proof of the analogous structure of the quaternary chelidonium bases and of the similar position of the O atoms attached to the aromatic nuclei. The structure of homochelidonine is more firmly established.



(I.)

Reply is made to von Bruchhausen and Bersch (this vol., 750). H. Wren.

Constitution of corydine, *iso*corydine, and corytuberine. Synthesis of corydine. E. Späth and F. Berger (Ber., 1931, **64**, [*B*], 2038—2048).—Corytuberine is converted by diazoethane into its amorphous *Et_2 ether*, which is oxidised by $KMnO_4$ to 4-methoxy-3-ethoxyphthalic acid (identified as the *ethylimide*, m. p. 85°), thus showing that the free phenolic groups are not present in the same C_6H_6 nucleus. If corytuberine is treated with that amount of diazoethane required for the essential production of the two monoethyl ethers and the product is energetically oxidised with $KMnO_4$, 4-methoxy-3-ethoxyphthalic acid and 5-methoxy-4-ethoxybenzene-1 : 2 : 3-tricarboxylic acid (*methylimide*, m. p. 160—161°) are formed, thus establishing the constitution (I) for the alkaloid. The synthesis of the tricarboxylic acid is effected as follows: opianic acid is converted by fuming HCl at 100° into 2-aldehydo-6-hydroxy-5-methoxybenzoic acid, m. p. 155—156°, and thence by diazoethane into 2-*aldehydo*-5-*methoxy*-6-*ethoxybenzoic acid*. 3-*Nitro*-2-*aldehydo*-5-*methoxy*-6-*ethoxybenzoic acid*, prepared by means of fuming HNO_3 in AcOH, is reduced by $SnCl_2$ to *anhydro*-6-*amino*-4-*methoxy*-3-*ethoxyphthalic acid*, m. p. 162—163° (decomp.). 3-Nitro-2-aldehydo-5-methoxy-6-ethoxybenzoic acid is oxidised by $KMnO_4$ in neutral solution to 6-nitro-4-methoxy-3-ethoxyphthalic acid (*Me* ester, m. p. 86—87°), whence successively *Me* 6-*amino*-4-*methoxy*-3-*ethoxyphthalate*, m. p. 130—131°, *Me* 6-*cyano*-4-*methoxy*-3-*ethoxyphthalate*, m. p. 98—99°, and 5-*methoxy*-4-*ethoxybenzene*-1 : 2 : 3-*tricarboxylic anhydride*, m. p. 150—151° (corresponding *methylimide*, m. p. 160—161°). 4-*Methoxy*-3-*ethoxyphthalmethylimide* has m. p. 136—137°.

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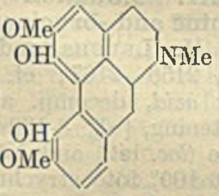
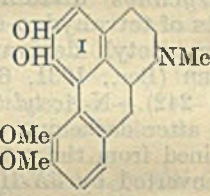
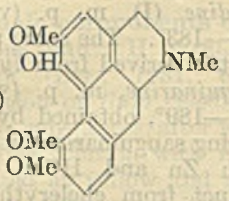
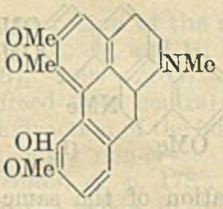


(II.)


Removal of the CH_2O_2: group from bulbocapnine Me ether with phloroglucinol and H_2SO_4 affords the phenolic *base* (II) (+MeOH), m. p. 118—120° with loss of MeOH, which is partly methylated to corydine, identified as the free base and hydrochloride. Since the 2 OH groups of the phenolic base must be situated in the nucleus (I) and corydine is obtained by partial methylation of corytuberine, the constitution (III)



(III.)



(IV.)

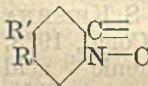
must be ascribed to corydine. This is in agreement with the observation that 3 : 4-dimethoxyphthalic acid is formed by oxidation of corydine or its Et ether. The establishment of the constitution of corydine and the conversion of corytuberine by partial methylation into *iso*corydine enable the constitution (IV) to be assigned to the last-named alkaloid. H. WREN.

Synthesis of sinactine. E. SPÄTH and E. MOSETTIG (Ber., 1931, **64**, [*B*], 2048—2050).—Cryptopine is transformed into *r*-tetrahydro*epi*berberine (improved method). The base cannot be resolved into its optically active components by *d*-camphor- or *d*-bromocamphor-sulphonic acid or by tartaric acid in EtOH. Resolution is readily effected by alternate use of *d*- and *l*-tartaric acid in MeOH. The optically active bases have m. p. (vac.) 178—179°, $[\alpha]_D^{15}$ ±302° in $CHCl_3$. For natural sinactine Goto and others (A., 1930, 98, 935) record m. p. 175°, $[\alpha]_D$ −312°. H. WREN.

***Strychnos* alkaloids. LXI. Oxidation products of tetrahydro-strychnine and -brucine and their acetyl derivatives.** H. LEUCHS and H. BEYER (Ber., 1931, **64**, [*B*], 2156—2167; cf. this vol., 242).—N-*Acetylstrychnic acid*, decomp. about 305° after darkening and softening, $[\alpha]_D^{16}$ +130·6°/*d*, obtained from the perchlorate (*loc. cit.*) and NaOH, is converted by 5*N*-H_2SO_4 at 100° into strychnine; the *methiodide*, m. p. 247—249° (decomp.), and the *Et* ester (as *perchlorate*) are described. It is reduced by H_2–PtO_2 to *dihydro*-N-*acetylstrychnic acid*, m. p. 245—248° (decomp.) after softening at 240°, $[\alpha]_D^{21}$ +95·0°/*d*, transformed by 5*N*-H_2SO_4 into dihydrostrychnine. The NH_2-acid, $C_{21}H_{22}O_4N_2$, is converted by HCl–EtOH into the *Et* ester, m. p. 178—180° after softening and darkening at 173° [*hydrochloride*; (?) *methiodide*, decomp. 296° after darkening at 220—290°]; it is hydrogenated to the *acid* $C_{21}H_{24}O_4N_2$, m. p. 280—285° (*hydrochloride*, $[\alpha]_D^{20}$ +30·6°; *oxime hydrochloride*; *Ac* derivative).

Brucine is reduced at a Pb cathode to brucidine (50%) and tetrahydrobrucine (30%). Oxidation of the last-named with CrO_3 and H_2SO_4 gives the base $C_{17}H_{20}O_4N_2$, m. p. 245—247° after softening (perchlorate, $[\alpha]_D^{20}$ +76·3°/*d*) (cf. *loc. cit.*), and a trihydrated *substance*, $C_{19}H_{22}O_5N_2$, m. p. 300—305° (decomp.) after softening at 285°, $[\alpha]_D^{20}$ +63·8°/*d* in H_2O (*perchlorate* +H_2O, $[\alpha]_D^{20}$ +38·8°/*d* increasing greatly when the salt is heated). The NH_2-acid readily absorbs 4H, giving the *compound* $C_{19}H_{26}O_5N_2$, softening above 315°, $[\alpha]_D^{23}$ +69·7°/*d*. The *base* $C_{17}H_{18}O_3N_2$, also obtained by the oxidation of tetrahydrobrucine, has m. p. 298—300° after darkening and softening, $[\alpha]_D^{24}$ +297°/*d* (*perchlorate*, $[\alpha]_D^{24}$ +209·5°/*d*); it is hydrogenated to 2-keto-3-hydroxydihydronucidine. The base $C_{17}H_{20}O_4N_2$ has been converted into its *Ac* derivative (*perchlorate* +H_2O, $[\alpha]_D^{20}$ +64·3°/*d*, passing after protracted heating into the salt of the base $C_{17}H_{18}O_3N_2$), its *methiodide*, m. p. 291—293° (decomp.) after darkening at 285°, and its *oxime hydrochloride*, $[\alpha]_D^{24}$ +74·1°/*d* in H_2O. It is reduced by Na–Hg and H_2O to 2-*keto*-2′ : 3′-*dihydroxynucidine*, m. p. 271—273° (decomp.), $[\alpha]_D^{20}$ −33·8°/*d* in H_2O, and by Zn–Hg and 6*N*-HCl to 2-keto-3-hydroxynucidine, m. p. 254° (decomp.), $[\alpha]_D^{24}$ −21·3°/*d* in H_2O. Hydrogenation in presence of PtO_2 affords the *substance* $C_{17}H_{24}O_4N_2$, m. p. 228—230° after softening, $[\alpha]_D^{27}$ +43·4°/*d* in H_2O (*perchlorate* of corresponding *Ac* derivative). Tetrahydrobrucine is converted by Ac_2O and NaOAc into its *Ac_2* derivative, m. p. 125—127° [*hydrochloride*, $[\alpha]_D^{20}$ +95·4°/*d*; *perchlorate* +$2H_2O$, $[\alpha]_D^{20}$ +85°/*d*; *methiodide*, m. p. 285—290° (decomp.)]. The Ac_2 substance is hydrolysed by NaOH to N-*monoacetyltetrahydrobrucine*, m. p. 130—135° [*hydrochloride*, $[\alpha]_D^{20}$ +95·3°/*d*; *perchlorate*, $[\alpha]_D^{20}$ +87·2°/*d*; *methiodide*, m. p. 305° (decomp.)]. H. WREN.

Three new *Strychnos* alkaloids [α- and β-colubrines, ψ-strychnine]. K. WARNAT (Helv. Chim. Acta, 1931, **14**, 997—1007).—The mother-liquors from the technical production of strychnine contain 3 new alkaloids: α-*colubrine* (I), $C_{22}H_{24}O_3N_2$ +$4H_2O$, m. p. 184°, $[\alpha]_D^{19}$ −66·4°, −76·5° (H_2O-free) in 80% EtOH (*hydrochloride* +$3H_2O$; *sulphate* +$10H_2O$); β-*colubrine* (II), $C_{22}H_{24}O_3N_2$, m. p. 222°, $[\alpha]_D^{19}$ −107·7° in 80% EtOH (*hydrochloride* +H_2O; *sulphate* +$9H_2O$); and ψ-*strychnine* (III), probably $C_{21}H_{22}O_3N_2$, m. p. 266—268° (decomp.), $[\alpha]_D^{23}$ −43·8° in EtOH, −85·9° in $CHCl_3$ (*hydrochloride* +$2H_2O$; *nitrate*; *NO*-derivative, m. p. 292—294°). Oxidation of (I) and (II) with alkaline $KMnO_4$ (cf. A., 1926, 1263; this vol., 242) and esterification of the acids formed with diazomethane gives *Me_2* N-*oxalyl*-4-, m. p. 163°, and N-*oxalyl-5-methoxyanthranilate*, m. p. 176°, respectively. These esters are synthesised from the requisite Me methoxyanthranilate and oxalic acid at 120—130° with subsequent esterification. The structure (*A*) is present, therefore, in (I) (where R=OMe and R′=H), (II) (R=H, R′=OMe), strychnine (R=R′=H), and brucine (R=R′=OMe).

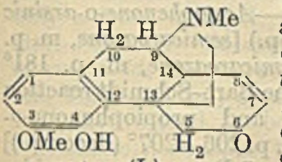


(*A*.)

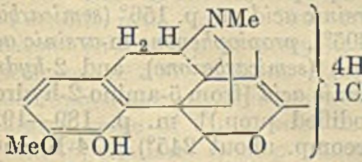
Dissolution of (III) in hot MeOH and EtOH gives, on cooling, *methyl*-, m. p. 198—200°, $[\alpha]_D^{21}$ −70·1° in $CHCl_3$, and *ethyl*-ψ-*strychnine*, m. p. 224—225°, respectively; 1 mol. of H_2O is replaced by 1 mol. of the alcohol, which cannot be removed at 110°.
H. BURTON.

Denigès–Oliver test for morphine. F. BAMFORD (Analyst, 1931, **56**, 586—589).—Both morphine and heroin give a red colour in the Denigès–Oliver test. For ordinary work the method of Denigès, using aq. $CuSO_4$, is more convenient, but in the case of extracts prepared from viscera etc. Oliver's modification with a Cu wire gives more definite results. The red colour developed is an intermediate product and is destroyed by an excess of H_2O_2. For 1 mg. of alkaloid the max. colour is produced by dissolving in 5 c.c. of H_2O, adding 4 c.c. of H_2O_2 (2/3 vol. O), 1 drop of 0·1% $CuSO_4$, and 1—4 drops of conc. aq. NH_3, and diluting the whole to 10 c.c. For qual. work this is matched against a solution of Congo-red (1 in 10^6), and for quant. work a solution of heroin (1 in 10^4). Quinine, if present, may be salted out by Na_2SO_4. If Na K tartrate is used to salt out quinine, the morphine or heroin must be extracted by an immiscible solvent, since tartaric acid interferes with the test. T. McLachlan.

Acid rearrangement of morphine alkaloids. II. Preparation of "true" thebainone, and action of concentrated hydrochloric acid on thebaine. C. Schöpf and H. Hirsch (Annalen, 1931, **489**, 224—251).—*Thebainone* (I) (+0·5H_2O), m. p. 151—152° [*hydriodide*, m. p. 258°; *methiodide*, m. p. 223°; *oxime* (+0·5H_2O), m. p. 185—186° (*hydrochloride*, m. p. 290—291°)], is obtained by the gradual addition of thebaine or codeinone to $SnCl_2,2H_2O$ in conc. HCl at room temp., and heating for a short time at 70°, or, in much smaller yield, by reduction of the red halochromic solution of thebaine in conc. HCl with $SnCl_2$ at 70°. That it has the formula assigned (I) is shown by its reduction with Pd–H_2 to dihydrothebainone, and by degradation of its methiodide to 3 : 4 : 6-*triacetoxyphenanthrene*, m. p. 165—167°, which is also obtained by hydrolysis and demethylation of acetylthebaol with HBr and acetylation of the product. Thebainoneoxime also gives this acetoxyphenanthrene on reduction. Codeinone, which is stable to cold conc. HCl, exists in the red solution of thebaine in HCl to the extent of about 7%, and therefore can be responsible for only a small proportion of the thebainone formed on reduction. From the general properties of the solution the existence in it of the substances (II) and (III) (in reversible equilibrium ?) is postulated; these are converted into (I) and metathebainone, respectively, on reduction. On the assumption that (III) is responsible for the halochromism of the solution, these views are supported by approx. polarimetric determinations. The conversion of morphine into *apo*morphine and of thebaine into thebenine is discussed in the light of these results. The reduction of thebaine with $SnCl_2$–AcOH gives methebenine in 59% yield, the course of the reaction being similar to that with HCl (*d* 1·07) except that the OMe group migrates from C_6 to C_8 without simultaneous hydrolysis. Avoidance of heating in the reduction of codeinone with $SnCl_2$–HCl leads to formation of an alkali-insol. *base*, $C_{18}H_{20-22}O_3N_2$, m. p. 155—158° (*oxime*, decomp. slowly, 305°). A *compound*, $C_{18}H_{19}O_3N,NH_2OH,H_2O$, m. p. 142—144°, (anhyd.) 210—212° (decomp.) (*hydrochloride*, m. p. 204°), is formed from codeinone and NH_2OH in acid solution. H. A. Piggott.



(I.)



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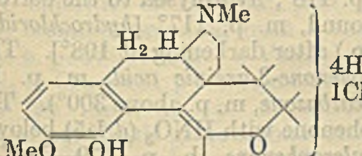


(III.)

Composition of oxonitin. E. Späth and F. Galinovsky (Ber., 1931, **64**, [*B*], 2201—2202; cf. this vol., 243).—The OMe content of oxonitin prepared according to Barger (J.C.S., 1915, **107**, 231) is usually somewhat low and falls when the substance is cryst. from $CHCl_3$–Et_2O or other agents. When precipitated by Et_2O from $CHCl_3$–MeOH const. vals. are obtained in good agreement with the formula $C_{32}H_{43}O_{12}N$, which therefore, contrary to Henry and Sharp (this vol., 636), is provisionally maintained. H. Wren.

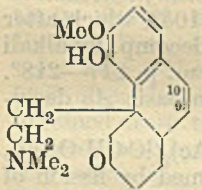
Phenolic alkaloids of *Cocculus trilobus*, D.C. I. H. Kondo and M. Tomita (Arch. Pharm., 1931, **269**, 433—442).—The total alkaloids of *C. trilobus* consist of trilobine, homotrilobine, an amorphous non-phenolic base, and two phenolic bases (*a*) *trilobamine* (I), $C_{31\ (or\ 32)}H_{22\ (or\ 24)}(\cdot O\cdot)_2(OH)_2(OMe)_2(NMe)_2$, m. p. 195°, decomp. 212°, $[\alpha]_D^{15}$ +356·6° in 2% AcOH [*dihydriodide*, decomp. 264°; *dimethiodide* (+H_2O); amorphous *Me_2 ether*, m. p. 169° (sinters at 130°), from (I) and diazomethane], and (*b*) a *base* (II), $C_{20\ (or\ 21)}H_{15\ (or\ 17)}O_3(OMe)(NMe)$, m. p. 223°, $[\alpha]_D^{18}$ +190·3° in $CHCl_3$. The product from (I) and Me_2SO_4 is decomposed by 20% NaOH to *dimethyltrilobaminemethylmethine*, amorphous, decomp. 105°, which after further treatment with Me_2SO_4 and decomp. by alkali gives NMe_3 and a N-free substance, m. p. 217—218°. (I) and Ac_2O at 70—80° give a non-basic *Ac* derivative, probably $C_{27\ (or\ 28)}H_{20(22)}O_2(OMe)_2(OAc)_2(NMeAc)_2(\vdots C\cdot\dot{C}H\cdot OAc)_2$, amorphous, decomp. 210—213°, formed by fission of 2 tetrahydro*iso*quinoline rings. Oxidation of methyltrilbaomine with 1% $KMnO_4$ affords 2-methoxy-5 : 4′-dicarboxydiphenyl ether. The absorption spectrum and colour reactions of (I) are similar to those of oxyacanthine and berbamine, probably $C_{31\ (or\ 32)}H_{22\ (or\ 24)}(\cdot O\cdot)_2(OH)(OMe)_3(NMe)_2$ (this vol., 242); the spectrum of (II) resembles that of menisarine. H. Burton.

Alkaloids of pereiro bark. I. Geissospermine. A. Bertho and G. von Schuckmann (Ber., 1931, **64**, [*B*], 2278—2286).—The finely-powdered bark is extracted with EtOH, the solvent evaporated, and the residue mixed with $Ca(OH)_2$ and H_2O and dried. Extraction of the product with ligroin gives a mixture of bases purified by dissolution in AcOH and precipitation with NH_3. Recrystallisation from aq. MeOH gives *geissospermine sesquihydrate*, $C_{40}H_{48}O_3N_4,1·5H_2O$, decomp. 145—147° (corr.) after softening, $[\alpha]_D^{20}$ −101·9° in 96% EtOH. Crystallisation of the sesquihydrate from AcOEt or C_6H_6 yields *geissospermine dihydrate*, m. p. 210—212° (corr., decomp.) after softening at about 160°, $[\alpha]_D$ −108·2° in 96% EtOH. The alkaloid can be cryst. only in the form of its hydrates. In the dihydrate the H_2O

is so firmly combined that normal mol. wt. is observed in freezing C_6H_6 or $CHBr_3$; when preserved, it passes slowly into the sesquihydrate. Both hydrates are derived from the same substance, since they are capable of interconversion, can be cautiously dehydrated whereby $1H_2O$ is shown to be firmly and chemically retained in the mol., and yield the same *sulphate* $X,H_2SO_4,6H_2O$ ($X=C_{40}H_{48}O_3N_4$), decomp. 226° (corr.) after incipient discoloration at 180°, $[\alpha]^{20}_{D}$ $-84{\cdot}2°$ in H_2O, *oxalate*, $X,(CO_2H)_2,5H_2O$, decomp. 193° (corr.), and *dimethiodide*, $X,2MeI,4H_2O$, decomp. 261—262° (corr.) after becoming yellow at 240°, $[\alpha]^{20}_{D}$ $-61{\cdot}5°$ in 96% EtOH. Geissospermine contains 1 OMe and a labile, basic NMe group. It cannot be benzoylated or acetylated and does not react with ketonic reagents. The two remaining O atoms are therefore present in bridges or in a masked CO group; the marked heat of hydration indicates the latter possibility. Losses during the recrystallisation of the substance and its sensitiveness towards acid indicate that the third O atom is probably present in a very labile CO·N· group. H. WREN.

Pereirine oxide. M. C. ROSA (Ann. soc. pharm. Chim. Sao Paulo, 1931, 2, 67—84).—Addition of 30% H_2O_2 affords the amine oxide of pereirine; on successive crystallisation the peroxide action disappeared. CHEMICAL ABSTRACTS.

Sinomenine and disinomenine. XXVIII. Hofmann decomposition of dihydrosinomenine. K. GOTO and H. SHISHIDO (Bull. Chem. Soc. Japan, 1931, 6, 229—233).—Dihydrosinomenine methiodide is converted by boiling 16·5% KOH into *dihydrosinomeninemethine* (I), m. p. 173° (sinters at 160°), $[\alpha]^{18}_{D}$ $-84{\cdot}32°$ (all rotations are in $CHCl_3$), the methiodide (not characterised) of which similarly gives 7-*methoxydehydro*-l-*thebenone* (II), m. p. 118° (sinters at 113°), $[\alpha]^{18}_{D}$ $-268°$ [*oxime*, m. p. 180° (decomp.)]. Catalytic reduction ($PdCl_2$–charcoal) of (I) in dil. HCl gives its 9 : 10-*dihydro*-derivative, m. p. 133° (sinters at 123°), $[\alpha]^{18}_{D}$ $+2{\cdot}09°$, the methiodide of which is decomposed to 7-*methoxy*-l-*thebenone* (III), m. p. 128° (sinters at 122—123°), $[\alpha]^{18}_{D}$ $-147{\cdot}66°$ [*oxime*, m. p. 168° (sinters at 145°); *oximino*-derivative], also prepared by catalytic reduction (as above) of (II). The step-wise inversion of rotation during the change sinomenine ⟶ (III) is explicable by the hypothesis previously suggested (this vol., 1172), which can only be applied to the simplest cases (*i.e.*, thebenone and thebenane series). H. BURTON.



(I.)

Precipitation of alkaloids in gels. B. JONSSON (Svensk farm. Tidskr., 1931, 35, 25—29, 45—49; Chem. Zentr., 1931, i, 2789).—If the alkaloid solution is allowed to diffuse slowly into a gel containing the precipitant, well-formed crystals are obtained. The prep. of the gels from Na silicate, various nitrophenols, and H_3PO_4 is described. A. A. ELDRIDGE.

Benzyloxyphenylarsinic acids. I. E. BALABAN (J.C.S., 1931, 2473—2475).—Attempts to prepare 3 : 4-dihydroxyphenylarsinic acid failed. *o*-Hydroxy-, *o*-amino-, di- and tri-amino-phenylarsinic acids give an olive-green colour with aq. $FeCl_3$. 2 : 4-Dinitrochlorobenzene, CH_2PhCl (I), and aq. KOH at 100° give 2 : 4-dinitrophenyl benzyl ether, m. p. 154° after softening (lit. 150°), reduced by $(NH_4)_2S$ in boiling EtOH in poor yield to 4-nitro-2-aminophenyl benzyl ether, m. p. 92° (crude) [*hydrochloride*, m. p. 220° (decomp.)]. 4-Hydroxyphenylarsinic acid, (I), and NaOH in aq. MeOH at 100° give 4-*benzyloxyphenylarsinic acid* (II), m. p. above 300° (*Ba* salt). 3-Nitro-4-hydroxyphenylarsinic acid yields similarly 3-*nitro*-4-*benzyloxyphenylarsinic acid* (*Ba* salt) [not obtained by nitration of (II)], which is reduced by $Fe(OH)_2$ at 80—90° to the corresponding NH_2-*acid*, decomp. about 220° (*Ac* derivative); the NH_2 group could not be replaced by OH; with $CH_2Cl{\cdot}CO{\cdot}NH_2$ it gives 3-*carbamylmethylamino*-4-*benzyloxyphenylarsinic acid*, m. p. 215° (decomp.), which did not yield a benz*iso*oxazine derivative. 2-Chloro-5-nitrophenol and $CH_2Ph{\cdot}OH$ in aq. KOH at 100° give a substance, $C_6H_6O_2NCl$, m. p. 175° (possibly 2-*chloro*-5-*hydroxylaminophenol*), in small yield. R. S. CAHN.

Benzaldehyde-*p*-arsinic acid, arsinic acid derivatives of acylphenylketones and their derivatives. Chemotherapeutic examination of these and other arsinic acids. C. S. GIBSON and B. LEVIN (J.C.S., 1931, 2388—2407).—*Acetophenone*-o-*arsinic acid*, m. p. 285—286° (decomp.) [*semicarbazone*, m. p. 234—235° (decomp.); *thiosemicarbazone*, m. p. 181° (decomp.)], was prepared by the Bart–Schmidt reaction from *o*-aminoacetophenone, and propiophenone-*o*-arsinic acid [*semicarbazone*, m. p. 206—207° (decomp.)] from *o*-aminopropiophenone. 5-Bromo-2-acetamidoacetophenone, m. p. 160° (modified prep.), gives on hydrolysis 5-*bromo*-2-*aminoacetophenone* (I), m. p. 86—88°, which by the Bart–Schmidt reaction affords a *substance*, $C_8H_7O_2N_2Br$, m. p. 278° (probably 5-*bromo*-2-*nitrosoaminoacetophenone*, but possibly 5-*bromo*-2-*amino*-*oximinoacetophenone*), and 5-*bromoacetophenone*-2-*arsinic acid*, decomp. incipient at 188° and complete at 291—293° (*Na* salt). The constitution of (I) was proved by conversion (Sandmeyer) into 2 : 5-dibromoacetophenone, m. p. 41°, oxidised to 2 : 5-dibromobenzoic acid. Directions are given for the prep. by analogous methods of *acetophenone*-m-*arsinic acid*, m. p. 156° (*semicarbazone*, not decomp. at 305°), *propiophenone*-m-*arsinic acid*, m. p. 212° (decomp.) (*semicarbazone*), and 2-*hydroxyacetophenone*-5-*arsinic acid* [from 5-amino-2-hydroxyacetophenone (modified prep.)], m. p. 189—192° (*semicarbazone*, decomp. about 245°). 4-Bromo-3-nitroacetophenone, m. p. 120° (lit. 116·5°), is unaffected by Na_3AsO_3 in aq. MeOH and is not reduced to the NH_2-compound by Fe and AcOH, or Sn and HCl; with $SnCl_2$ and Ac_2O it yields 4-*bromo*-3-*acetamidoacetophenone*, m. p. 118°, hydrolysed to the corresponding 3-NH_2-compound, m. p. 117° [*hydrochloride*, m. p. 206° (decomp.) after darkening at 198°]. This led to 4-*bromoacetophenone*-3-*arsinic acid*, m. p. 198° (decomp.) (*semicarbazone*, m. p. above 300°). Treatment of *iso*valerophenone with HNO_3 (d 1·5) below 0° gives m-*aminoisovalerophenone*, b. p. 179—181°/14 mm. (*di*-p-*toluenesulphonyl* derivative) (converted into m-*bromoisovalerophenone*, b. p. 153—155°/19 mm., and thence by oxidation into *m*-bromobenzoic acid), together with some o- and p-NH_2-derivatives (converted into the mixed Br compounds and thence into *o*- and *p*-bromobenzoic acid). Acetophenone-*p*-arsinic acid (II) [oxime, m. p. about 188° (lit. 157°, decomp.); *semicarbazone*, froths at 210° without change of colour; *thiosemicarbazone*, m. p. above 290°; *ketazine*, m. p. above 290°; *semioxamazone*, decomp. about 217°; *phenylhydrazone*, yellow, m. p. 225° (decomp.); p-*bromophenylhydrazone*, m. p. 227° (decomp.)] was prepared (*a*) from *p*-aminoacetophenone (obtained from NHAcPh, AcCl, and $AlCl_3$ in CS_2), and (*b*) from aq. Na_3AsO_3 and *p*-bromoacetophenone at 160—170°. The last-mentioned compound was prepared from PhBr, AcCl, and $AlCl_3$; an analogous reaction with *p*-dibromobenzene afforded oily *p*-bromoacetophenone (*semicarbazone*, m. p. 201°). Acetophenone-*p*-dichloroarsine and warm aq. NaOH give *acetophenone*-p-*arsenious oxide*, m. p. above 300°. *m*-Nitroanisole (from *m*-nitrophenol, aq. NaOH, and Me_2SO_4) is reduced by Sn and a trace of graphite in HCl (1 : 1) to *m*-anisidine, the Ac derivative of which with AcCl and $AlCl_3$ in CS_2 affords 4-*acetamido*-2-*hydroxyacetophenone*, m. p. 91° (yield variable, up to 35%), hydrolysed by hot 15% HCl to the corresponding 4-NH_2-compound (III), m. p. 122—123°. A Friedel–Crafts reaction with acet-*o*-anisidide gave only a trace of cryst. material. (III) gives, by the Bart–Schmidt reaction, 2-*hydroxyacetophenone*-4-*arsinic acid*, m. p. 156°. *p*-Acetamidoacetophenone and HNO_3 (*d* 1·5) give the 3-NO_2-compound, m. p. 137°, hydrolysed by boiling conc. HCl to 3-*nitro*-4-*aminoacetophenone*, m. p. 148—149°, and oxidised by $KMnO_4$ to 3-nitro-4-acetamidobenzoic acid. The 4-NH_2-compound, by a modified Bart–Schmidt reaction, affords 3-*nitroacetophenone*-4-*arsinic acid* (IV), m. p. 228—230°; this could not be obtained by nitration of acetophenone-*p*-arsinic acid, which under certain conditions gives carboxyphenyl-*p*-arsinic acid. Reduction of (IV) by $Fe(OH)_2$ and NaOH gives 3-*aminoacetophenone*-4-*arsinic acid*, m. p. above 290° (lit. decomp. 230°), which could not be prepared from 4-bromo-3-aminoacetophenone, Na_3AsO_3, and Cu powder. 3-Bromo-4-aminoacetophenone (prepared by hydrolysis of the NHAc-compound with 20% HCl) gives, by the Bart–Schmidt reaction, 3-*bromoacetophenone*-4-*arsinic acid*, m. p. 190—191° (decomp.) [*semicarbazone* (*Na* salt)]. 4-*Acetyldiphenylamine*-6′-*arsinic acid*, m. p. 205—208°, is obtained (*a*) from *p*-bromoacetophenone, *o*-aminophenylarsinic acid, K_2CO_3, and a trace of Cu powder in boiling amyl alcohol, and (*b*) similarly from *p*-aminoacetophenone and *o*-bromophenylarsinic acid. *Propiophenone*-p-*arsinic acid*, m. p. above 295° (*semicarbazone*), is obtained from *p*-aminopropiophenone. *p*-Acetamido-*n*-valerophenone could not be obtained from NHAcPh, *n*-valeryl chloride or bromide, and $AlCl_3$ in CS_2. n-*Valeryl bromide*, prepared from *n*-valeric acid and PBr_3, has b. p. 64°/66 mm. *n*-Valeryl chloride, PhBr, and $AlCl_3$ in CS_2 yield p-*bromo*-n-*valerophenone*, b. p. 168—169°/20 mm., m. p. 37—38°, which with Na_3AsO_3 in aq. MeOH gives a small amount of a *substance*, m. p. 203°, containing As. The last ketone with HNO_3 (*d* 1·5) and conc. H_2SO_4 at −5° gives 4-*bromo*-3-*nitro*-n-*valerophenone*, m. p. 196—197°, which did not condense with Na_3AsO_3 under the above conditions. By a modified Bart–Schmidt reaction, *p*-aminobenzaldehyde gives *benzaldehyde*-p-*arsinic acid*, m. p. above 280° [*oxime*, m. p. 157° (decomp.); *semicarbazone*, m. p. above 300° (*Na* salt); *thiosemicarbazone*, m. p. above 300°; *phenylhydrazone*, m. p. 186°; p-*bromophenylhydrazone*, m. p. 233° (decomp.); *semioxamazone*, m. p. above 300°].

Many of the above and other arsinic and arsazinic acids have been examined for activity against *T. equiperdum* in mice, but few show marked curative action. Those having the AsO_3H_2 group in the *p*-position to another group are less toxic than their *m*- and *o*-isomerides; the latter are not curative. Acetophenone- and benzaldehyde-*p*-arsinic acid are moderately toxic and slightly curative; their semicarbazones and thiosemicarbazones are less toxic and more curative, but the phenylhydrazones are not curative. R. S. CAHN.

Pyridine derivatives. XVI. *N*-Substituted pyridonearsinic acids. A. BINZ, H. MAIER-BODE, and A. RAST (Z. angew. Chem., 1931, **44**, 835—840; cf. this vol., 1071).—The following *N*-substituted 2-pyridone-5-arsinic acids were prepared by treating the unsubstituted acid and appropriate alkyl halide with KOH in MeOH or H_2O; all products are amorphous: Bu^{β}-, m. p. about 213°; iso*amyl*-, m. p. about 154—155°; *carboxymethyl*-, +0·5H_2O (I) (from $CH_2Cl{\cdot}CO_2H$) (*Na_2* salt), which on reduction by SO_2 without isolation gives the corresponding *arsenious acid* (II), decomp. about 191° [-*arsenious oxide*, m. p. 230—234° (decomp.)], also obtained from (I) by boiling with As, $CuSO_4$, and aq. KOH, and oxidised to (I) by H_2O_2; *allyl*- (III), m. p. about 154—155°; *acetamido*- (from $CH_2Cl{\cdot}CO{\cdot}NH_2$), decomp. from 222°; *$CH_2Ph$*-, m. p. 227—228°; *acetanilido*- (from $CH_2Cl{\cdot}CO{\cdot}NHPh$), decomp. from 240°. The following *N*-substituted derivatives (all amorphous) of 2-pyridone-3-arsinic acid were similarly prepared: *carboxymethyl*-, m. p. above 270° [prepared only by way of the *arsenious oxide* (from $CH_2Cl{\cdot}CO_2H$, followed by reduction by SO_2), decomp. 231°]; Bu^{α}- (IV), m. p. 188—189°; *allyl*-, m. p. about 178—179°; *CH_2Ph*-, m. p. about 237—238°, also obtained by diazotisation etc. of 3-amino-2-hydroxypyridine, and by fusion of 2-pyridone with H_3AsO_4; *acetamido*-, decomp. about 262—263°. 3-Amino-4-pyridone, when diazotised in HCl, treated with As in NaOH, and then with hot H_3PO_2 and HI, gives the arseno-compound, which is oxidised by H_2O_2 to 4-*pyridone*-5-*arsinic acid*, cryst. [reduced by warm H_3PO_2 and HI to 4 : 4′-*dihydroxy*-5 : 5′-*arsenopyridine* (*dihydrochloride*, cryst., hydrolysed by H_2O)], from which the following cryst. *N*-substituted derivatives were prepared: *Me*-, decomp. 285° after darkening at 273°; Bu^{α}-, m. p. 107—108°; *acetamido*-, decomp. about 232°; *CH_2Ph*-, m. p. about 221—222°. The following compounds were prepared by reduction of the corresponding arsinic acids by hot H_3PO_2 and HI: NN′-*di*-n-*butyl*-5 : 5′-*arseno*-2 : 2′-*pyridone*, m. p. 250—251°, large colourless and small yellow crystals (giving cryst. *X*-ray diagram), the former bimol., the latter unimol. in camphor (arsenobenzene is bimol. in camphor); NN′-*diacetamido*-3 : 3′-*arseno*-2 : 2′-*pyridone*, decomp. about 267°, cryst. (confirmed by *X*-ray diagram); 1 : 1′-*di*(*carboxymethyl*)-5 : 5′-*arseno*-2 : 2′-*pyridone*, m. p. 210—215°. (I) with thiophenol gives 1-*carboxymethyl* 5-*di*(*phenylthiol*)*arseno*-2-*pyridone*, m. p. 176° (aq. solution of Na salt unstable). (II), when oxidised with H_2O_2 and treated with Br, gives 3 : 5-*dibromo*-1-*carboxymethyl*-2-*pyridone*, m. p. 240—241°, and 3-*bromo*-1-*carboxymethyl*-2-*pyridone*-5-*arsinic acid*, $+0{\cdot}5H_2O$, losing H_2O at 125° and decomp. at 250°; the latter was also obtained from 3 - bromo - 2 - pyridone - 5 - arsinic acid and $CH_2Cl{\cdot}CO_2H$. (I) with warm conc. H_2SO_4 and fuming HNO_3 gives 3-*nitro*-N-*methyl*-2-*pyridone*-5-*arsinic acid*, m. p. above 250°, which when warmed in MeOH with 4% Na–Hg and subsequently acetylated in the cold, affords 3-*acetamido*-N-*methyl*-2-*pyridone*-5-*arsinic acid*, m. p. above 270°.

The toxic doses for most of the above arsinic acids are recorded. Only (III) and (IV) are curative against trypanosomes. R. S. Cahn.

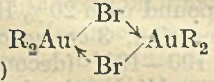
Introduction of arsenic into the coumarin nucleus. I. M. Goswami and H. N. Das-Gupta (J. Indian Chem. Soc., 1931, 8, 417—422).—The Bart reaction with 6-aminocoumarin gives *tricoumarylarsine oxide*, m. p. 200° (slight decomp.); the toxicity of its Na salt is determined. 6-Chloromercuricoumarin and $AsCl_3$ give coumarin. H. Burton.

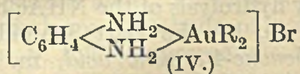
10-Chloro-5 : 10-dihydrophenarsazine and its derivatives. XV. Monoacyl derivatives. L. A. Elson and C. S. Gibson (J.C.S., 1931, 2381—2388; cf. this vol., 501).—5 : 10 - Dihydrophenarsazine derivatives, prepared by condensation of the substituted $NHPh_2$ with $AsCl_3$ and by reduction of substituted diphenylamine-6′-arsinic acids in HCl, are homogeneous in the cases hitherto reported and when obtained by reduction of 3-*acetyl*-, -*propionyl*-, and -*butyryl-diphenylamine*-6′-*arsinic acid* (I), (II), and (III), respectively. m-*Acetyldiphenylamine* (IV), however, gives a mixture of 1- and 3-substituted isomerides; the structure of the latter is proved by synthesis from NH_2Ph and 3-bromoacetophenone-4-arsinic acid (V). The structure of the other phenarsazine derivatives described below follows by analogy and because of similar colour reactions. A number of other As compounds were prepared.

m-Bromoacetophenone, *o*-aminophenylarsinic acid, anhyd. K_2CO_3, and a trace of Cu powder in boiling amyl alcohol give (I), m. p. 154°, also obtained similarly from *m*-aminoacetophenone (VI) and *o*-bromophenylarsinic acid. Reduction of (I) (SO_2, I, EtOH, HCl) yields 10-*chloro*-3(or 1)-*acetyl*-5 : 10-*dihydrophenarsazine* (VII), m. p. 268—270° (decomp.) [corresponding 10-*Br*-compound, m. p. 269 °(decomp.)]. The 10-Cl-compound with “ chloramine-*T* ” in cold aq. $COMe_2$ yields 3(or 1)-*acetylphenarsazinic acid*, not decomp. at 290°. *m*-Bromopropiophenone gives similarly (II), m. p. 160°, and 10-*chloro*-3(or 1)-*propionyl*-5 : 10-*dihydrophenarsazine*, m. p. 227° after sintering and darkening, whilst *m*-bromobutyrophenone gives (III), m. p. 125—126°, and 10-*chloro*-3(or 1)-*butyryl*-5 : 10-*dihydrophenarsazine*, m. p. 210°. (V), NH_2Ph, K_2CO_3, and a trace of Cu powder in boiling amyl alcohol afford (VII). K *o*-chlorobenzoate, (VI), and a trace of Cu powder in boiling amyl alcohol yield 3-*acetyldiphenylamine*, m. p. 93°; this condenses with $AsCl_3$, best in PhCl, giving 10-*chloro*-1-*acetyl*-5 : 10-*dihydrophenarsazine*, m. p. 280°, and a mixture, probably containing (VII).

Acetophenone-*p*-arsinic acid with SO_2–HI–HCl gives p-*acetylphenyldichloroarsine*, m. p. 100°, b. p. 212—215°/30 mm., unaffected by Br in CCl_4 at 100°. Addition of phenylarsenious oxide and NaOH to diazotised *p*-aminoacetophenone and warming affords p-*acetyldiphenylarsinic acid*, m. p. 182° [*semicarbazone*, +(?) H_2O, m. p. indefinite]. *p*-Acetylphenylarsenious oxide gives similarly acetophenone-*p*-arsinic acid and a little 4 : 4′-*diacetyldiphenylarsinic acid*, m. p. 194°. Acetophenone-*p*-arsinic acid with Br (1 mol.) in warm $CHCl_3$ gives a *Br* derivative, m. p. 187—190°, and with an excess of Br in boiling CCl_4 gives an impure Br_2 derivative, m. p. 196—198°. R. S. Cahn.

Organic compounds of gold. II. Co-ordination compounds. C. S. Gibson and W. M. Colles (J.C.S., 1931, 2407—2416; cf. this vol., 78).—Analyses show that the material previously described as “ gold tribromide ” (*loc. cit.*) or “ auric bromide ” (this vol., 1172) is $HAuBr_4,3H_2O$ (I). Because of the facts mentioned below it is suggested that Au^{+++} does not exist; that Au always has a co-ordination no. of 4, and that gold tribromide is $(AuBr_3)_n$ (II), where *n* is at least 2. (II) is almost insol. in dry Et_2O with or without anhyd. HBr, and in H_2O, but sol. in aq. solutions of inorg. bromides. Addition of H_2O to (II) in Et_2O containing anhyd. HBr gives a solution of (I) in Et_2O. (II) does not react with Grignard reagents. The prep. of (I) from Au, for synthetic purposes, is modified. The yield of gold diethyl bromide (III; R=Et) is highest (17·4%) if 6 mols. of MgEtBr are used, but some unchanged (I) and Au are also obtained. An ethylenediamine bromide with aq. HBr gives a quant. yield of (III). *Gold ethylenediaminedi*-n-*propyl bromide* (IV; $R=Pr^{a}$) (prepared by the Grignard reagent) becomes violet about 130° and decomp. about 190°, and with aq. HBr gives gold di-*n*-propyl. The analogous *di*-n-*butyl* compound (IV; $R=Bu^{a}$), decomp. about 190° (similarly prepared), gives similarly gold di-*n*-butyl bromide. The following compounds were prepared by adding the appropriate base to aq. $KAuBr_4$: *gold pyridine tribromide*, $C_5H_5N,AuBr_3$, scarlet, decomp. about 150°, which, best with 3 mols. of MgEtBr in Et_2O and pyridine, gives (III), and when recryst. from pyridine gives *gold dipyridinodibromo-bromide*, $[(C_5H_5N)_2AuBr_2]Br$, deep red; gold pyridinetrichloride, giving similarly gold dipyridinodichlorochloride, which at 135° loses pyridine and gives a reddish-yellow substance; *gold quinoline tribromide*, deep red, decomp. above 200°; *gold* iso*quinoline tribromide*, violet-red plates or brick-red powder; *gold 2-aminopyridine tribromide*, black, decomp. about 160° (probably co-ordinated by the pyridine-N); *gold di-2-pyridylamine tribromide*, scarlet; *gold diethylenediamine tribromide*, $[Au(NH_2{\cdot}C_2H_4{\cdot}NH_2)_2]Br_3$, bright yellow, which with aq. HBr gives $HAuBr_4$; $NHPh_2$ gives a dark green compound containing


(III.)



$$\left[C_6H_4{<}^{NH_2}_{NH_2}{>}AuR_2\right]Br$$

(IV.)

2 mols. of base. The above co-ordination compounds are only slowly attacked by aqua regia or aq. SO_2.
R. S. Cahn.

Organic lead compounds. II. Oxidation reactions. P. R. Austin (J. Amer. Chem. Soc., 1931, **53**, 3514—3518).—Oxidation of Pb tri-*p*-tolyl with $KMnO_4$ in $COMe_2$ gives *Pb tri-p-tolyl acetate*, m. p. 158—159° (AcOH is presumably formed by oxidation of $COMe_2$ and then reacts with the intermediate hydroxide), which with HCl in EtOH affords *Pb tri-p-tolyl chloride*, m. p. 140—141° (from Pb tetra-*p*-tolyl and HCl in $CHCl_3$). Similar oxidation of Pb tri-*o*-tolyl furnishes a product which is converted by HCl into *Pb tri-o-tolyl chloride*, m. p. 141—142°, also obtained from Pb tetra-*o*-tolyl and HCl. Mg allyl bromide and $PbPh_3Cl$ give *Pb triphenylallyl* (I), m. p. 76—77°, oxidised by $KMnO_4$ in $COMe_2$ containing a little H_2O to $PbPh_3OH$ (main product) and *Pb triphenyl-βγ-dihydroxypropyl* (II), m. p. 124—125°. (I) and O_3 in light petroleum afford probably Pb triphenyl oxide, since treatment of this with AcOH yields *Pb triphenyl acetate*, m. p. 206—207°. (I) and (II) are converted by HBr in EtOH into $PbPh_3Br$. Definite products could not be obtained by oxidation of Pb triphenyl-*p*-tolyl, tri-*o*-tolyl chloride, and tetra-*o*- and -*p*-tolyl; much unchanged material is recovered. *Pb di-o-tolyl dichloride*, m. p. 178—179°, is obtained from Pb tetra-*o*-tolyl and excess of HCl or from Pb tri-*o*-tolyl and conc. HCl in $CHCl_3$.
H. Burton.

Basic amino-acids of silk fibroin. Determination of basic amino-acids yielded by proteins. H. B. Vickery and R. J. Block (J. Biol. Chem., 1931, **93**, 105—112).—Ag_2SO_4 is unsuitable for the precipitation of arginine and histidine from protein hydrolysates rich in monoamino-acids owing to the difficulty of maintaining a $[Ag^{\cdot}]$ adequate for complete precipitation of arginine. Replacement by $AgNO_3$ and the use of Ag_2SO_4 for subsequent re-precipitation and separation of the two bases is recommended. By this method silk fibroin yields 0·74% of arginine, 0·07% of histidine, and 0·25% of lysine (relative proportions approx. as in wool). F. O. Howitt.

Basic amino-acids of proteins. Chemical relationship between the various keratins. R. J. Block and H. B. Vickery (J. Biol. Chem., 1931, **93**, 113—117).—The arginine, histidine, lysine, and cystine contents of keratins derived from human hair, sheep wool, goose feathers, snake epidermis, *Plexaurella dichotoma*, *Gorgonia flabellum*, and silk fibroin were determined (preceding abstract). The mol. ratio of the first 3 acids is approx. 1 : 4 : 12 for these keratins; the cystine content is variable. F. O. Howitt.

Precipitation of proteins and of their degradation products with tannin. H. Lundin and J. Schröderheim (Biochem. Z., 1931, **238**, 1—23).—The effects of acidity, $[H^{\cdot}]$, particular acid used, amount and nature of precipitant, temp., and presence of EtOH, salts, or sugars on the precipitation by tannin of proteins and protein degradation products as well as on the co-precipitation of substances not directly precipitable from milk, blood, flesh hydrolysate, wort, and beer have been studied and the methods best adapted to the varying conditions and materials have been worked out. Tannin produces no ppt. in normal urine. W. McCartney.

Electrolyte-free proteins. X. Electrochemical constitutive characterisation of proteins by the Ag activity of their silver salts. E. Goigner and W. Pauli (Biochem. Z., 1931, **235**, 271—302; cf. this vol., 856).—The electrochemical differences in the "zwitterion" forms of proteins and in the multivalent negative ions may be studied by a comparison of the activity changes produced by addition of $AgNO_3$ or of AgOH, respectively. In serum-albumin all the negative groups are engaged on addition of $1·7\times10^{-3}N$-AgOH. Egg-albumin shows strong inactivation of Ag. It is practically complete at $1\times10^{-3}N$-$AgNO_3$. Inactivation by gelatin is far behind that of serum-albumin (about 60%). Gelatose shows still weaker inactivation (40%), considerably below that of the simpler NH_2-acids (78%). The somewhat unexpected behaviour of the NH_2-acids may be due to internal metal-complex salt formation. J. H. Birkinshaw.

Proteins. I. Importance of ions for the inner stability of the protein molecule (caseinogen). G. Ettisch and G. Schulz (Biochem. Z., 1931, **239**, 48—73).—The behaviour of the protein mol. over a certain p_H range is a reversible function of its electric charge, the space occupied by the mol. increasing with the charge, the process leading to reversible fission of the mol. Increase of p_H beyond this range causes irreversible disintegration of the mol. (chemical action of OH′). The alkali-fixing power of caseinogen is due to the primary ionic reaction and a secondary irreversible slower reaction. The irreversible reaction is not brought about by neutral salts. The viscosity under the action of alkali increases at first and then slowly decreases. The splitting of caseinogen by alkali can be inhibited with NaCl over a p_H range of 7·4—11 but not above this p_H (cf. this vol., 426, 427, 503). P. W. Clutterbuck.

Structure of simple nucleic acid. II. *h*- and *t*-Adenylic acid. H. Steudel and R. Wohinz (Z. physiol. Chem., 1931, **200**, 82—86; cf. A., 1930, 1307).—The plant-(*h*-)nucleic acids (yeast-nucleic acid, *h*-guanylic acid, *h*-adenylic acid, *h*-inosic acid) give 60—75% of the theoretical yield of furfuraldehyde (from the pentose). Animal-(*t*-)inosic acid affords only 8—11% of the theoretical, but the *t*-inosine obtained after hydrolysis and its Ac_3 derivative give 63—70%. Probably the different point of attachment of the H_3PO_4 constitutes the difference between *h*- and *t*-adenylic acid. J. H. Birkinshaw.

Synthesis of the histone of the thymus gland. IV. K. Felix and H. Rauch (Z. physiol. Chem., 1931, **200**, 27—40; cf. A., 1930, 939).—Histone picrate from the calf's thymus gland was converted by means of HCl in MeOH into the *Me ester hydrochloride*, $[\alpha]_D^{20}$ −95·5°. Comparison with preps. produced in another way and subsequently esterified by MeOH and HCl or by Me_2SO_4 showed that no change occurred in the mol. apart from a conversion of SH into S·S groups. The mol. contains, per 100 atoms of N, 7·5 free esterifiable CO_2H, 5 preformed Me groups attached to N, and a basicity of 20 equivs. (calc. from the Cl content of the ester hydrochloride).
J. H. Birkinshaw.

Change of rotatory power of purified egg-albumin as evidence of the mode of combination of acid and alkali with proteins. H. J. Almquist and D. M. Greenberg (J. Biol. Chem., 1931, 93, 167—170).—Purified egg-albumin (3·5% aq. solution) has a min. $[\alpha]_D^{22}$ —30·8 at p_H 5·04. This val. is not changed by addition of alkali to p_H 11·0, whilst from 11·0 to 12·6 it increases to a max. of —60·6°. With addition of acid the rotation rises sharply to —35·1° at p_H 3·15 and then remains const. to p_H 1·72. The change on both sides of the isoelectric point is reversible. At p_H 12·6 the albumin has attained its max. base combination. On the acid side the attainment of a max. at p_H 3·15 is not in agreement with that of max. acid combination, due to a complex change and not to simple ionisation of the protein.

F. O. Howitt.

Determination of protein by differential opacimetry. P. Mounier (Bull. Biol. Pharm., 1931, 2, 196—197).—The greater part of the protein is precipitated by standard K iodomercurate. The residual protein in the centrifugate is precipitated by a solution of $CCl_3 \cdot CO_2H$ and the opacity contrasted with that produced by a known wt. of protein. C. C. N. Vass.

Determination of small quantities of acetylene. W. Riese (Z. angew. Chem., 1931, 44, 701—703).—An account of the use of Ilosvay's reagent for the determination of traces of C_2H_2; by a new method of prep. of the reagent, and under the conditions described, 0·0005 vol.-% may be determined.

H. F. Gillbe.

Determination of water. J. Lindner.—See this vol., 1257.

Halogen determinations. K. Heller and others. —See this vol., 1257.

Determination of smallest amounts of ethyl alcohol in very dilute solution by a modified micro-Ziesel method. J. B. Niederl and B. Whitman (Z. anal. Chem., 1931, 86, 65—68).—The modified procedure for the determination of EtOH as EtI (or KI) is most satisfactory for about 1 mg. of EtOH at a concentration of 0·02%, but can be conducted with a 0·06 mg. sample in 0·001% aq. solution.

E. S. Hedges.

Determination of ethyl alcohol. M. Nicloux. —See this vol., 1327.

Electrometric micro-determination of amino-nitrogen. J. Roche and (Mme.) A. Roche (Bull. Soc. Chim. biol., 1931, 13, 835—840).—By electrometric titration to a definite p_H a more accurate end-point is reached than is possible with indicators. By use of extrapolation methods 0·05 to 5 mg. of NH_2-N can be determined with an accuracy of 1—2%. C. C. N. Vass.

Micro-method for determination of nitro-groups in aromatic compounds. S. Maruyama (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, 16, 196—199).—Reduction with $TiCl_3$ is employed. The following new compounds are recorded: *6-nitro-2-chlorolepidine*, m. p. 209—209·5°; *5-nitro-6-methoxy-α-lepidone*, m. p. 295° (decomp.); *β-(m-nitroanilino)crotonyl-m-nitroanilide*, m. p. 155°; and *4-chloroquinaldine picrate*, m. p. 176—177°.

A. A. Levi.

Determination of 2:4-dinitrophenol. A. Suchier (Z. anal. Chem., 1931, 85, 434—435).—The solution is titrated at the b. p. with 0·5N-NaOH in presence of phenolphthalein, the end-point being reached when the orange colour becomes red. It is desirable to titrate to a standard tint.

R. Cuthill.

Micro-determination of cholesterol. M. Yasuda (J. Biol. Chem., 1931, 92, 303—312).—Okey's method (A., 1930, 1303) is modified in that lipins and excess of digitonin are removed by dissolution in $COMe_2$, and the remaining cholesterol digitonide is dissolved in hot EtOH and filtered from impurity. The residue on evaporation of the EtOH solution is determined by oxidation with $K_2Cr_2O_7$. The results for a number of tissue extracts are about 15% lower than those given by the colorimetric method. A. Cohen.

Action of iodine monochloride on cholesterol. Determination of the iodine value. H. Werner (Z. Unters. Lebensm., 1931, 61, 321—337).—I vals. of cholesterol have been determined by a variety of methods, of which Kaufmann's, employing an EtOH solution of NaBr and Br (cf. B., 1926, 447), was found to be the most suitable, the next best being that of Rosenmund and Kuhnhenn (cf. B., 1923, 798a) employing pyridine sulphate dibromide, with Winkler's method (cf. B., 1922, 473a) third in order of merit. Methods involving the use of ICl or IBr (Hanus, Hübl, Wijs) were unsuitable owing to simultaneous substitution. Attempts to determine the relative proportions of substitution and addition by titrating the halogen acid formed were unsuccessful. H. J. Dowden.

Colour reaction of adrenaline. B. Azzolini (Boll. chim.-farm., 1931, 70, 665—667).—4—5 c.c. of a neutral solution are acidified with 1 drop of HCl and 2—3 c.c. of EtOH containing 4% of aq. NH_3 are added. In presence of adrenaline in a limiting dilution of 1 : 500,000 a rose-peach coloured ring is obtained, spreading through the solution on shaking and changing to yellowish-brown. R. K. Callow.

Detection of organic compounds. IV. Micro-chemical reactions of mezcaline. L. Rosenthaler (Pharm. Ztg., 1931, 76, 653—654).—Several reactions of mezcaline (β-3 : 4 : 5-trimethoxyphenylethylamine) are given and the crystal form of some of the ppts. is sketched.

Determination of small amounts of camphor. M. L. Nichols and A. Stubblefield (Z. anal. Chem., 1931, 86, 30—34).—Camphor affects the surface tension of a mixture of H_2O and EtOH (3 : 1 by weight) in proportion to its concentration. Surface tension measurements by the ring-tensiometer method permit the determination of the camphor content of EtOH solutions containing 0·05—13% of camphor.

E. S. Hedges.

Potentiometric determination of some compounds precipitable by potassium mercuric iodide. L. Maricq (Bull. Soc. chim. Belg., 1931, 40, 361—370).—Stovaine, novocaine, pyramidone, antipyrine, and atophan can be determined potentiometrically by means of an acid solution of HgI_2 in KI.

The first three compounds give complexes of the type HgI_2,X,HI and the last two of the type $HgI_2,2X,HI$. Antipyrine and pyramidone can be determined simultaneously. E. S. Hedges.

Use of ferric salts for the detection of morphine. L. Rossi (Anal. Farm. Bioquim., 1930, 1, 106—110; Chem. Zentr., 1931, i, 2789).—$Fe^{\cdot\cdot\cdot}$ salts (in conc. solution) give with morphine salts (solid) a blue colour. A. A. Eldridge.

Micro-chemistry of stereoisomerides. L. Rosenthaler (Z. anal. Chem., 1931, 86, 61—65).—*l*-Ephedrine and ephetonine can be distinguished by microscopical examination of the products formed with picrolonic acid, $NaClO_4$, KCNS, Reinecke's salt, and $Na_3Co(NO_2)_6$. E. S. Hedges.

Biochemistry.

Production of methæmoglobin and increased respiration by organic dyes. L. Michaelis (Biochem. Z., 1931, 239, 186—188).—The author's paper (this vol., 857) is supplemented. P. W. Clutterbuck.

Rôle of copper in hæmoglobin regeneration and in reproduction. H. L. Keil and V. E. Nelson (J. Biol. Chem., 1931, 93, 49—57).—In rats with anæmia, due to a diet of whole milk uncontaminated by contact with metals, hæmoglobin regeneration is effected by addition of small amounts of $FeCl_3$ supplemented by $CuSO_4$, but not when supplemented by salts of V, Ti, Mn, Ni, As, Ge, Zn, Cr, Co, Sn, or Hg (cf. A., 1929, 206; this vol., 247). The subnormal reproduction of rats on a milk and Fe diet is corrected by addition of Cu. F. O. Howitt.

Preparation of nitric oxide-hæmoglobin. H. Hartridge (Analyst, 1931, 56, 571—572).—NO-hæmoglobin is most readily prepared by adding to blood a dil. solution of $NaNO_2$ and $(NH_4)_2S$ as a reducing agent. On heating a solution of CO-hæmoglobin coagulation commences at about 65°, whereas NO-hæmoglobin changes at 50° to methæmoglobin, which then coagulates. T. McLachlan.

Preparation of standard acid-hæmatin solutions from hæmin. C. A. Elvehjem (J. Biol. Chem., 1931, 93, 203—210).—Hæmin is prepared by the action of conc. AcOH on defibrinated blood at 90° and from it a solution of acid-hæmatin is obtained by dissolving in dil. HCl with the addition of gelatin as protective agent. The hæmoglobin equiv. of such a solution is given by the Fe content, and it may be used as a standard for the colorimetric determination of hæmoglobin or as a means of calibration of the glass standards of the Newcomer method (A., 1919, ii, 179). F. O. Howitt.

Determination of volatile substances in blood. N. V. Lazarev, A. J. Brussilovskaja, and J. N. Lavrov (Biochem. Z., 1931, 240, 12—18).—A method for determination of C_6H_6 in air depending on the conductometric titration of the CO_2 formed on burning it in an electric furnace is adapted for determination of hydrocarbons, Et_2O, and $COMe_2$ in blood. P. W. Clutterbuck.

Relative composition of sea-water and of the blood of *Limulus polyphemus*. M. E. Dailey, F. Fremont-Smith, and M. P. Carroll (J. Biol. Chem., 1931, 93, 17—24).—The blood-serum of *L. polyphemus* is isotonic with sea-water, the isotonicity being maintained even when the sea is diluted by heavy rain. The distributions of Cl' and $Na^{\cdot}$ between sea-water and the serum agree with the theoretical Donnan ratio. F. O. Howitt.

Occurrence of proteolytic enzymes in serum. J. Wohlgemuth (Biochem. Z., 1931, 239, 493—494).—The procedure of Fuchs and von Falkenhausen (this vol., 1080) was unsatisfactory. Their results and their criticism of the work of Yokota (this vol., 641) must be rejected. W. McCartney.

Physico-chemical properties of the globulin fraction of serum and plasma precipitable by acetic acid. A. Roche (Bull. Soc. Chim. biol., 1931, 13, 962—970).—Addition of 10% AcOH to serum diluted × 10 causes complete precipitation of the globulins at p_H 7·0—7·2, as compared with about p_H 6·0 in the case of plasma. The globulins obtained in this way from serum contain no mucoprotein and give no NH_2-carbohydrate on hydrolysis; the isoelectric point is p_H 5·8—6·0. P. G. Marshall.

Determination of the protein composition of blood-serum. J. von Darányi and B. von Gözsy (Biochem. Z., 1931, 239, 110—127).—The method described uses 2 c.c. of serum and permits the determination of 4 protein fractions of 4 to 8 sera in 36—48 hr. The results compare favourably with those by the gravimetric method. P. W. Clutterbuck.

Refractometric investigation of serum-protein. VII. Effect of dilution and of ammonium sulphate concentration on the protein fractions of horse-serum. D. von Deseö (Biochem. Z., 1931, 239, 329—349; cf. this vol., 1176).—When serum-protein is precipitated with $(NH_4)_2SO_4$ a vol. contraction, probably of the same order as that which occurs when such solutions are mixed with distilled H_2O, takes place and the ppt. contains less $(NH_4)_2SO_4$ than does the mother-liquor. The change in the $(NH_4)_2SO_4$ concentration of the liquid which occurs after the precipitation is due to the binding of H_2O by the ppt. The amount of the protein precipitated varies with the dilution of the serum and the concentration of the $(NH_4)_2SO_4$ used. At the same time the amounts of eu- and pseudo-globulin especially are greatly changed. W. McCartney.

Precursor of ammonia arising in blood and muscle. J. K. Parnas (Biochem. Z., 1931, 239, 18—20).—Criticism of the results and conclusions of Freund and Lustig (this vol., 641). P. W. Clutterbuck.

Approximate determination of blood-urea by opacimetry. P. Mounier (Bull. Biol. Pharm., 1931, 2, 191—192).—The opacity produced by the precipitation of the urea as dixanthylcarbamide from 1—2 drops of blood in presence of egg-white and glycerol is compared with that produced by a 0·02% solution of urea. C. C. N. Vass.

Acetylcholine in ox-blood. III. C. Bischoff, W. Grab, and J. Kapfhammer (Z. physiol. Chem., 1931, **200**, 153—165; cf. this vol., 1080).—Acetylcholine was isolated from 20 samples of fresh ox-blood by precipitation as the Reinecke salt, conversion into the Au salt, then into the chloride. It was present in all samples examined, the average amount being 27·4 mg. per litre of blood. In 11 cases the physiological test on the blood showed little or no acetylcholine present, although the isolated chloride was physiologically active. The acetylcholine content of blood decreases on keeping according to the method of isolation. J. H. Birkinshaw.

Determination of choline in blood. M. Maxim (Biochem. Z., 1931, **239**, 138—139).—A method for separation of blood-choline as periodide is described, titration of the I liberated therefrom on treatment with HNO_3 giving a measure of the choline content.
P. W. Clutterbuck.

Distribution of serum-phosphatide and of cholesterol in the ultra-filtrates obtained by filtration through large-pored collodion filters. S. Went and L. Goreczky (Biochem. Z., 1931, **239**, 441—448).—When horse-serum is ultra-filtered through collodion membranes having large pores the P, phosphatide, cholesterol, lecithin, and protein (in its various fractions) contents indicate that in serum the phosphatides and sterols exist in different types of combination with proteins, since the lipin content of the ultra-filtrates is dependent on the protein content and the concentration of cholesterol in them decreases in direct proportion as the protein content decreases. Also, as regards their phosphatide content, the ultra-filtrates can be divided into two groups sharply divided at the point where the euglobulin content falls to zero. In the one group the lecithin content equals that of the original serum and the protein content exceeds 40—50% of the total protein; in the other, the lecithin content is much lower and the protein content falls to zero. Ultra-filtrates which are free from protein contain Et_2O-sol. P equiv. to 30—40% of the total phosphatide but no cholesterol. The lipin content of the ultra-filtrates is independent of the pressure used. W. McCartney.

Total non-protein-sulphur in whole blood, plasma, and serum, and the glutathione content of blood. I. S. Lorant, N. Hajdu, and W. Weil (Z. physiol. Chem., 1931, **200**, 121—125).—The non-protein-S in plasma or serum from the blood of healthy persons after a 12-hr. fast is 2·5 mg. per 100 c.c. Since the non-protein-S in whole blood is 6·8 mg. the val. for glutathione-S is 5·42—4·30 mg. for men and 5·30—4·30 mg. for women.
J. H. Birkinshaw.

Determination of total base in serum. M. Chatron (J. Pharm. Chim., 1931, [viii], **14**, 236—240, and Bull. Biol. Pharm., 1931, **3**, 290—291).—Serum is heated with H_2SO_4–$HClO_3$ mixture and the residue dissolved in H_2O, neutralised to bromothymol-blue with 0·2N-NaOH, and boiled, neutralising with a known vol. of 0·02N-NaOH if necessary. SO_4'' is determined by Fiske's method. Phosphates are removed by the method of Stadie and Ross (A., 1926, 100). C. C. N. Vass.

Determination of reducing sugars in blood and milk by the Fleury–Boutot method. L. Boutot (Bull. Biol. Pharm., 1931, **2**, 177—183).—Proteins are precipitated by $HgSO_4$ and after neutralisation with NaOH the filtrate is freed from excess of Hg by addition of powdered Zn. An excess of Bertrand's alkaline Cu solution is added and the mixture is warmed under definite conditions. The excess of the Cu solution is measured iodometrically and the difference between this val. and the blank measures the amount of reducing sugars present.
C. C. N. Vass.

Determination of dextrose in blood. G. Rodillon (Bull. Biol. Pharm., 1931, **2**, 216—219).—After precipitation of proteins with $CCl_3{\cdot}CO_2H$, the sugar is determined by titration with alkaline $Cu_2Fe(CN)_6$.
C. C. N. Vass.

Compensation dialysis *in vivo*; state and character of the blood-serum. C. H. Greene and M. H. Power (Proc. Staff Mayo Clinic, 1931, **6**, 123).—Examination of the protein-free dialysates of dog's blood indicated the absence of "labile" dextrose. Only 1—2 mg. of the reducing material per 100 c.c. was non-fermentable. Chemical Abstracts.

Prevention of glycolysis of blood by iodoacetic acid. A. D. Marenzi and W. A. Mundt (Anal. Farm. Bioquim., 1931, **2**, 100—102).—Addition to dog's blood of $CH_2I{\cdot}CO_2H$ or its Na salt in the proportion 1 : 2000 prevents glycolysis at 37° for 24 hr. (cf. Lundsgaard, A., 1930, 954, 958). T. H. Pope.

Influence of arsenate on phosphorus exchange and glycolysis in blood. A. E. Braunstein (Biochem. Z., 1931, **240**, 68—93).—Addition of arsenate (0·00016—0·005M) to whole blood and erythrocyte suspensions containing dextrose causes a rapid liberation of inorg. PO_4''' from the pyrophosphate and glycerophosphate fractions. The action of serum-phosphatase and the liberation of PO_4''' in non-glycolysing erythrocytes are not affected by arsenate. Addition of arsenate (0·0002—0·007M) increases the rate of disappearance of sugar and formation of lactic acid in whole blood and erythrocytes. PO_4''' exchange and glycolysis are influenced by vanadate in the same way as by arsenate. The hydrolysis of hexosediphosphate by the phosphatase, the formation of methylglyoxal by the *apo*zymase of dried erythrocyte preps., and the activity of the glyoxalase of erythrocytes are not influenced by arsenate.
P. W. Clutterbuck.

Determination of lactic acid in tissue and blood. F. Matakas (Biochem. Z., 1931, **239**, 417—423).—In the method of Mendel and Goldscheider (A., 1926, 212), which is fairly satisfactory, the HPO_3 can with advantage be replaced by 0·5N-H_2SO_4 and 5% $NaPO_3$ solution. Colorimetric are not necessarily more accurate than titrimetric processes, circumstances determining which is preferable.
W. McCartney.

Enzymes and blood groups. II. F. Schiff and G. Weiler (Biochem. Z., 1931, **239**, 489—492;

cf. this vol., 1174).—The agent in human fæces which inactivates the substance A_1 is not affected in 20 hr. (in some cases also in much longer periods) by the following substances at the dilutions given or by $CHCl_3$–H_2O or glycerol: quinine hydrochloride, 0·5%, KCN 0·5%, 30% formalin 1%, thymol 0·1%, atoxyl 0·1%, PhOH 0·1%. Consequently sterile suspensions of fæces in which the activity of the agent remains undiminished can be prepared. The action of the agent on A_1 is not affected by 0·1% solutions of any of the following substances, but is inhibited by KCN (0·5%) or by salicylic acid (0·1%): quinine, cocaine, atoxyl, sympatol (α-4-hydroxyphenyl-β-methylaminoethyl alcohol hydrochloride), PhOH. Probably the agent is a "blood group" enzyme. W. McCartney.

Serum anaphylaxis. Chemical nature of the anaphylactising substance. Desplanques, Simonnet, and Verge (Ann. Inst. Pasteur, 1931, **48**, 332—338).—Anaphylaxis of guinea-pigs by horse-serum is due to the serum-globulin, serum-albumin being inactive after precipitation of the globulin. A. Cohen.

Mineral content of the developing avian embryo. W. R. Mankin (Med. J. Austral., 1930, 2, 41—48).—The Na and K contents of the 4-day embryo are much higher than those of the fully developed chick; for Ca the reverse holds. About the 13th day the Ca increases slightly and the other constituents fall. The H_2O content is closely parallel with the K content. Chemical Abstracts.

Phosphatides. III. Fatty acids of the ether-soluble phosphatides and of the protagon fraction of brain. E. Klenk (Z. physiol. Chem., 1931, **200**, 51—68; cf. this vol., 251).—The saturated fatty acid fraction of the Et_2O-sol. phosphatides was a mixture of palmitic and stearic acids. The unsaturated fatty acid fraction, on catalytic hydrogenation, yielded, in addition to stearic and behenic, small amounts of palmitic and *n*-eicosoic acid. The last must have arisen from an unsaturated C_{20} acid.

In the protagon fraction the amount of unsaturated fatty acid is small. The chief constituents are palmitic and stearic together with a little nervonic acid. The portion in amide-linking consists of the 4 fatty acids of the C_{24} group: cerebronic, lignoceric, hydroxynervonic, and nervonic acids. Stearic acid was also present, and possibly an acid of higher mol. wt. Apart from the latter the acids present are those recognised as fission products of cerebrosides and sphingomyelins. The acids of the C_{18} and C_{24} series predominate. J. H. Birkinshaw.

Phosphorus in glycogen. T. C. Taylor and J. J. McBride (J. Amer. Chem. Soc., 1931, **53**, 3436—3440).—Glycogen isolated from rat-liver and sea scallop by Pflüger's method and then subjected to long dialysis contains 0·013—0·24% of P, which is attached to some nitrogenous residue of const. composition. H. Burton.

Iodine content of commercial desiccated anterior pituitary preparations. K. Closs (J. Pharm. Exp. Ther., 1931, **43**, 131—138).—The accurate determination of I in org. material is discussed and a modification of the micro-method of von Fellenberg (A., 1926, 1052) is given. All but one prep. (with 0·00198—0·00996%) of those examined contained 0·00008—0·00019% I. F. O. Howitt.

Production of homogeneous skeletal material for analysis of the whole skeleton and the presence in it of small amounts of calcium soaps. F. Fischler, A. Wild, and H. Kaussler (Biochem. Z., 1931, **239**, 213—223).—The bone material is prepared by hydrolysis of the whole animal with 2% KOH and the ratios of Ca : PO_4 : MgO show great constancy in composition. It contains 0·5—1·0% of Ca soaps. The ratios for teeth show a higher PO_4 and MgO val. P. W. Clutterbuck.

Organic chlorine compounds in animal tissues. W. Hogartz (Z. physiol. Chem., 1931, **200**, 119—120).—The org. Cl compounds are not removed from tissue by simple Et_2O extraction of the powdered dried material (cf. Amer. J. Physiol., 1929, **90**, 375). J. H. Birkinshaw.

Copper content of human organs. H. Kleinmann and J. Klinke (Arch. path. Anat. Physiol., 1930, **275**, 422—435; Chem. Zentr., 1931, i, 2777—2778).—The livers of prematurely and newly-born infants (up to 3 days old) contained up to 11 times as much Cu as the normal val. Perfusion experiments also showed that the Cu content of the liver is high. PhBr was used instead of $CHCl_3$ in Schönheimer and Oshima's method for the determination of Cu. A. A. Eldridge.

Loss of weight of the human body during the six hours following death. L. Hébert (Bull. Biol. Pharm., 1931, 2, 151—152).—The loss is attributed to loss of H_2O and CO_2 by the oxidation of lactic acid produced in the muscle after the heart has ceased to beat. C. C. N. Vass.

Fission of arcaine by micro-organisms. F. Linneweh (Z. physiol. Chem., 1931, **200**, 115—118; cf. this vol., 1178).—A mixed culture of saprophytic bacteria hydrolysed arcaine to putrescine and urea. J. H. Birkinshaw.

Pigments of *Haliotis californiensis*. R. Lemberg (Z. physiol. Chem., 1931, **200**, 173—178).—*H. californiensis* yields *A*, green in acid $CHCl_3$ solution, absorption max. at 623 mμ, weaker band at 498 mμ, in neutral solution bands at 555 and 496 mμ; *B*, greenish-blue in acid solution, band at 622 mμ. J. H. Birkinshaw.

Salts of heavy metals as fixatives. J. J. Sheinin and H. A. Davenport (Stain Tech., 1931, **6**, 131—148).—Heavy metal salts were used for tissue fixation and their precipitating action on albumin and gelatin solutions was studied. Precipitation of proteins is generally influenced by the at. wt. of the cation of an electrolyte. A relatively good protein precipitant is not necessarily a good tissue-hardening agent, but the reverse is true. H. W. Dudley.

Insect waxes. IV. Coccerin, the wax of the cochineal insect (*Coccus cacti*). M. Becker (Biochem. Z., 1931, **239**, 235—242).—Coccerin is a compound of 1 mol. of cocceryl alcohol, $C_{32}H_{64}(OH)_2$ (*monoacetate*, m. p. 78—79°), with 1 mol. of coccerinic acid, $C_{31}H_{62}(OH)\cdot CO_2H$ (*Et* ester, m. p. 72—73°). The second OH group of the alcohol is very difficult to esterify (cf. this vol., 975). P. W. Clutterbuck.

Composition of the silk-worm pupa. S. Wada (Acta Schol. Med. Kyoto, 1931, 13, 201—210).—The material contained H_2O 8·8; the dry substance contained protein 63·2, neutral fats 19·9, unsaponifiable substances 0·8, glycogen 1·2, ash 3·3%. The following NH_2-acids were isolated: glutamic acid 4·17, glycine 1·01, leucine 2·47, alanine 0·78, valine 0·95, *iso*leucine 1·71, *l*-proline 1·85, *dl*-proline 0·4, phenylalanine 1·21, *dl*-aspartic acid 0·11, *l*-aspartic acid 0·26, serine ?, tyrosine 1·84, cystine 0·19, tryptophan 1·2, histidine 0·07, arginine 0·15, lysine 0·02, guanine 0·03, adenine 0·03%, hypoxanthine ?, choline ?
Chemical Abstracts.

Effect of respiratory injury on biophysical properties of the body fluid and digestive fluid of silk-worm larvæ. T. Gamô (J. Sci. Agric. Soc. Japan, 1928, 124—149, 177—187).—Changes in p_H and electrical conductivity are recorded.
Chemical Abstracts.

"Kaijo" of cocoons and their sericin particles. H. Kaneko (Bull. Sericult. Japan, 1931, 4, 2—6).—The physical properties of their sericin solutions are used to characterise the "kaijo" of cocoons. A better "kaijo" gives a greater p_H, and, in an electric field, greater cataphoretic velocity and biuret colour-change in the anodic compartment. H. Davson.

Distribution of various forms of nitrogen in wild silk, and in fibroin and sericin of true silk. R. Inouye and K. Sakamoto (Bull. Sericult. Japan, 1931, 4, 10—12).—The N of wild silks dissolved in conc. HCl is less than that of true silks, whilst humin and amide are the same. More arginine than histidine and lysine is found in each silk. N distribution is similar in fibroin and sericin, also in Yamamai and Tussah silks, and different in *Attacus cynthia* and *Caligula japonica*. H. Davson.

Nature of the enzyme secreted by the hatching gland of plagiostomes (*Scylliorhinus canicula*). O. T. Yio (Compt. rend., 1931, 193, 545—546).—The enzyme resembles trypsin in digesting mixtures of gluten with albumin and gelatin at p_H 7·0—7·2. It is, however, active at a lower temp. (13°). A. Cohen.

Equilibrium between cerebrospinal fluid and blood-plasma. VI. Distribution of sodium between cerebrospinal fluid and blood-serum. M. E. Dailey (J. Biol. Chem., 1931, 93, 5—15).—Human serum-Na tends to vary directly with the serum-Cl. The cerebrospinal fluid-Na is generally higher (1·03 : 1) than the serum-Na, whilst the average ratio of serum-Cl to cerebrospinal fluid-Cl is 0·82. Meningitis is associated with a decrease in Cl content and a less marked decrease in Na content of both serum and fluid. Acute changes in the serum by blood dilution are followed by corresponding changes in the cerebrospinal fluid, the change in Na content being proportional to that in Cl.
F. O. Howitt.

Photometric determinations of different constituents of body-fluids. G. Rodillon (Bull. Biol. Pharm., 1931, 2, 163—175).—Details for the application of the photometric method for the micro-determination of urea, uric acid, dextrose, Cl′, PO_4''', Ca, and phenols in body-fluids are recorded.
C. C. N. Vass.

Milk secretion. (A) Influence of inanition. (B) Influence of insulin and phloridzin. J. W. Gowen and E. R. Tobey (J. Gen. Physiol., 1931, 15, 45—66, 67—85).—(A) Cows when starved but supplied freely with H_2O secrete milk with a high content of total solids, especially of fat and ash, the increase in protein being usually small. The vol. of milk secreted and the concentration of lactose are decreased. Administration of "parathormone" (1000 units) had no significant effect on the blood or the milk.

(B) Milk secretion is altered by a large dose of insulin sufficient to lower the blood-sugar (500—1200 units) in a manner somewhat similar to that observed during starvation, the chief difference being that the marked rise in total solids, butter-fat, and ash and the fall in rate of secretion are more immediate. Administration of phloridzin during inanition temporarily increases the % of total solids and butter-fat. The results are in conformity with the view that the lactose is derived from the blood-dextrose and that a balance is maintained between the osmotic pressure of the milk and that of the blood. W. O. Kermack.

Absorption spectrum of bilirubin in various solvents. II. P. Müller and L. Engel (Z. physiol. Chem., 1931, 200, 145—152; cf. this vol., 1082).—Bilirubin in all solvents examined shows a sharply defined absorption band, the position of which varies for each solvent. With increasing alkalinity of the solution the absorption band moves towards the violet, decreases in strength, and becomes less clearly defined. J. H. Birkinshaw.

Bile salts in urine. P. Mounier (Bull. Biol. Pharm., 1931, 2, 153—160).—Surface tension measurements afford the only means of determining minute quantities of bile in urine. A statistical val. for normal urine has been determined; max. vals. of surface tension are obtained in urine acidified with 0·05*N*-HCl. The presence of bile is shown by an increased surface tension; free org. acids also increase the surface tension, but to a much smaller extent. Hay's test is extremely sensitive, corresponding with a concentration of 0·05 g. of bile salts per litre. Difficulties may be met in urine containing min. concentrations of bile and max. concentrations of keto-acids. C. C. N. Vass.

Distinction between dextrose and lactose in urine. G. Rodillon (Bull. Biol. Pharm., 1931, 2, 185—187).—Lactose and dextrose are differentiated by means of their osazones. C. C. N. Vass.

Diacetyl, acetylmethylcarbinol, and βγ-butylene glycol in human urine. H. Schmalfuss and H. Schaake (Z. physiol. Chem., 1931, 200, 169—172).—These substances occur in small amounts in the urine of healthy persons. J. H. Birkinshaw.

Colorimetric determination of phenols in urine. A. D. Marenzi (Anal. Farm. Bioquim., 1931, 2, 81—90).—A modification of Benedict and Theis' method (A., 1918, ii, 461) serves for the determination of free PhOH and, after hydrolysis, of conjugated PhOH in urine. Folin and Denis' (A., 1915, ii, 802) and Goiffon and Nepveux' methods (A., 1924, ii, 706) yield high results. T. H. Pope.

Micro-determination of total urinary nitrogen. G. Rodillon (Bull. Biol. Pharm., 1931, **2**, 192—193).—1 c.c. of urine is heated with 1·5 c.c. of H_2SO_4 in presence of $KHSO_4$ and $HClO_3$. After dilution the solution is neutralised to phenolphthalein and the concentration of NH_3 determined by formol titration. C. C. N. Vass.

Determination of total nitrogen in urine. M. Wirbel (Bull. Biol. Pharm., 1931, **3**, 325).—Urine is heated with H_2SO_4–$HClO_3$ mixture, the residue dissolved in H_2O, and the NH_3-N determined by formol titration. C. C. N. Vass.

Photometric determination of total and inorganic phosphorus in urine. C. Urbach (Biochem. Z., 1931, **239**, 28—41).—The process depends on examining the P–molybdic acid complexes by means of the step photometer. The method is superior to the colorimetric method in accuracy and rapidity. P. W. Clutterbuck.

Determination of organic phosphorus in urine by means of the step photometer. C. Urbach (Biochem. Z., 1931, **239**, 182—185).—The method is described and claimed to be superior to others in accuracy, rapidity, and in the avoidance of the use of standards. P. W. Clutterbuck.

Anæmias. I. Porphyria and red cell generation. II. Anæmias and liver substance. R. Duesberg (Arch. exp. Path. Pharm., 1931, **162**, 249—279, 280—295).—I. Clinical and experimental anæmias are divided into two classes. Those caused by distilled H_2O injection, phenylhydrazine, and jaundice are marked by an increase in reticulocytes and O_2 consumption, without an increase in porphyrin excretion. Pernicious, sulphonal, and Pb anæmias do not show increased regeneration of blood-cells, whilst porphyrin in the urine increases.

II. Liver preps. have no therapeutic action on anæmias due to experimental bleeding, distilled H_2O, loss of blood, $NHPh{\cdot}NH_2$, and jaundice. Favourable reactions are observed in anæmias where blood-cell regeneration is inhibited, *e.g.*, pernicious, sulphonal, and Pb anæmias. A. Cohen.

Methæmoglobin formation by antianæmic organ extracts. R. Duesberg and W. Koll (Arch. exp. Path. Pharm., 1931, **162**, 296—306).—Several liver preps. and organ extracts of clinical therapeutic val. in anæmia convert hæmoglobin into methæmoglobin in the presence of O_2 *in vitro*; cyanohæmoglobin is formed by the addition of HCN. Fe, Cu, SH compounds, or disulphides are not responsible for the conversion. A. Cohen.

Production of nutritional anæmia in rats. C. A. Elvehjem and A. R. Kemmerer (J. Biol. Chem., 1931, **93**, 189—195; cf. A., 1928, 790).—In rats weaned at 17 days of age and fed on whole cow's milk *ad libitum*, blood-hæmoglobin decreases to a level of 2—3·5% within 2 weeks, when, if no additions are made to the diet, death ensues. On addition of Fe and Cu to the milk fed to such rats the hæmoglobin returns to normal levels. Such anæmic rats possess a low Mn storage (0·0026—0·0064 mg. per animal). F. O. Howitt.

Ineffectiveness of purified glutamic acid as a supplement to iron in the correction of nutritional anæmia. C. A. Elvehjem, H. Steenbock, and E. B. Hart [with E. van Donk] (J. Biol. Chem., 1931, **93**, 197—201).—Contrary to Drabkin and Miller (cf. this vol., 247; also following abstract) the addition of pure glutamic acid to a diet of whole milk and Fe does not correct nutritional anæmia in the rat. F. O. Howitt.

Hæmoglobin production. III. Relief of anæmia, due to milk diet, by feeding amino-acids and related compounds. D. L. Drabkin and H. K. Miller (J. Biol. Chem., 1931, **93**, 39—48; cf. this vol., 247, 510).—Rats develop anæmia on a diet of either raw or boiled milk. The onset of the disease is retarded by administration of 0·18 mg. Fe per rat per day; this amount is ineffective, either alone or supplemented with leucine, cystine, glycine, α-aminovaleric acid, or glutaric acid, in curing the anæmia once produced. Fe and succinic acid or succinimide are partly effective. Rats receiving milk supplemented with Na glutamate, but not with Fe, are more resistant to anæmia than those receiving Fe alone or Fe and alanine. Glutamic acid (70 mg. per rat per day) stimulates hæmoglobin formation in anæmic rats when administered with as little as 0·05 mg. of Fe. F. O. Howitt.

Blood studies in hæmorrhagic anæmia. H. S. Mayerson and H. Laurens (J. Nutrition, 1931, **3**, 453—463).—The effect of various diets on hæmoglobin production in dogs is recorded. Chemical Abstracts.

Metabolism of cancer tissue. G. Harker (J. Cancer Res. Comm. Sydney, 1931, **3**, 114—118).—A review. C. C. N. Vass.

Tumour immunity. Effects of eu- and pseudo-globulin fractions of anti-cancer sera on tissue cultures. T. Lumsden (J. Path. Bact., 1931, **34**, 349—355).—The euglobulin contains all the antibodies which are specifically toxic to cancer cells and all the heterotoxins which have escaped destruction during fractionation. The pseudoglobulin contains the anti-species bodies. Chemical Abstracts.

Cancer-producing substances of Rous sarcoma. E. Fränkel (Z. physiol. Chem., 1931, **200**, 126—132).—Certain dyes of known constitution (Hansa-yellow, lack-orange, and thioindigo colours) adsorb the cancer-producing agent. Except in the case of lack-orange the eluates are active. J. H. Birkinshaw.

Non-enzymic nature of entity transmitting chicken sarcoma. W. Nakahara and H. Yaoi (Gann, 1930, **24**, 318—336).—Repeated freezing (−18° for 20 min. or −75° for 10 min.) and thawing (37° for 5—10 min.) of tissue reduces the tumour-transmitting action of the saline extract of Rous chicken sarcoma tissue or its sediment. If an enzyme-like substance is responsible for the formation of the sarcoma, extracts obtained from disrupted cells should be more active than those obtained from intact cells. Chemical Abstracts.

Capability of serum to dissolve carcinoma lipins. R. Willheim and K. Stern (Biochem. Z., 1931, **239**, 473—483; cf. A., 1930, 1611).—The lipins which are derived from cancer cells are dissolved by normal sera, whilst cancer sera not only lose this power, but even readily deposit the lipins which they contain. Lipins from different tumours exhibit considerable differences as regards solubility in sera, whereas those from normal cells or from the whole carcinoma tissue do not. It is concluded that, since attempts to separate the lipins into fractions fail, the differences are not due to differing contents of a chemical substance, but to the combination of various constituents to form a physicochemical unit.

W. McCartney.

Experimentally produced changes in the behaviour of serum towards cancer cells. R. Willheim and K. Stern (Biochem. Z., 1931, 239, 484—488; cf. A., 1930, 1611).—When human carcinoma cells or lipins extracted from human tumours are injected into rabbits and curves of the type previously described are drawn, these are of the same type as those obtained in the case of persons suffering from cancer. W. McCartney.

Effect of sodium fluoride on the metabolism of tumours. C. Sellei and J. Jány (Biochem. Z., 1931, 239, 94—99).—Glycolysis in kidney tissue is decreased and respiration but little affected by NaF. The respiration of carcinoma tissue with a high concentration of NaF is similarly effected, but with more dil. solutions (0·001—0·0001*N*) is increased and the glycolysis decreased, the heat coeffs. $W^{O_2}_{CO_2}/W$ and $W^{N_2}_{CO_2}/W_{O_2}$ being similar to those of normal tissue without NaF. P. W. Clutterbuck.

Cancer chemotherapy. X. Effect of thorium, cerium, erbium, yttrium, didymium, praseodymium, manganese, and lead on transplantable rat tumours. L. C. Maxwell and F. Bischoff [with E. M. Ottery] (J. Pharm. Exp. Ther., 1931, 43, 61—70).—The lethal dose and the action on cancer tumours of compounds of the above metals have been investigated in rats. All are essentially negative in checking cancer growth. F. O. Howitt.

Respiratory quotient. Value in diagnosis of diabetus mellitus. M. Wishnofsky and C. S. Byron (Arch. Int. Med., 1931, 48, 470—477).—Vals. for R.Q. less than 0·88 after the ingestion of dextrose are considered as indicative of diabetus mellitus. Where the presence of glycosuria and hyperglycæmia is inadequate owing to other factors, such as high renal threshold, hypertension, nephritis, or hyperthyroidism, the R.Q. is the ultimate criterion in the diagnosis of diabetus mellitus. A. Lawson.

Intermediate fat metabolism in diabetes and disorders of the liver. L. Cannavó (Biochem. Z., 1931, 239, 100—109).—Almost all aliphatic acids are acidogenic and all acids having an even no. of C atoms are very ketogenic. The acidosis caused by acids having an odd no. of C atoms is due to acids (not keto-acids) formed during metabolism. Acidosis is accompanied by increased urinary NH_3. In all the liver cases some ketonæmia and ketonuria were observed. P. W. Clutterbuck.

"Parathormone" dosage and serum-calcium and -phosphorus in experimental chronic hyperparathyroidism leading to ostitis fibrosa. A. Bodansky and H. L. Jaffe (Proc. Soc. Exp. Biol. Med., 1930, 27, 797).—On a low Ca intake hypercalcæmia tended to disappear in chronic hyperparathyroidism on a given dose of parathormone; an increase of Ca intake or hormone dosage increased the serum-Ca. The serum-P in chronic hyperparathyroidism in young puppies continued at or rose above the normal high level. The effects of single doses and of prolonged treatment with parathormone are described. Chemical Abstracts.

Native complement in hyperthyroidism. N. Novick (Arch. Int. Med., 1931, 48, 462—469).—A method of determining the complement val. by hæmolytic titration is described. In disagreement with the results of Hadjopoulos and Burbank (J. Lab. Clin. Med., 1928, 14, 131), no increase of complement val. in hyperthyroidism is found. No relationship is apparent by comparing the post-operative and preoperative complement vals. with the basal metabolic rates. A. Lawson.

Significance of the potassium–calcium ratio and of the inorganic phosphorus and cholesterol of the blood-serum in arterial hypertension. A. A. Weinstein and S. Weiss (Arch. Int. Med., 1931, 48, 478—499).—Slight improvements in the Fiske–Logan (unpublished) and Taylor methods of determining Ca and K respectively are given, the former being found to give lower vals. than the Kramer–Tisdall or Jansen methods owing to the elimination of org. acids, MgC_2O_4, and excess $C_2O_4H_2$. In the cases examined, the average rise in K is 2·15 mg. per 100 c.c. of serum, this being most marked in hypertension with cardiac involvement. Allowing for factors other than hypertension, no appreciable rise in either Ca or cholesterol levels is found, a fact which does not support the hypothesis that these are fundamental in the development of arterial hypertension. Elevation of the K and cholesterol levels in one group of cases is considered as the result rather than the cause of changes in the cardiovascular system. A. Lawson.

Blood-cholesterol in acute malaria. R. D'Alessandro (Arch. Farm. sperim., 1931, 52, 258—268).—Acute malaria is generally accompanied by hypercholesterolæmia, which is intensified during fever in benign tertian or quartan malaria, but the reverse effect occurs in malign tertian malaria or mixed infections including this form. R. K. Callow.

Significance of cerebrospinal-fluid sugar. E. F. Wahl (Arch. Int. Med., 1931, 48, 446—461).—A high val. for the cerebrospinal-fluid sugar is not diagnostic of any given disease, but decreasing vals. are obtained as tuberculous and purulent meningitis progress. A. Lawson.

Pathological physiology of pellagra. I—V. R. H. Turner (J. Clin. Invest., 1931, 10, 61—70).—Serum-albumin tends to be low owing to digestive disturbance; serum-Ca is abnormal. Plasma-Cl′ and total acids are low. Chemical Abstracts.

Chemical changes in the blood of the dog in experimental bile peritonitis. A. M. Ziegler and T. G. Orr (J. Exp. Med., 1931, 53, 865—868).—The changes are similar to those found in experimental peritonitis. The increase in blood-non-protein- and -urea-N is probably due to increased tissue destruction, and the fall in Cl' to vomiting.

Chemical Abstracts.

Metabolism in pneumonia. II. Mechanism of retention of chloride. III. Excretion of anions and total base. I. Greenwald (Arch. Int. Med., 1931, **48**, 418—439, 440—445).—II. Using dogs injected intratracheally with *Pneumococcus*, increase of Cl' and subsequent retention in the urine is confirmed. Approx. agreement is shown between the retained Cl' val. and that of the estimated increased body-fluid content.

III. The fact that there is no marked change in the anion–cation balance in pneumonia is confirmed.

A. Lawson.

Ammonia content of the blood of women during pregnancy, labour and delivery, and childbed. L. Stanojević (Biochem. Z., 1931, **239**, 257—272).—The NH_3 content of the blood of women rises just perceptibly in the 8th and 9th months of pregnancy, but quite distinctly during labour and delivery. During the first few days after delivery the content returns to its normal val. The part of the "mother substance" of the blood-NH_3 which gives up its NH_3 at room temp. seems to decrease during labour and delivery. W. McCartney.

Colloidal benzoin reaction for the diagnosis of neurosyphilis. G. Rodillon (Bull. Biol. Pharm., 1931, **3**, 313—318).—The flocculation produced by decreasing amounts of cerebrospinal fluid in a colloidal benzoin solution varies with the nature of the disease.

C. C. N. Vass.

Calcium and phosphorus metabolism in a case of non-tropical sprue with associated tetany. A. Marble and W. Bauer (Arch. Int. Med., 1931, **48**, 515—532).—Low serum-Ca and -P, the osteoporosis and tetany in sprue are not due to parathyroid deficiency, but to the inadequate absorption of Ca and P from the gastrointestinal tract because of existing diarrhœa. A very low val. of 124 mg. per 100 c.c. for total base in serum is reported.

A. Lawson.

Relationship of guanidine metabolism and the activity of liver-arginase in tetany after parathyroidectomy in dogs. A. von Beznák and K. Szeöke (Biochem. Z., 1931, **239**, 159—162).—The activity of liver-arginase is the same for normal and parathyroidectomised dogs and the accumulation of guanidine in tetany of this type cannot arise from arginine. It is probably formed from the choline group of lecithin. P. W. Clutterbuck.

Thrombo-angiitis obliterans (Buerger). VI. Chemistry of the blood. M. Friedlander and S. Silbert (Arch. Int. Med., 1931, **48**, 500—506).—The blood in 40 cases shows increases in total ash, total protein, Ca, and cholesterol content. Cl' and sugar content is normal. A. Lawson.

Chemical view of pathogenesis of tuberculosis. E. R. Long (Amer. Rev. Tuberculosis, 1930, **22**, 467—490).—A discussion. Chemical Abstracts.

Plasma-protein, red-cell sedimentation, and serum lability of the blood in tuberculosis. L. R. Jones (Amer. Rev. Tuberculosis, 1931, **23**, 325—332).—The plasma-protein was normal; fibrin was increased in 19 and (of these) globulin in 7 of 20 cases. Albumin was normal in 13 and low in 7 cases. In tuberculosis the average val. of the protein quotient was 1·47 (normal, 2·39). Chemical Abstracts.

Accumulation of iron in tuberculous areas. V. Menkin and M. F. Menkin (J. Exp. Med., 1931, **53**, 919—927).—Repeated intravenous injection of $FeCl_3$ is followed by accumulation of Fe in tuberculous areas of the lungs. Chemical Abstracts.

Differential quantitative tuberculin test. J. E. Blair and W. J. Galland (Amer. Rev. Tuberculosis, 1931, **23**, 1—2). Chemical Abstracts.

Oxygen consumption of tissues from rats fed with a diet deficient in cystine. R. Gerschmann (Rev. soc. argentina biol., 1930, **6**, 50—62).—A diet low in cystine diminishes O_2 consumption, glutathione, and oxidation–reduction power of tissues.

Chemical Abstracts.

Rôle of phosphate in biological oxidations. M. Barmore and J. M. Luck (J. Gen. Physiol., 1931, **15**, 97—105).—The rate of oxidation of glyceraldehyde by methylene-blue, α-naphthol-2-sulphonate-indophenol, and phenol-indophenol in presence of borate, phenylalanine, or carbonate at p_H 7·9 is increased by the addition of phosphate, whereas at p_H 4·77 in presence of phthalate buffer no catalytic effect of phosphate appears except in the case of α-naphthol 2-sulphonate-indophenol. Quant. observations on the rate of oxidation of glyceraldehyde by phenol-indophenol in presence of borate buffer over a range of p_H vals. are in agreement with the view that the PO_4''' ion is responsible for the catalysis of oxidation. W. O. Kermack.

Conservation of rainfall as carbohydrates. W. A. Osborne (Nature, 1931, **128**, 378).—In arid countries of high temp. a fraction of the rainfall is locked up in carbohydrate mols. and becomes available for animal life. L. S. Theobald.

Regulatory action of yeast in deficient nutrition of rats. T. Osuka (Biochem. Z., 1931, **239**, 163—171).—When glycogen utilisation is increased, *e.g.*, in bodily activity and when the type of diet influences the formation of glycogen unfavourably (in fat and in protein diets) addition of yeast to the diet increases the formation of glycogen. Yeast slightly decreases liver-glycogen of an animal on a mixed diet, but increases it by several times on a pure fat or protein diet. The fat contents of the fresh liver of rats on a mixed diet with or without addition of yeast are almost identical. On a pure protein diet, yeast causes an increase of body-fat and a slight decrease of liver-fat. On a carbohydrate diet the body-fat is greatly increased and the liver-fat slightly decreased.

P. W. Clutterbuck.

Relation of glycogen to water storage in the liver. E. M. Bridge and E. M. Bridges (J. Biol. Chem., 1931, **93**, 181—187).—The variation in the glycogen content of the liver of rabbits induced by modifications of diet is accompanied by changes in one or more of the other components, a high glycogen content being associated with a low protein and, to a smaller extent, fat and H_2O concentration. Thus the glycogen : H_2O ratio is not even approx. const., although the liver-H_2O per kg. body-wt. is fairly steady. Hence changes in body-H_2O are more likely due to changes in the metabolism of fats than that of carbohydrates. F. O. Howitt.

Fate of histidine in the animal organism. E. Abderhalden and S. Buadze (Z. physiol. Chem., 1931, **200**, 87—100).—Administration of *l*-histidine to dogs causes an increase in the total creatinine excreted in the urine, although the N metabolism remains const. Only a portion of the glyoxaline-N of *l*- and *d*-histidine reappears as such in the urine. Glycerol extracts of liver tissue attack *l*- and *d*-histidine. The enzyme has a broad optimum p_H 8—9. By the usual methods for NH_3 determination, the NH_3 recovered does not correspond with complete deamination. With more conc. alkali at 60° the amount of NH_3 obtained indicates a removal of N from the glyoxaline ring.

J. H. Birkinshaw.

Methylamine as intermediate product of glycine degradation in the surviving liver. R. Kohn (Z. physiol. Chem., 1931, **200**, 191—208).—Glycine added to blood used for perfusion of the surviving liver of dogs gives rise to NH_2Me, which is detected by the carbylamine reaction, and determined by distillation after removal of NH_3 with HgO. In perfusion experiments only about 1% of the glycine yields NH_2Me. Considerable amounts of NH_2Me are rapidly withdrawn from circulation by the liver. No increase in NH_3 and only a small increase in urea are observed. J. H. Birkinshaw.

Absorption and utilisation of the carbohydrate of *Arctium lappa* as shown by a protein-sparing action on the diet of dogs. J. C. Krantz, jun., and C. J. Carr (J. Pharm. Exp. Ther., 1931, **43**, 187—191).—The drop in N output (7·6%) of dogs fed a protein diet when burdock (*A. lappa*) root is added indicates a protein-sparing action comparable with that of pure inulin (cf. A., 1922, i, 82).

F. O. Howitt.

Nitrogen metabolism in infants on graded intake of soya-bean "milk" proteins. E. Tso and F. T. Chu (Chinese J. Physiol., 1931, **5**, 287—294).—In young infants fed on soya-bean "milk" furnishing 120—150 g.-cal. per kg. body-wt., adequate N retention is obtained when 18% of the cals. is provided in the form of protein. On cow's milk feeding, in which 10—14% of the cals. is furnished in the form of protein, 38—42% of the N intake was retained, whilst on soya-bean "milk" in which 8—18% of the cals. was provided as protein 14—30% of the N ingested was retained. At different levels of intake with soya-bean "milk" the ratio of N absorbed to N ingested is approx. const. at 80%, the corresponding figure in the case of cow's milk being 95%.

W. O. Kermack.

Salts and protein metabolism. E. Gerhartz (Biochem. Z., 1931, **239**, 404—416).—Administration of $CaCl_2$ or KCl to dogs favours or reduces excretion of N according as there are or are not sufficient salts in the food consumed. The N balance is impaired by administration of PO_4'''. The unfavourable results are probably due to the interference with the electrolyte equilibrium. In case of $CaCl_2$ administration corresponding changes take place in the utilisation of N, but distinct results are not obtained with other salts.

W. McCartney.

Influence of growth on a number of constituents of the white rat. A. Chanutin (J. Biol. Chem., 1931, **93**, 31—37).—The variations in the following constituents with age of the animal were studied from birth in normal rats, eviscerated before analysis: total solids, org. (*i.e.*, dry, fat- and ash-free) tissue, org. and wet tissue-creatine, -N, and ash and the Et_2O-extractable substances of the org. tissue. The greatest increase in all the constituents investigated occurred during suckling. Creatine reached a max. in 30—40 days and the fat and ash in 20 days, whilst the N concentration remained const. throughout life. F. O. Howitt.

Normal retention of food-iron during growth and the utilisation of the iron of protein foods. R. C. Miller (Proc. Amer. Soc. Animal Produc., 1928, 21—25).—The Fe content of rats decreases very rapidly during suckling, rapidly rising to a const. val. when solid food is ingested. Meat diet leads to a high, and milk powder to a low, Fe content.

Chemical Abstracts.

Significance of minerals in the mixed foods of domestic animals. N. Hansson (Bied. Zentr., 1931, B, **3**, 137—173).—Analyses of numerous fodder and other crops show that the essential mineral constituents of animal rations may be ensured by the properly regulated use of these feeding stuffs. Where insufficient grass or hay is available mixtures of bone meal, $CaCO_3$, Na phosphates, and NaCl are satisfactory supplements and cod-liver oil may be used in extreme cases. A. G. Pollard.

Phosphatic limestone and other rock products as mineral supplements. C. Tolle and L. A. Maynard (Proc. Amer. Soc. Animal Produc., 1928, 15—21).—Phosphatic limestone (Ca phosphate 23, $CaCO_3$ 70%), bone meal, and limestone were equally effective as sources of Ca for bone development in rats, but rock phosphate was much less effective. The presence of F causes changes in tooth structure.

Chemical Abstracts.

Phosphorus metabolism in embryonic life. I. Invertebrate eggs. J. Needham and D. M. Needham (J. Exp. Biol., 1930, **7**, 317—347).—Considerable differences in P distribution are recorded.

Chemical Abstracts.

Effect on abnormal skeletal mineral metabolism of the Ca Mg salts of inositolphosphoric acid together with biologically active plant extracts. B. Bleyer and F. Fischler (Biochem. Z., 1931, **239**, 224—231).—By administration of McCollum's diet to rats, a decrease of total mineral content of the bones and an abnormal composition in individual bone constituents are obtained. Normality is completely restored in 4 weeks by administration of Ca Mg inositolphosphate.

P. W. Clutterbuck.

Calcium content of the body in relation to that of the food. H. C. Sherman and L. E. Booher (J. Biol. Chem., 1931, **93**, 93—103).—Ca determinations were made on the ash of eviscerated rats raised on diets of varying Ca content. With full diets varying only in Ca content the body-Ca varied in accordance with the food-Ca. Rats on a Ca-poor diet increased very slowly in body-wt. and consequently had a higher body-Ca than those on a diet richer in Ca. Hence with a Ca-poor diet the average normal adult body-Ca (1·09% for males and 1·23% for females) was attained at a late age. With certain lower levels of Ca intake the appearance and growth were normal but the bodies were poor in Ca. F. O. Howitt.

Calcium. V. Blood and urine levels after peroral and deep muscular administration of calcium gluconate in man. A. L. Lieberman (J. Pharm. Exp. Ther., 1931, **43**, 139—145).—Whilst there is no direct quant. correlation between the blood- and urine-Ca the latter can serve as a qual. index of the former. Thus a urinary Ca output greater than 10 mg. per hr. indicates a rise of blood-Ca.

F. O. Howitt.

Absorption and retention of calcium chloride and phytin. J. C. Forbes and H. Irving (J. Pharm. Exp. Ther., 1931, **43**, 79—83).—When $CaCl_2$ or phytin was fed to young rats on a diet of known Ca content the retention of Ca was of the same order for each salt. F. O. Howitt.

Relationships between parathyroids, calcium metabolism, and bone-growth. E. Bülbring (Arch. exp. Path. Pharm., 1931, **162**, 209—248).—In normal rats, serum-Ca and retention of Ca are not increased by a Ca-rich diet, and the Ca : P ratio varies with the diet-Ca. Parathyroidectomy causes a temporary increase in Ca and P retention in the soft parts, a fall in serum-Ca which is intensified by a Ca-rich diet, and a fall in bone-Ca which is prevented by Ca feeding. " Parathormone " decreases Ca and P retention and Ca and P content of bone, the effects being more marked on Ca-rich, and modified or reversed by Ca-poor, diet. The increased serum-Ca caused by the hormone is most pronounced on a Ca-rich diet. A. Cohen.

Muscle structure and aërobic carbohydrate formation. A. Hahn, H. Belmonte, and H. Niemer (Z. Biol., 1931, **91**, 491—495).—Carbohydrate formation by the frog sartorius muscle immersed in lactate-Ringer solution and in presence of O_2 is reduced to 33% in isotonic and to 13% in hypertonic solution by transverse section of the fibres, whilst longitudinal section gives vals. agreeing with the intact muscle. Thus the non-formation of carbohydrate by pulped muscle is explained (cf. this vol., 258). The process of recovery is also probably dependent on the structure. F. O. Howitt.

Formation of lactic acid in muscular work after removal of the suprarenal glands. A. von Árnay and L. Lengyel (Biochem. Z., 1931, **239**, 128—137).—The formation of lactic acid in 67 muscles taken from adrenalectomised rats during rest, work, after tetanic stimulation, and in rigor is very greatly decreased. P. W. Clutterbuck.

Phosphorylation and production of lactic acid in muscles and organs. B. Tankó (Biochem. Z., 1931, **239**, 318—323; cf. A., 1929, 1106).—When human striped muscle and striped muscle from the pigeon, pig, rat, and guinea-pig are compared as regards phosphorylation, it is found that the process takes place most strongly in pigeon breast-muscle, which also yields most lactic acid from glycogen. In human muscle (from the leg) also phosphorylation usually proceeds rather strongly with production of lactic acid, but in cases where this is not so addition of boiled muscle-juice containing co-enzyme stimulates the process considerably. Phosphorylation and lactic acid production proceed strongly in fresh heart-muscle (dog) and even more strongly in pig heart-muscle, whilst in pig liver the process is less pronounced, although here also phosphorylation can be stimulated by addition of boiled muscle-juice. This juice also causes phosphorylation and lactic acid production in pig abdominal muscle, kidneys, and brain, in which, otherwise, these processes do not occur.

W. McCartney.

Insulin and phosphorylation. J. Bodnár and B. Tankó (Biochem. Z., 1931, **239**, 314—317; cf. this vol., 520).—Since it exerts no influence on phosphorylation under physiological conditions (no glycogen or NaF added, low phosphate concentration) in fresh muscle pulp, muscle powder, or muscle powder poor in co-enzyme and since phosphorylation proceeds briskly in the leg muscle of dogs from which the pancreas has been removed, insulin cannot be regarded as a sp. activator of muscle-phosphatase.

W. McCartney.

Fate of *p*-chlorobenzoic acid in the animal organism. J. Wührer (Arch. exp. Path. Pharm., 1931, **161**, 719—729).—Na *p*-chlorobenzoate administered to dogs or rabbits is excreted in the urine partly unchanged and partly combined with glycine in the form of p-*chlorohippuric acid*, m. p. 148°.

W. O. Kermack.

Poisoning by acetic acid. R. W. Blair (Analyst, 1931, **56**, 596—597).—The symptoms are described. To identify AcOH the stomach and intestines are steam-distilled, the distillate is made just alkaline with NaOH and evaporated, and the AcOH is esterified with EtOH. T. McLachlan.

Behaviour of bees towards honey-dew containing melezitose. F. E. Nottbohm and F. Lucius (Z. Unters. Lebensm., 1931, **61**, 314—321).—A destructive criticism of Elser's statement (cf. *ibid.*, 1930, **60**, 332) that melezitose is non-injurious to bees (cf. B., 1929, 955). H. J. Dowden.

Poisonous action of ingested saponins. A. J. Ewart (Counc. Sci. Ind. Res. Austral., Bull. 1931, **50**, 28 pp.).—The toxic action of saponin and saponin-containing plant extracts on guinea-pigs and stock is described. Ingested saponin is hydrolysed in the alimentary canal and only a small fraction is absorbed. It acts indirectly on the central nervous system. The liver, in affording protection from the toxic effects, undergoes fibrosis. Saponin-containing plants are probably responsible for certain stock diseases.

A. Cohen.

Ethyl alcohol. I. Micro-determination. II. Oxidation in a small homeotherm and in a poikilotherm at different temperatures. M. Nicloux (Bull. Soc. Chim. biol., 1931, **13**, 857—918).

—For complete oxidation of EtOH to AcOH a slight excess of standard $K_2Cr_2O_7$ is added to 5 c.c. of the dil. EtOH mixed with 0·5 vol. of 66% H_2SO_4, and the mixture heated in a stoppered bottle at 85° for 1 hr. After cooling, a slight known excess of $Fe(NH_4)_2(SO_4)_2$ is added and the excess titrated with standard $KMnO_4$.

II. With subcutaneous injection of small quantities of EtOH in mice (1 c.c. per kg.), oxidation is rapid and only 3·7% is eliminated by way of the lungs and skin in 2 hr., as opposed to 10% in 8 hr. in the case of larger quantities (about 7 c.c. per kg.). In a frog 24 hr. are required at 30° to effect complete oxidation of a quantity of EtOH which is oxidised in 2 hr. in a mouse, whilst at 12° only 31·3% is oxidised.

P. G. Marshall.

Anæsthetic action of furan. J. F. A. Johnston (J. Pharm. Exp. Ther., 1931, **43**, 85—88).—Inhalation of furan vapour in cats induces an unsuitable type of anæsthesia. F. O. Howitt.

Anæsthetic potency in the *cyclo*-hydrocarbon series. V. E. Henderson and J. F. A. Johnston (J. Pharm. Exp. Ther., 1931, **43**, 89—92).—The anæsthetic potency of *cyclo*hexane is 4·8 times that of *cyclo*propane for anæsthetic concentrations and 3·2 times for fatal concentrations (cf. A., 1929, 1104; 1930, 639). F. O. Howitt.

Reversible coagulation in living tissue. W. D. Bancroft and J. E. Rutzler, jun. (Proc. Nat. Acad. Sci., 1931, **17**, 482—484).—The effect of anæsthetisation is a reversible coagulation of proteins in both plants and animals. In plants there is a preliminary stage of excitation before anæsthetisation sets in. The sensitivity of *Mimosa pudica* can be increased by the addition of peptising agents (*e.g.*, NaCNS) and by coagulating agents (*e.g.*, Na citrate). Bernard's theory of anæsthesia is applicable to plants as well as animals. A. J. Mee.

Physiology of phenol. B. A. Houssay and A. D. Marenzi (Anal. Farm. Bioquim., 1931, **2**, 75—80).—The disappearance of PhOH, after intravenous injection into dogs, from the blood is due to the action of the kidneys and its conjugation (*e.g.*, with H_2SO_4) is a very general action and proceeds rapidly in the small intestine. T. H. Pope.

Action of rarefaction of air on the hæmoglobin and resistance of the erythrocytes in rabbits treated with "pyrodin." F. Heimann (Arch. exp. Path. Pharm., 1931, **161**, 686—691).—The red blood-corpuscles of normal rabbits which have been kept in a partly exhausted chamber have a max. resistance to hæmolysis by hypotonic NaCl solution much above normal and an approx. normal min. resistance. The max. resistance increases further after administration of "pyrodin." The red blood-corpuscles of rabbits which have been poisoned with "pyrodin" have a low hæmoglobin content and a min. resistance above normal. When these rabbits are kept in a partly exhausted chamber, the min. resistance decreases and the max. resistance rises.

W. O. Kermack.

Antipyretic action of *p*-acetamidourethanes. R. F. B. Cox, C. R. Eckler, and R. L. Shriner.—See this vol., 1287.

Influence of cinchophen derivatives on the uric acid excretion in the bile of rabbits. M. Yamagami (Folia Pharmacol. Japon., 1931, **12**, 53—66).—After subcutaneous injection of erycon (0·2 g.) into rabbits the bile-uric acid is considerably increased, but the quantity of bile is practically unaltered. The changes following splanchnectomy and vagotomy are recorded; there is a close connexion between the splanchnic and vagus nerves and uric acid excretion. Chemical Abstracts.

Detection and separation of barbituric acid derivatives in toxicological examination. J. J. L. Zwikker (Pharm. Weekblad, 1931, **68**, 975—983).—The deep blue complex Ba Co compound formed when the extract is treated in MeOH solution with $CoCl_2$ and $Ba(OMe)_2$ is sp. Quant. separation from Et_2O extracts of urine is effected by dissolving the residue after evaporation of Et_2O in H_2O containing pyridine, precipitating a Cu pyridine barbiturate, collecting, washing, and treating with acid. S. I. Levy.

Sensitiveness to alkali as a distinction between choline and acetylcholine. K. Velhagen (Arch. exp. Path. Pharm., 1931, **161**, 697—702).—Acetylcholine is more sensitive to dil. alkali than is choline. This observation is of use in the detection of acetylcholine in cell extracts. W. O. Kermack.

Production of a compound with histamine-like action from histidine by cathode rays. F. Ellinger (Arch. exp. Path. Pharm., 1931, **161**, 703—712).—By irradiation of solutions of histamine hydrochloride or of the solid salt by cathode rays a compound is formed resembling histamine in its actions on the intestine and the uterus (cf. A., 1930, 638, 1472). W. O. Kermack.

Blood-electrolytes during histamine shock in dogs. D. W. Atchley, D. W. Richards, jun., and E. M. Benedict (J. Clin. Invest., 1931, **10**, 1—7).—Concentration of blood, uncompensated lactic acidosis with increase in serum-total base and decrease in serum-HCO_3', increase in serum-inorg. phosphate, and decrease in O_2-saturation are observed.

Chemical Abstracts.

Antagonism between the action of atropine and that of acetylcholine, pilocarpine, and physostigmine on the isolated rabbit's uterus. M. Takahashi (Folia Pharmacol. Japon., 1931, **12**, no. 1, 102—110).—The action of acetylcholine is increased and of pilocarpine decreased. When the action of physostigmine is weak it is not completely inhibited by atropine. Chemical Abstracts.

Action of pilocarpine on the rabbit's blood-sugar. G. Carbonaro and F. Salamone (Arch. Farm. sperim., 1931, **53**, 1—16).—Doses of 0·01—0·05 mg. of pilocarpine per kg. body-wt. exert a hypoglycæmic effect without causing other apparent disturbance; 0·1 mg. per kg. has slight and inconstant effects, whereas 5 mg. exhibit a biphasic effect, namely, primary hyperglycæmia accompanied by the manifestations of general pilocarpine action, followed by hypoglycæmia. From the pharmacodynamic viewpoint pilocarpine must, therefore, be regarded as having amphotropic action. T. H. Pope.

Blood-sugar in animals after administration of morphine and the theoretical basis of the dextrose–insulin treatment of morphinism. G. Anton (Arch. exp. Path. Pharm., 1931, **161**, 646—668).—The rise in blood-sugar which occurs in dogs after the administration of morphine runs parallel with increased blood acidity and is not inhibited by pituitary or ergotamine, but may be reduced by the administration of alkali. W. O. Kermack.

Influence of the nervous system on blood-sugar. II. Action of ergotamine on blood-sugar level and arecoline hyperglycæmia. G. Carbonaro (Arch. Farm. sperim., 1931, **52**, 241—257).—Subcutaneous injection of ergotamine into rabbits causes a considerable hypoglycæmia, due to its paralysing action on the sympathetic. The hyperglycæmia produced by arecoline is prevented by first injecting ergotamine, and the effect of arecoline is, therefore, produced by action on the sympathetic. R. K. Callow.

Toxicological detection of coniine. O. Krayer (Arch. exp. Path. Pharm., 1931, **162**, 342—372).—A forensic study. The similarity in properties of coniine and bases present in putrefied material from a corpse is discussed. Coniine hydrochloride may be separated by micro-sublimation. A. Cohen.

Coniine-like properties of some amines. O. Krayer and W. Koll (Arch. exp. Path. Pharm., 1931, **162**, 373—384).—Coniine cannot be distinguished chemically from a number of volatile basic putrefaction products. The contracting effect on the abdominal muscle of the frog is also possessed by *iso*amylamine, β-phenylethylamine, and pyrrolidine. A. Cohen.

Distribution and excretion of coniine hydrochloride. S. Thaddea (Arch. exp. Path. Pharm., 1931, **162**, 385—394).—The distribution of coniine in guinea-pigs at varying times after administration has been determined quantitatively by micro-sublimation of the hydrochloride. The lethal subcutaneous and oral doses are 4 and 15 mg. per 100 g. body-wt., respectively. Subcutaneously, coniine is quickly and widely distributed in the blood and organs, and 75% of coniine *per os* is absorbed from the gastro-intestinal tract in 45 min. In a few hr. 80—90% of the alkaloid (by either route) is destroyed in the body whilst 10% is excreted in the urine in 24 hr. in quantities increasing in the first 4—5 hr. Traces only are excreted in the fæces. A. Cohen.

Determination of traces of strychnine. W. Koll (Arch. exp. Path. Pharm., 1931, **162**, 307—319).—Strychnine is precipitated in H_2SO_4 solution by neutral phosphomolybdate. The ppt. gives a bluish-violet colour with NH_4 vanadate in conc. H_2SO_4, changing to orange, which serves for the colorimetric determination of the alkaloid (±3%). A. Cohen.

Detection of strychnine in organs. W. Koll (Arch. exp. Path. Pharm., 1931, **162**, 320—341).—EtOH extraction yields only 15—40% of the strychnine content of organs, as shown by colorimetric determination (cf. preceding abstract). This is due to adsorption of the alkaloid on protein and on filters used in manipulation. A method is described whereby proteins are first digested with pepsin and trypsin. Strychnine is then extracted by dil. H_2SO_4 and HCl, and from the latter by $CHCl_3$. Of 2 mg. of strychnine added to 100 g. of tissue, 90% is recovered. An extraction apparatus for solvents heavier than H_2O is described. A. Cohen.

Potentiation of toxicity of strychnine by quinine. R. I. Grantham and J. C. Munch (J. Assoc. Off. Agric. Chem., 1931, **14**, 295—296).—Mixtures of strychnine and quinine cannot be assayed by their toxicity to rats, owing to potentiation of toxicity. The lethal dose of mixtures containing 83% or more of quinine, injected subcutaneously into white rats, is about 1·0 mg. of strychnine per kg. body-wt., the lethal doses of strychnine and quinine being 2·5 mg. and 1000 mg. respectively. W. J. Boyd.

Spermicidal powers of contraceptives. II. J. R. Baker (J. Hyg., 1931, **31**, 189—214).—The toxic effect of pure substances on guinea-pig sperm was determined. The $[H^{\cdot}]$ of acids is the determining factor. Substances which reduce surface tension may be effective. Chemical Abstracts.

Carbon monoxide poisoning. Its detection, and the determination of percentage saturation in blood, by means of the Hartridge reversion spectroscope. R. C. Frederick (Analyst, 1931, **56**, 561—571).—For each instrument a curve must be plotted connecting the span with % saturation. The span for CO-hæmoglobin is plus compared with oxy-hæmoglobin and cannot be confused with that of NO-hæmoglobin, which is negative. T. McLachlan.

Investigation of carbon monoxide poisoning. J. S. Haldane (Analyst, 1931, **56**, 571).—The use of a spectroscope for the determination of CO-poisoning is unnecessary. NO-poisoning may be detected in blood samples taken during life by the presence of methæmoglobin, and in the cadaver by the colour of the clot on boiling. T. McLachlan.

Detection of hydrogen cyanide and its alkali salts in viscera and other products by formation of Prussian-blue. G. Magnin (J. Pharm. Chim., 1931, [viii], **14**, 233—236).—Air is drawn through the substance under investigation and passed over a strip of filter-paper moistened with 5%KOH. The paper is then treated with a few drops of very dil. aq. $FeSO_4$ and a few drops of 10% HCl. The intensity of the blue colour is proportional to the amount of HCN present. 1 part HCN in 1,000,000 parts can be detected by this method. C. C. N. Vass.

Effect of prolonged iodine feeding on the iodine content of animal organs. S. Weiser and A. Zaitschek (Bied. Zentr., 1931, B, 3, 275—297).—Prolonged feeding of KI (35—125 mg. daily) increased the I content of all organs and tissues (but not bones) of goats and their suckling kids. Cessation of I administration decreased the I content of the thyroid gland, blood, milk, liver, bile, spleen, pancreas, and reproductive organs to vals. which remained above normal. In other organs vals. returned to normal. Skin, hair, and hoofs retained an increased I content. Changes in the I contents of the organs of suckling kids were not always of the same order as those of their dams. A. G. POLLARD.

Iodine tolerance of goats. S. WEISER and A. ZAITSCHEK (Bied. Zentr., 1931, B, 3, 298—301; cf. A., 1930, 495).—For goats of all ages and both sexes the optimum daily dose of I is 1 mg. per kg. live wt. Administration may be continued indefinitely. For milch goats 2 mg. per kg. live wt. was used for several weeks without ill effects. A. G. POLLARD.

Pharmacology of iodine. I. Action of iodine on cholesterol and ergosterol sclerosis. H. SEEL and G. CREUZBERG (Arch. exp. Path. Pharm., 1931, 161, 674—685).—Sclerosis produced in animals by administration of cholesterol or irradiated ergosterol is favourably influenced by I either in inorg. (KI) or in org. ("Iodotropin") form, the effect being more marked in the case of cholesterol than of irradiated ergosterol. W. O. KERMACK.

Detoxication of phosphorus by sugar. R. SCHOLL (Biochem. Z., 1931, 240, 62—67).—The lethal dose of P when subcutaneously injected into rats is 8 mg. per kg. but increases when inulin is fed to 12—15 mg. per kg. The toxicity of As derivatives is not similarly influenced by a rich carbohydrate diet. P. W. CLUTTERBUCK.

Effect of intravenous injection of "novarsenobenzol" on blood-nitrogen, -sugar, and -cholesterol. A. LEULIER, J. GATE, and P. LINARD (Compt. rend. Soc. Biol., 1930, 105, 12—13; Chem. Zentr., 1931, i, 2780).—No changes were observed. A. A. ELDRIDGE.

Effects of varying calcium and phosphorus intake on the œstrus cycle and reproduction in the rat. H. R. GUILBERT and G. H. HART (Hilgardia, 1930, 5, no. 5, 101—118).—A diet containing 0·22% P and Ca : P=4 : 1 fed to female rats from weaning seriously interfered with growth and sexual maturity. In mature rats receiving a diet having 0·18—0·22% P and Ca : P=4 : 1 up to 100 days old, ovulation was irregular or ceased entirely. This proportion of P, however, suffices to maintain a normal œstrus cycle after 110 days of age. With a diet containing Ca : P=8 : 1 ovulation ceased in mature rats. Lowering the Ca content of the ration from 0·82 to 0·22% did not limit growth or reproductive functions. A. G. POLLARD.

Influence of irradiation on the behaviour of silver in the organism. II. Silver in the organs of full-grown rats. L. PINCUSSEN and W. ROMAN (Biochem. Z., 1931, 239, 374—403; cf. this vol., 652).—When Ag (as Ag_2SO_4) is injected in 6- or 12-mg. doses into full-grown male rats the proportions of the three Ag fractions found in the blood, liver, kidneys, spleen, heart, lungs, skin, and hair are independent of the size of the dose, although the total amount of Ag found in these organs is greater when the dose is 6 than when it is 12 mg. The liver retains most, the blood least of the Ag. Except in the liver, where most of the Ag is retained as Ag–protein compound, most of the metal occurs as ionised Ag. Irradiation of the rats after administration of the Ag decreases the amount of the metal recovered in the organs and alters the proportions of the various Ag fractions in them. The magnitude of the decrease depends on the intensity, duration, and type of radiation. Moderate irradiation favours increase in the Ag–protein fraction, strong irradiation leads to increase in the metallic Ag fraction. Clipped rats are more strongly affected by irradiation than are unclipped. W. McCARTNEY.

Action of X-rays on the material of inner secretion and organ poisons. B. TERATA and R. ITO (Folia Pharm. Japon., 1931, 12, no. 1, 67—73).—The effect of adrenaline on blood-pressure is increased by "moderate" X-rays but inhibited by "strong" rays; that of pituitrin and thyroid extract is increased, whilst that of histamine and peptone is decreased, by the rays. CHEMICAL ABSTRACTS.

Metabolic changes produced by irradiation. VIII. Effect of irradiation and of insulin on the substances in the organs which affect the sugar content of the blood. L. PINCUSSEN. **IX. Glutathione content of the organs.** L. PINCUSSEN and S. YOKOTA (Biochem. Z., 1931, 239, 290—302, 303—309; cf. this vol., 872).—VIII. From the pancreas, liver, hind-leg muscle, lungs, spleen, and skin of the treated guinea-pigs (donors) extracts were made and injected into other guinea-pigs (the receivers), in which the blood-sugar content was then determined. All the extracts from normal donors living in diffused light reduced the blood-sugar in the receivers, the pancreas extract having the greatest effect. The blood of the donors also always contained agents which altered the blood-sugar in the receivers. Extracts from the organs of donors kept in the dark increased the blood-sugar in the receivers. In donors (especially in those kept in the dark) to which insulin was administered the blood-sugar was reduced, but extracts from these donors increased the blood-sugar in the receivers. Very similar effects were obtained with donors irradiated with a "vitalux" lamp. Irradiation of the donors with various types of light and with heat rays reduced the sugar content of the blood except when the irradiation was by a quartz lamp and was of short duration. In the latter case the blood-sugar was increased whilst if the irradiation lasted longer it was reduced. Extracts from the organs of donors irradiated with the quartz lamp increased or reduced the blood-sugar in the receivers according as the period of irradiation had been short or long. Although in the case of irradiation by quartz and "vitalux" lamps extracts from all the organs of the donors acted alike, in that of the Ne and Na lamps and of the heat rays extracts of different organs had different effects. It is concluded that the effects produced may be attributed to the production and action of a substance similar to adrenaline which acts antagonistically to insulin, and the similarity between the effects of insulin and those of irradiation is emphasised.

IX. In guinea-pigs irradiation with a Hg-vapour lamp appears to cause increase in the glutathione content of the liver, lungs, and muscle, but to have no effect on that of the spleen. In white rats the increases are very distinct in liver and lungs, whilst there is no change in the amount of glutathione in the muscle, but a slight decrease in the amount in the spleen. In general, the stimulating effect of irradiation on the metabolism has been confirmed.

W. McCartney.

Influence of sweet material on biocatalysis and metabolic processes. II. Action on blood-sugar and liver-glycogen in rabbits. W. Diemair and F. Fischler (Biochem. Z., 1931, 239, 232—234).—No disturbance occurs in the carbohydrate metabolism of rabbits receiving large doses of saccharin for a long time. P. W. Clutterbuck.

Amylases of malt and potato. H. Borchardt and H. Pringsheim (Biochem. Z., 1931, 239, 193—200).—The prep. of maltase-free amylases and their characterisation are described.

P. W. Clutterbuck.

Viscosimetric method of estimating enzyme concentration, with special reference to amylase. W. R. Thompson, C. E. Johnson, and R. Hussey (J. Gen. Physiol., 1931, 15, 1—7).—The viscosimetric method for the determination of enzyme concentration has been improved and applied to the determination of amylase (cf., A., 1923, ii, 271). W. O. Kermack.

Effect of radiations from a mercury arc in quartz on enzymes. II. Effect of ultra-violet radiation on amylase in solution. W. R. Thompson and R. Hussey (J. Gen. Physiol., 1931, 15, 9—13).—The activity of pancreatic amylase solutions decreases under the influence of the radiation of a quartz–Hg-vapour lamp exponentially with time (cf. A., 1926, 202). The sensitiveness to irradiation is greater than with pepsin solutions.

W. O. Kermack.

Influence of temperature on the formation of reducing material in the autosaccharification of rye meal. S. Pronin (Biochem. Z., 1931, 240, 94—97).—The max. autosaccharification, expressed as maltose % of the meal starch, is for two kinds of rye meal 46·34 and 52·24%. The process has an optimum temp. zone at 55—64°.

P. W. Clutterbuck.

Amylosynthease. S. Nishimura and T. Minagawa (Proc. Imp. Acad. Tokyo, 1931, 7, 258—260).—A 1% solution of achroodextrin at p_H 6·2 was treated in the presence of $CHCl_3$ with a filtrate from autolysed yeast. After keeping at 25—26°, a ppt., which formed in 84% yield, was collected, washed with EtOH and Et_2O, and dried; it gave a bluish colour with I. Amylosynthease is destroyed at 60°. It is present in wine, press, and distiller's yeasts, and in *Saccharomyces Biwa* and *Mycoderma*.

C. C. N. Vass.

Disaccharide fission by α-glucosidase. R. Weidenhagen (Z. physiol. Chem., 1931, 200, 279).—A neutral phosphate extract of the dry prep. of *B. coli* I. used by Myrbäck (this vol., 983) was inactive but a PhMe autolysate hydrolysed weakly both maltose and sucrose. J. H. Birkinshaw.

Contraction constants of enzyme–substrate reactions. M. Sreenivasaya and H. B. Sreerangachar (Nature, 1931, 128, 585).—The contraction per g.-mol. of substrate is a const. for each enzyme–substrate system; for urea–urease the const. is 24, and for sucrose–invertase, 6. L. S. Theobald.

Rôle of pectase in the fermentation of coffee. A Perrier (Compt. rend., 1931, 193, 547—549).—The spontaneous elimination of the undesirable mucilaginous layer on coffee seeds is not due to direct microbic action. It is solubilised by the digestion of its pectins by pectase under favourable temp. conditions arising from simultaneous fermentation occurring in the seed. A. Cohen.

Animal phosphatase and sulphatase. C. Hommerberg (Z. physiol. Chem., 1931, 200, 69—81).—Enzyme material from different organs shows the same ratio between phosphatase and sulphatase activity. Brain preps. of the pig, calf, and rabbit show no greater activity than those of pig's kidney. Phosphatase but not sulphatase was found in autolysates or eluates. Shaking dry preps. of pig's kidney with H_2O or dil. aq. NH_3 increases their activity. The washed prep. contains less P than the original; when the original P is restored, inhibition is observed. Addition of $MgCl_2$ to the dry prep. activates phosphatase and inhibits sulphatase. The inhibition may be due to the formation of $MgCO_3$ since $CaCO_3$ is present as sulphate acceptor.

J. H. Birkinshaw.

Gluco-sulphatase. T. Soda and C. Hattori (Proc. Imp. Acad. Tokyo, 1931, 7, 269—270).—In the autolysates of some Japanese snails (*Eulota* spp.) is an enzyme which exerts a sp. hydrolysis of dextrose-monosulphate, optimum p_H 7. C. C. N. Vass.

Presence of a gelatin-liquefying enzyme in crude pepsin preparations. J. H. Northrop (J. Gen. Physiol., 1931, 15, 29—43).—An amorphous fraction isolated from crude pepsin preps. shows high gelatinase activity, being 400 times as active in liquefying gelatin as is cryst. pepsin. The initial val. of the ratio (decrease in viscosity)/(increase in "formol-N") is much greater in the case of gelatinase than in the case of cryst. pepsin. Its action on caseinogen, edestin, and ovalbumin is relatively weak. It is more stable to alkali than is cryst. pepsin, being inactivated at p_H 11—12 and partly reactivated when its solution is brought back to p_H 6. W. O. Kermack.

Action of trypsin on solutions of monoamino-acids, alone or in mixtures. A. Blanchetière (Compt. rend., 1931, 193, 549—550; cf. this vol., 1090).—Under the influence of trypsin at p_H 8·0, NH_2-N slowly decreases in solutions of glycine, alanine, and a mixture of both, alanine showing the greatest loss (10%). The formation of diketopiperazines is demonstrated by the Abderhalden and Kamm reaction.

A. Cohen.

Effect of temperature on the degradation of collagen by pancreatin. F. Stather and H. Machon (Biochem. Z., 1931, 239, 430—433).—The action of pancreatin in an enzyme mixture from fish viscera on collagen in the presence of borate–HCl buffer exhibits a max. at about 50°. In the absence of the buffer the action also reaches a max. which is shifted towards high temp. as the concentration of the enzyme is increased. W. McCartney.

Influence of heavy metals and metal complexes on proteolytic processes. L. Michaelis and K. G. Stern (Biochem. Z., 1931, 240, 192—217).—Further work (cf. this vol., 874) is described on the effect of heavy metals (varying amounts of Hg^{II} salts, complexes containing Zn, Co, Fe, etc.) on the degradation of dissolved organ proteins by tissue proteinase (cathepsin), the process being followed nephelometrically. Certain complex compounds, especially Zn and Fe dipyridyl complexes, accelerate the early stages of degradation more strongly than the same metal in the ionic form. With Fe^{II} and Fe^{III} compounds of varying complex types every effect is obtained from activation to complete inactivation, the valency of the Fe not playing any decisive rôle. The degradation of gelatin by trypsin is studied in terms of the NH_2-groups liberated. At p_H 8, Zn, Hg, and Mn salts inhibited the enzyme but $FeSO_4$ activated it.

P. W. CLUTTERBUCK.

Effect of oxygen, carbon dioxide, and cysteine on arginase. S. SALASKIN and L. SOLOVIEV (Z. physiol. Chem., 1931, **200**, 259—260).—CO_2 inactivates arginase slightly, O_2 more strongly. Cysteine reactivates the arginase after passage of O_2 or CO_2, but subsequent O_2 treatment again inactivates. Cysteine has no effect. Probably the O_2 oxidises cysteine to cystine, thus destroying the activating effect.

J. H. BIRKINSHAW.

Enzymes and light. XVII. Tyrosinase. L. PINCUSSEN and T. HAMMERICH (Biochem. Z., 1931, **239**, 273—289).—A modification of Raper's method (A., 1926, 977) for the prep. of tyrosinase and of Raper and Wormall's method (A., 1923, i, 1146) for its (micro-)determination are described. Methods are also given for the volumetric determination of 3 : 4-dihydroxyphenylalanine, of this compound and tyrosine together, and of the red intermediate product (colorimetrically) produced by the action of tyrosinase on these two substances. The activity of tyrosinase and the production of the red substance are greatly reduced by irradiation, which also decomposes both compounds, tyrosine particularly in the acid region and dihydroxyphenylalanine particularly in the alkaline. The formation of melanin from the compounds is favoured by the presence of Fe. In a mixture of the two acids containing tyrosinase the dihydroxyphenylalanine content increases at first as a result of the oxidation of the tyrosine and the oxidation of the latter is favoured by the presence of the former. It follows that the production of melanin from tyrosine or similar substances in the skin is not due to the effect of ultra-violet light on tyrosinase.

W. MCCARTNEY.

Mitogenetic spectrum analysis. III. Detailed glycolytic spectrum. J. PONOMAREVA (Biochem. Z., 1931, **239**, 424—429; cf. this vol., 1083).—The technique of mitogenetic spectrum analysis is described. Results are tabulated for *B. acidi lact.* from whey; rabbit blood; rabbits' eyes; and an EtOH solution of an active wine yeast from beer wort. In each case five prominent bands comprise the glycolytic spectrum occurring at 1900—1910, 1910—1920, 1940—1950, 1960—1970, and 2170—2180 Å.

W. R. ANGUS.

Action of yeast on fumaric acid. K. P. JACOBSOHN (Biochem. Z., 1931, **239**, 449—455).—When yeast acts on fumaric acid the amounts of CO_2 evolved and lactic acid produced are so small and so slowly formed that there is no ground for supposing that the decarboxylation is other than a very secondary process. The conclusions of Jung and Müller (A., 1922, i, 486) must be rejected. Possibly their yeast was infected.

W. MCCARTNEY.

Mechanism of the phosphorylation of sugars by yeast. Changes during the period of total phosphorylation. S. VEIBEL (Biochem. Z., 1931, **239**, 350—373).—When fresh bottom yeast acts on dextrose, NaH_2PO_4, and $NaHCO_3$ in presence of PhMe, hexosemono-, hexosedi-, and trehalosemono-phosphate are produced and can be isolated. At first the ratio of di- to mono-phosphate is less than 1, but rises in about 2 hr. to 1 and in 4 hr. to its max., 1·5. The time at which the ratio reaches its max. coincides with the max. binding of PO_4'''. Between the 4th and the 14th hr. the amount of the diphosphate decreases and that of monophosphate increases, so that after about 8 hr. the ratio is again 1 and elimination of inorg. PO_4''' becomes appreciable. After 14 hr. the amount of monophosphate reaches its max. and the ratio falls to 0·5—0·7, at which val. it remains for the remainder of the experiment. After 32 hr. half of the phosphate used is again in inorg. combination. No trehalosemonophosphate can be detected during the first 4 hr., but appreciable amounts are present after 8 hr. and these increase up to the end (32 hr.). The monophosphate fraction consists chiefly of Robison's ester after 4 hr., but after 8 hr. chiefly of Neuberg's ester. Trehalosemonophosphate crystallises with $7H_2O$ which are lost at 110° and 15 mm. The bearing of the results on the theories of phosphorylation is discussed.

W. MCCARTNEY.

Phytochemical production of δε-octanediol from butyroin. S. VEIBEL (Biochem. Z., 1931, **239**, 456—460; cf. Neuberg and Kobel, A., 1926, 96).—δε-Octanediol can be obtained in 43% yield from butyroin by the action of bottom yeast. The product is a mixture of the *meso*-form (m. p. 123—124°) and the *d*-form ($[\alpha]_{D}^{23}$ +32° at least) (cf. Bouveault and Locquin, A., 1906, i, 783). During the process practically all the butyroin disappears.

W. MCCARTNEY.

Function of magnesium in enzymic carbohydrate degradation. H. VON EULER, R. NILSSON, and E. AUHAGEN (Z. physiol. Chem., 1931, **200**, 1—26).—Mg is essential in the yeast fermentation of dextrose, lævulose, and sucrose, the optimum concentration being about 10^{-2} mols. of $MgCl_2$. For varying amounts of co-zymase added to Mg-free *apo*zymase, the rate of fermentation at optimum Mg activation is proportional to the amount of Mg required. Mg is also essential for the production of hexosephosphoric acid. Reduction of methylene-blue occurs in absence of Mg, but is activated by it; reduction of MeCHO proceeds without Mg and its addition has little effect. Inhibition of fermentation by F′ is not due to the withdrawal of Mg. MeCHO reduction is stimulated by NaF in a yeast containing Mg, but is inhibited in a Mg-free yeast. It is definitely activated by MgF_2. The latter produces a slight activation of fermentation by Mg-free yeast.

Methylene-blue reduction is stimulated by muscle-adenylic acid in presence of hexosediphosphoric acid, but not in absence of the latter or of co-zymase. Adenylic acid activates the fermentation of hexosephosphates but not that of dextrose.

J. H. Birkinshaw.

Nomenclature of the catalysts of alcoholic fermentation. C. Neuberg and H. von Euler (Biochem. Z., 1931, **240**, 245).—The term holozymase (panzymase) is used for the whole system concerned in alcoholic fermentation; zymase is restricted to the purely enzymic constituents, and *apo*zymase to the holozymase freed from co-zymase, *apo*zymase thus still containing Mg. P. W. Clutterbuck.

Effect of sea-water irradiated with ultra-violet light on the velocity of alcoholic fermentation of dextrose solutions. L. Sanzo and F. Pirrone (Atti R. Accad. Lincei, 1931, [vi], **13**, 613—617).—This fermentation is activated by sea-water only if exposure of the latter is limited, under the conditions employed, to 3 hr. The activity depends partly on the sea-water, considered as a salt solution, and partly on an unknown factor which loses its effect if the irradiated sea-water is either boiled for 20 min. or evaporated to dryness and made up to its original vol. with sterile, distilled H_2O (cf. this vol., 1091).

T. H. Pope.

Action of imine-producing substances on the decomposition of sugar by yeast. Action of co-zymase. I. F. Zuckerkandl and L. Messiner-Klebermass (Biochem. Z., 1931, **239**, 172—181).—Yeast fermentation inhibited by $CH_2I\cdot CO_2H$ or NaF can be reactivated by addition of NH-forming amines, *e.g.*, *p*-phenylenediamine hydrochloride, NH_2Ph hydrochloride, tyrosine. EtOH and glycerol are formed. It is considered that the action is analogous to that of the NH-groups of adenine in the adenine nucleotide of co-zymase.

P. W. Clutterbuck.

Action of halogen derivatives on alcoholic fermentation. P. Cayrol (Compt. rend., 1931, **193**, 446—447).—The sp. inhibition of the alcoholic fermentation of yeast by $CH_2Br\cdot CO_2H$ is compared with that of other halogenated fatty acids. Bromides, bromates, and some halogen-containing hypnotics are inactive. Inhibition is confined to α-halogenated monocarboxylic acids. A. Cohen.

Vital properties of yeast plasma: preparation and biochemical importance of some new yeasts. V. Jonáš (Biochem. Z., 1931, **239**, 140—158).—The culture and properties of some new yeasts are described and it is claimed that the life of the organism is bound, not with the cell, but with the plasma.

P. W. Clutterbuck.

Yeast fat. I. J. Weichherz and R. Merländer (Biochem. Z., 1931, **239**, 21—27).—The presence of valeric acid and probably also of decoic acid is detected. P. W. Clutterbuck.

Glycogen from yeast. Cell membrane of yeast. K. M. Daoud and A. R. Ling.—See this vol., 1277.

Alkaloid content of *Claviceps purpurea* grown on artificial media. H. Kreitmair and W. Küssner (Biochem. Z., 1931, **239**, 189—192).—The presence of alkaloids of ergot in cultures of *C. purpurea* grown on artificial media is detected by chemical and biological methods. P. W. Clutterbuck.

Insensitivity of *Paramecium* to cyanide and effects of iron on respiration. C. S. Shoup and J. T. Boykin (J. Gen. Physiol., 1931, **15**, 107—118).—The rate of respiration of *P. caudatum* is not depressed by KCN at from $N/200$ to $N/10{,}000$, but a slight stimulating action is usually observed. This effect is not related to the p_H of the medium, which, within limits, does not sensibly influence the rate of respiration. Fe^{III} and Fe^{II} salts are usually toxic to *Paramecium* even at low concentrations and in no case stimulate respiration. *Paramecium* probably does not contain a respiratory catalyst containing Fe sensitive to CN'. W. O. Kermack.

Importance of iron for the growth of fungi. B. B. Mundkur (Proc. XV Indian Sci. Cong., 1928, 230).—Fe stimulates the growth of *Fusarium vasinfectum*, Atkinson. Chemical Abstracts.

Dependence of the nitrogen assimilation of some fungi on [H˙]. K. Rippel (Arch. Mikrobiol., 1931, **2**, 72—135).—The N-assimilation of fungi was a function of the p_H of the nutrient, but the Robbins effect was not similarly applicable to all fungi. No selective power of assimilation was observed. NH_2-acids are not preferentially assimilated. The position of the growth optima of the fungi examined was to the left of the isoelectric points. A. G. Pollard.

Decomposition of the various chemical constituents of complex plant materials by pure cultures of fungi and bacteria. S. A. Waksman (Arch. Mikrobiol., 1931, **2**, 136—154).—Certain classes of organisms act on the H_2O-sol. substances, hemicelluloses, and N-complexes of plant tissues, others decompose cellulose, and a few attack lignin. The decomp. of proteins is accompanied by a synthesis of new materials and the extent of decomp. cannot be judged by wt. losses alone. A. G. Pollard.

Formation of citric acid by moulds. V. Formation of citric from acetic acid. K. Bernhauer and H. Siebenäuger (Biochem. Z., 1931, **240**, 232—244).—The power to form citric acid from acetates (especially NaOAc) is a general one for all strains of *Aspergillus niger* used, in several cases the yield being up to 16% on the AcOH disappearing. EtOH, fumaric, malic, and glycollic acids are all converted into citric acid. P. W. Clutterbuck.

Relation between p_H and citric acid formation by *Aspergillus niger* and *Citromyces glaber*. A. Frey (Arch. Mikrobiol., 1931, **2**, 272—309).—Citric acid production by *C. glaber* is favoured by the buffer action of Ca citrate and by p_H 3—4. Addition of acid to produce p_H 2 inhibits the activity of the organism. For *A. niger* the optimum p_H is 2·0. Inorg. N aids citric acid formation and the addition of $CaCO_3$ to produce p_H 6 favours the production of gluconic acid. Max. yields of citric acid are obtained by partial neutralisation of the acid with $CaCO_3$, while maintaining the $p_H \nless 3$. The temporary reduction of [H˙] during the first 12—24 hr. of growth is ascribed to the transition of inorg. to org. P. A. G. Pollard.

Mechanism of the synthesis of fats from carbohydrates. P. R. Bohn (Compt. rend., 1931, **193**, 441—442).—The fat content of cells of *Aspergillus niger* increases markedly when the lævulose in the medium is increased from 3 to 40%. Although the N content decreases, the efficiency of the fat synthesis is of the same order as is observed with dextrose (A., 1927, 797). A. Cohen.

Production of a growth regulator by *Aspergillus niger*. P. Boysen-Jensen (Biochem. Z., 1931, **239**, 243—249; cf. this vol., 1091).—*A. niger* produces considerable amounts of the regulator in both solid and liquid nutrient media, of which peptone and hæmoglobin solutions are amongst the best. No regulator is produced by peptic digestion of fibrin, hæmoglobin, or caseinogen, or by *A. niger* when the only N available is inorg. or when solutions of malt extract and ovalbumin form the medium. W. McCartney.

Oligodynamic action of copper. W. Schwartz and H. Steinhart (Arch. Mikrobiol., 1931, **2**, 261—271).—During its growth *Aspergillus niger* takes up Cu from nutrient solutions. The absorption curve is largely independent of the initial concentration of Cu in the nutrient. The max. intake of Cu is reached during the first day's growth and with subsequent growth the Cu content of the mycelium declines. A. G. Pollard.

Influence of calcium and strontium on the catalysis of nitrogen fixation by *Azotobacter*. D. Burk and H. Lineweaver (Arch. Mikrobiol., 1931, **2**, 155—186).—The fixation of N by *Azotobacter* demands 25—50 p.p.m. of Ca or Sr in the medium. The suitability of numerous Ca and Sr salts for this purpose is examined. No other elements can replace Ca or Sr. For the growth of *Azotobacter* in fixed N Ca and Sr are not required provided there is a sufficiency of other elements (*e.g.*, Mg, Ba, Be). The rate of growth of the organism in free N_2 depends on the concentration of the organism present. In this respect the ratio concentration of organism : concentration of Ca is important, but plays no part when the organism grows in fixed N. The action of Ca and Sr is exerted within the cell, but the greater part of the Ca required is probably concerned in metabolic processes and not actually in N fixation. In the latter process Ca may have a catalytic action. A. G. Pollard.

Oxidation–reduction potentials in cultures of *Es. coli*. E. M. Boyd and G. B. Reed (Canad. J. Res., 1931, **4**, 605—613; cf. this vol., 527).—In anaërobic buffered broth cultures free from dextrose the beginning of the logarithmic growth period coincides with a sudden fall in oxidation–reduction potential. In presence of dextrose the fall in potential to the limiting negative val. is more rapid and starts at the same time as the evolution of gas, which suggests that the primary aërobic metabolism gradually becomes anaërobic when dextrose is present. There is also present in the cultures a non-gaseous reversible oxidation–reduction system. R. Cuthill.

Bacteria producing trimethylene glycol. C. H. Werkman and G. Gillen (J. Bact., 1931, **21**, 6—7).—Fermentation of glycerol by certain organisms of the *Coli–aerogenes* group yielded 30% of trimethylene glycol. A. G. Pollard.

Oxidation of alcohols by acetic bacteria as a form of cellular respiration. H. Quéré (Compt. rend., 1931, **193**, 445—446).—The O_2 consumption of a type of *B. acetigenum* increases from zero in mineral or dextrose media to vals. in alcoholic media which are inversely proportional to the mol. wt. of the alcohol. The acid fermentation is inhibited by $0{\cdot}0001M$-KCN but not by $0{\cdot}01M$-$CH_2Br{\cdot}CO_2H$. The mechanism of alcohol oxidation is therefore similar to that of respiration. A. Cohen.

Factors influencing the free acidity and p_H of the medium of a lactic–acetic fermentation. V. Bolcato (Giorn. Chim. ind. appl., 1931, **13**, 405—408).—The acidity and p_H developed in a medium undergoing fermentation by the ordinary *Lactobacillus* depend on the contents of buffer salts, colloids, and electrolytes. Buffer salts increase markedly the free acidity and lower the final p_H. Org. compounds having a buffering action and capable of forming colloidal solutions act similarly to salts, but exert also a protective action against the depressing influence of the acids on the organisms. Addition of an electrolyte such as NaCl almost suppresses this protective effect of colloids. It is thus not possible to establish *a priori* the limits of resistance of a micro-organism to acids without a knowledge of the defensive elements—buffer salts and colloids—present in the medium. T. H. Pope.

Reducing substances in milk determine the predominating development of lactic fermentation in milk. P. Mazé and P. J. Mazé, jun. (Compt. rend. Soc. Biol., 1930, **105**, 518—519; Chem. Zentr., 1931, i, 2777).—If a gelose test-tube is inoculated with a young culture rich in lactic acid bacteria, cultures separated by a sterile layer (0·5—1 mm. thick) are obtained. On addition of 2—3 drops of 1% methylene-blue solution the layer becomes thicker and nearer to the surface. A. A. Eldridge.

Action of free oxygen on anaërobic lactic acid bacteria. P. Mazé and P. J. Mazé, jun. (Compt. rend. Soc. Biol., 1930, **105**, 519—520; Chem. Zentr., 1931, i, 2777).—The sterile layer (preceding abstract) is due to the anaërobic metabolic products becoming converted by the action of O_2 into an antiseptic substance, probably derivatives of lactic acid. A. A. Eldridge.

Biological and chemical studies of the *Lactobacillus* genus with special reference to xylose fermentation. L. Weinstein and L. F. Rettger (J. Bact., 1931, **21**, 4—5).—In the fermentation of pentoses by strains of *L. pentoaceticus* from various sources, max. acid production occurred at 33°, the addition of $CaCO_3$ being necessary. 90—95% of the xylose was destroyed in 14—16 days and the yield of acids was equiv. to 85—92% of the carbohydrate. A. G. Pollard.

Rhamnose-fermenting bacillus. A. Castellani (Ann. Inst. Pasteur, 1931, **48**, 297—305).—"*Bacillus rhamnosifermentans*," isolated from certain pathological human fæces, ferments rhamnose with evolution of gas. It has no action on several other carbohydrates and glucosides, and is suggested as a means of identifying rhamnose. A. Cohen.

Gaseous fermentation of erythritol by symbiotic bacteria. A. Castellani and D. Mackenzie (Ann. Inst. Pasteur, 1931, **48**, 306—310).—Mixed cultures of *B. kandiensis* and *B. morgani* ferment erythritol with production of gas containing CH_4 but no CO_2. A. Cohen.

Biological filtration of dilute sucrose solutions. N. W. Barritt (Biochem. J., 1931, **25**, 1419—1446).—The determination of carbohydrate in terms of O_2 absorption is vitiated by the fact that org. synthesis takes place in the process. The nature of the inoculum also affects the relative amounts of oxidation and synthesis. The org. acids formed during the decomp. of sugar are rapidly destroyed by an efficient filter-bed. Lactic and acetic acids are more rapidly oxidised than sucrose. The formation of oxidised N in presence of org. matter promotes the dehydrogenation of lactic acid and probably of other compounds. The film formed accounts for 15% of the sucrose supplied. Aëration is the dominant factor in biological filtration. The rate of flow is the best means of controlling the time of contact and purification. The growth efficiency of film depends on the C/N and C/P_2O_5 ratios. N fixation occurs in the filter-bed, but results in the growth of film of low N content and low purification. A low C/N ratio and a high concentration of org. matter promote the rapid development of the film and attainment of high purification. Both stages of nitrification occur in the filter-bed and are subject to considerable fluctuations not correlated with the supply of N in solution. S. S. Zilva.

Changes in blood-sugar and -phosphorus in rabbits following injection of suspensions of *B. äertrycke*. M. E. Delafield (J. Path. Bact., 1931, **34**, 177—194).—Hyperglycæmia is followed by fatal hypoglycæmia. Inorg. P at first diminishes and then increases. Org. acid-sol. blood-P often tends to increase during hyperglycæmia and decreases during hypoglycæmia. Treatment of the bacterial substances with EtOH, $COMe_2$, or by steaming or autoclaving does not alter the type of chemical response, although the enzyme activity is reduced. Chemical Abstracts.

Possible rôle of micro-organisms in the precipitation of calcium carbonate in tropical seas. C. B. Lipman (Science, 1931, **74**, 151).—A criticism (cf. this vol., 930). L. S. Theobald.

Metabolism of *S* and *R* forms of pneumococcus. P. Finkle (J. Exp. Med., 1931, **53**, 661—676).—A study of the respiration and glycolytic metabolism of various types of pneumococcus. Chemical Abstracts.

Specific and non-specific polysaccharides of type IV pneumococcus. M. Heidelberger and F. E. Kendall (J. Exp. Med., 1931, **53**, 625—639).—Autolysed cultures afford three N-containing polysaccharides: a type-sp. carbohydrate (I), a chemically similar carbohydrate (II) without sp. function, and the *C*-substance (III). (I) had $[\alpha]_D$ +17·0° to 35·0°, N 4·7—5·9%, acid equiv. 1250—3330; (II) had $[\alpha]_D$ +10°, N 5·9%, acid equiv. 4540; (III) had $[\alpha]_D$ +42°, N 6·1%, acid equiv. 1050; the hydrolytic products in each case are AcOH and an amino-sugar derivative, and also glucosamine from (II) and H_3PO_4 from (III). Chemical Abstracts.

Combination of bacterial polysaccharides and collodion particles as antigens. J. Zozaya (Science, 1931, **74**, 270—271).—Anthrax polysaccharide adsorbed on collodion particles is antigenic. L. S. Theobald.

Carbohydrates in biological processes. Fractions of the tubercle bacillus. T. B. Johnson and A. G. Renfrew (Amer. Rev. Tuberculosis, 1930, **22**, 655—663).—Sugars probably form one of the most important classes of bacterial cell constituents; they function in all the fractions which have been separated. Chemical Abstracts.

Carbohydrates produced by tubercle bacilli. M. Dorset and R. R. Henley (J. Amer. Vet. Assoc., 1930, **29**, 696—699).—Tuberculin prepared from cultures of human type on a sugar-free synthetic medium contains a polysaccharide which gives Molisch's test and pentose reactions, but fails to give the naphthoresorcinol test for glycuronic acid. The biuret test is usually positive. The tuberculin potency is decreased by attempts to remove protein. Hydrolysis with HCl affords arabinose and mannose. These sugars were also found in tuberculins of the bovine and avian types. Chemical Abstracts.

Carbohydrates associated with the ether-soluble lipins of tubercle bacilli. R. J. Anderson and E. G. Roberts (Amer. Rev. Tuberculosis, 1930, **22**, 664—668).—The carbohydrates in the phosphatide fraction from avian and bovine tubercle bacilli are described. The Et_2O-sol. constituents of the lipins consist of palmitic acid, oleic acid, and phthioic acid, liquid, saturated, and of high mol. wt. The H_2O-sol. constituents consist of glycerophosphoric acid, mannose, inositol, invert sugar, *d*-arabinose, glucosamine, and unidentified carbohydrates. Chemical Abstracts.

Bacterial derivatives. XII. Preparation of human tubercle bacillus polysaccharide MB-200 and some of its biological properties. P. Masucci, K. L. McAlpine, and J. T. Glenn. **XIII. Occurrence of mannose and *d*-arabinose in the polysaccharide. XIV. Preparation and composition of timothy bacillus polysaccharide MB-200.** P. Masucci and K. L. McAlpine (Amer. Rev. Tuberculosis, 1930, **22**, 669—677, 678—681, 682—684).—XII, XIII.—The gum, $[\alpha]$ +67°, contains 30% of pentose; the sol. sp. N-free substance appears to contain units of mannose, *d*-arabinose, and a sugar acid.

XIV. The polysaccharide, when hydrolysed, affords mannose and *d*-arabinose; it is comparable with that isolated from tubercle bacillus cultures. Chemical Abstracts.

Attempt to influence the growth of tubercle bacillus in the animal body by modifying the concentration of a growth-promoting substance (glycerol) in the tissues. E. R. Long and A. J. Vorwald (Amer. Rev. Tuberculosis, 1930, **22**, 636—654).—Glycerol (fed or injected) enhanced the growth

of tubercle bacilli in lesions in rats; on administration of palmitic acid the extent of tuberculosis was in general decreased, although the fatty acid was deleterious to general health.
CHEMICAL ABSTRACTS.

Ammonium malate as source of nitrogen for tubercle bacilli in cultures. R. R. HENLEY and P. W. LE DUC (Amer. Rev. Tuberculosis, 1930, 22, 568—570).—NH_4 malate can replace asparagine; a medium having p_H 7 is specified.
CHEMICAL ABSTRACTS.

Composition of the active principle of tuberculin. XIV. Analysis of the colloidal components of tuberculin with special reference to the relation of protein and carbohydrate. F. B. SEIBERT and B. MUNDAY (Amer. Rev. Tuberculosis, 1931, 23, 23—40).—The tuberculin action of tuberculin protein appears to be due to a sp. portion of the protein mol. present only in the first hydrolytic cleavage product. Polysaccharide is chemically associated chiefly with these early cleavage products, and cannot be removed by washing, but is released at p_H 4·8. A very potent H_2O-sol. tuberculin has been prepared; the N content is 16% and the polysaccharide content <2·7%. CHEMICAL ABSTRACTS.

Precipitation of diphtheria toxoid by potash alum. A. T. GLENNY and M. BARR (J. Path. Bact., 1931, 34, 131—138).—The amount of sp. toxoid precipitated varied with the quantity of alum in relation to the vol. of a given toxoid. At certain alum concentrations the ppt. is relatively pure, but becomes associated with non-sp. material when kept. The quantity of alum required differs for different toxoids.
CHEMICAL ABSTRACTS.

Ability of aluminium hydroxide *B* to adsorb diphtheria toxin. E. MASCHMANN, E. KÜSTER, and W. FISCHER (Ber., 1931, 64, [*B*], 2174—2178).—Diphtheria toxin is readily adsorbed by $Al(OH)_3$ *A*, *B*, and *C*, but prep. *B* has the most marked selective action. The best results are obtained from dil., faintly acid solutions. With increasing age of $Al(OH)_3$ *B* preserved under H_2O, the adsorptive power decreases greatly, sinking to less than 42% after 4 months. The phenomenon is ascribed, not only to alteration in size of the particles, but also to the conversion of the prep. into another individual of different chemical constitution. This assumption is in agreement with the gradual transformation of dialuminium hydroxide into bayerite (this vol., 1020). H. WREN.

Combined action of silver nitrate and formaldehyde on proteins and micro-organisms. M. DEGANELLO (Arch. Farm. sperim., 1931, 52, 269—282; cf. *ibid.*, 1929, 47, 177).—Addition of $AgNO_3$ and CH_2O to serum causes slow coagulation of the protein, but only in the light and concurrently with reduction of the Ag salt. $AgNO_3$ and CH_2O also increase the viscosity of serum and exert bactericidal action on *Staphylococcus pyogenes aureus*. In all these cases the effects produced by $AgNO_3$ and CH_2O together are greater than the sums of the effects produced by each separately. R. K. CALLOW.

Bactericidal efficiency of certain organic peroxides. B. E. PROCTOR and N. A. MILAS (J. Bact., 1931, 21, 55).—The germicidal power of org. peroxides varied somewhat according to the chemical nature of the parent substances. A. G. POLLARD.

Bactericidal properties of monoethers of dihydric phenols. I. Monoethers of resorcinol. E. KLARMANN, L. W. GUTYAS, and V. A. SHTERNOV.—See this vol., 1289.

Preparation and bacteriological study of *sym.* organic sulphides. F. DUNNING, B. DUNNING, jun., and W. S. DRAKE.—See this vol., 1289.

Effect of adrenaline on some phosphorus compounds of muscle. S. I. VINOKUROV and S. F. EPSTEIN (Arch. exp. Path. Pharm., 1931, 161, 669—673).—In the presence, but not in the absence, of dextrose, muscle perfused with Ringer's solution containing adrenaline shows a decrease of total inorg. P associated with a rise of $H_4P_2O_7$, the acid-sol. P remaining approx. const. W. O. KERMACK.

Origin of dextrose liberated by adrenaline in depancreatised animals. J. L. BOLLMAN, F. C. MANN, and C. M. WILHELMJ (J. Biol. Chem., 1931, 93, 83—91).—Depancreatised dogs were maintained in good condition by large doses of insulin and an appropriate diet including pancreas. The insulin was then withdrawn and after 4 days the liver, muscle, and blood before and after continuous administration of adrenaline for 12 hr. were examined for dextrose and glycogen, whilst the D : N ratio of the urine was determined during the experimental period. Little change occurred in the liver-dextrose and -glycogen or in the blood- and muscle-dextrose, whilst the increase in glycosuria due to the adrenaline could not be accounted for by conversion of protein or fat into dextrose. A marked decrease in the muscle-glycogen corresponded with, and hence was responsible for, the extra dextrose appearing in the urine during adrenaline administration. F. O. HOWITT.

Effect of ultra-violet rays on adrenaline and related products. P. L. EWING, P. BLICKENSDORFER, and H. A. MCGUIGAN (J. Pharm. Exp. Ther., 1931, 43, 125—129).—Adrenaline suffers a decrease in pressor activity, "synephrin" (*p*-hydroxyphenylmethylaminoethanol) an increase when irradiated as the tartrate, citrate, oxalate, or succinate, but not as the base (when it is unchanged), ephedrine a reversal to depressor activity, whilst *ψ*-ephedrine, its sulphate, and *l*-methylephedrine hydrochloride are unchanged. Such changes are probably due to oxidation and may be effected by H_2O_2. F. O. HOWITT.

Influence of electrolytes on the permeability of tissues to crystalline insulin. R. J. HAMBURGER (J. Pharm. Exp. Ther., 1931, 43, 233—243).—A frog's intestinal loop was filled with salt solution containing insulin and the vessels of the mesentery and intestinal walls were perfused by a solution which was subsequently examined by its action on the blood-sugar of the rabbit. Insulin dissolved in Ringer's solution is absorbed, the absorption being decreased by an increase of KCl concentration to 0·1% and nearly inhibited by increase of Ca to 0·1% $CaCl_2,2H_2O$. Replacement of Ringer's by NaCl solution indicates that the permeability of the intestinal mucosa to insulin is increased by $K^{\cdot}$ and decreased by $Ca^{\cdot\cdot}$.
F. O. HOWITT.

Action of thyroxine. K. Oberdisse (Arch. exp. Path. Pharm., 1931, **162**, 150—168).—In rats which have had the dorsal cord cut thyroxnie causes the same increase in CO_2 production as in normal rats. Thyroxine does not act, therefore, through the central nervous system, but directly on the cell. There is a quant. relationship between dosage of thyroxine and its effect on metabolism. A. Cohen.

Influence of intravenous injection of thyroxine on the blood-iodine level and on the urinary iodine excretion in man. J. Bøe and A. W. Elmer (Biochem. Z., 1931, **240**, 187—191).—After intravenous injections of thyroxine (2 mg.) in man, the blood-I increases, the increase being limited to the EtOH-insol. components, but returns to normal in 2 hr. About $\frac{1}{5}$ of the I is excreted in the urine, the excretion being ended after 24 hr.

P. W. Clutterbuck.

Detection of thyroid hormone in the blood in pregnancy. K. J. Anselmino and F. Hoffmann (Arch. Gynäkol., 1931, **145**, 95—103; Chem. Zentr., 1931, i, 2779).—The increase, in rats, of the blood-$COMe_2$ substances after injection of serum of pregnancy is due to the presence of thyroxine, the concentration of which is max. at the end of pregnancy and falls rapidly after parturition. Thyroxine was not detected in fœtal blood. A. A. Eldridge.

Detection of thyroid hormone in the blood of pregnancy. F. Hoffmann and K. J. Anselmino (Arch. Gynäkol., 1931, **145**, 104—113; Chem. Zentr., 1931, i, 2779).—The residue of ultra-filtered serum of pregnancy, when injected into rats, caused a 30% increase in basal metabolism. The active substance (thyroxine) appears in the third or fourth month.

A. A. Eldridge.

Detection of thyroid hormone in the blood of pregnancy, and the effect of increased thyroid activity on the metabolism, course, and nervous irritability of pregnancy. K. J. Anselmino and F. Hoffmann (Arch. Gynäkol., 1931, **145**, 114—131; Chem. Zentr., 1931, i, 2779).

Properties and stability of a powder prepared from anterior pituitary lobe. A. Loeser (Arch. exp. Path. Pharm., 1931, **161**, 730—731).—An active powder prepared from the anterior lobe of the pituitary showed no deterioration when kept for 18 months. W. O. Kermack.

Action of the hormone of the anterior lobe of the pituitary on the oxygen utilisation of guinea-pigs. F. Verzár and V. Wahl (Biochem. Z., 1931, **240**, 37—49).—The hormone increases the metabolism of guinea-pigs (especially of male) by causing increased secretions of the thyroid. The effect is not obtained with thyroidectomised animals but is replaced by a decrease of metabolism. "Prolan" does not produce the effect. P. W. Clutterbuck.

Gonad-stimulating substances of the anterior lobe of the pituitary body and of pregnancy-urine. Z. Wallen-Lawrence and H. B. van Dyke (J. Pharm. Exp. Ther., 1931, **43**, 93—123).—The term "hebin" is proposed for the gonad-stimulating principle of the anterior pituitary lobe. A method of assay of hebin based on the increase in wt. of the seminal vesicles in the male rat or of the ovaries in the female is described. Extraction of the desiccated gland by $M/7{\cdot}5$ acetate buffer at p_H 4·5 and treatment of the extract with 90% EtOH gives an active ppt. with fresh rat, sheep, or pig pituitary glands, but not with fresh ox or rat glands frozen for 9—36 days. The active principle, which initiates follicular maturation, corpus luteum formation, uterine hypertrophy, and œstrus in the hypophysectomised rat, does not dialyse through parchment or collodion and is heat-stable. Hebin prepared from urine of pregnancy by precipitation with EtOH following acidification to p_H 4·5 by AcOH is also non-dialysable, but deteriorates on boiling in aq. solution. Its stimulating action on the testis is equal to, whereas that of pituitary hebin is less than, the effect on the ovary, indicating a extra-hypophyseal origin for the gonad-stimulating principle of urine of pregnancy.

F. O. Howitt.

Increase of metabolism by ovarian hormone. F. Verzár and A. von Árvay (Biochem. Z., 1931, **240**, 28—36).—The basal metabolism of female rats is increased by 10—20% on injection of either of the ovarian hormone preps. menoformon or theelin. Ovarian hormone does not increase the basal metabolism of normal or castrated male rats. The increase of metabolism is obtained after extirpation of the ovaries and the thyroid, but disappears if the genital organs are removed. P. W. Clutterbuck.

Crystalline follicular hormone (ovarian or œstrus hormone). A. Butenandt and G. F. Marrian (Z. physiol. Chem., 1931, **200**, 277—278).—The new triol ("theelol") of Doisy and his co-workers (this vol., 879) has already been characterised by the authors (A., 1930, 1320). J. H. Birkinshaw.

Œstrus-producing hormones. G. F. Marrian and A. Butenandt (Nature, 1931, **128**, 305).—The view of Doisy and co-workers (cf. this vol., 879) that the substance previously described (A., 1930, 1320) is a mixture of both the active substances found in urine of pregnancy is untenable.

L. S. Theobald.

Action of ovarian hormone on plants. W. Schoeller and H. Goebel (Biochem. Z., 1931, **240**, 1—11).—Hyacinths grown in H_2O to which was added 200 mouse units of hormone per week showed development of bloom considerably earlier than the controls. Addition of 100 units per week had no effect, but of 300 units caused injury to roots and general development. This injury was due, however, to lipoidal impurities in the prep. Similar experiments with onions and maize are described.

P. W. Clutterbuck.

Absorption spectrum characteristic of vitamin-*A*. J. W. Woodrow and H. L. Cunningham (Physical Rev., 1930, [ii], **35**, 125).—Fresh cod-liver oil and spinach juice give prominent absorption bands with max. at 310 and 326 mμ, and minor bands at 320, 330, and 337 mμ. Extraction with Et_2O shifts the bands by 3 mμ towards the shorter wave-lengths. Egg-yolk and butter also give these bands. Exposure of cod-liver oil to a quartz–Hg arc for 20 min. or treatment with a current of air at 90° for 1 hr. caused the bands at 310, 320, 326, and 330 mμ to disappear. L. S. Theobald.

Vitamin-B_1. I. Concentration of vitamin-B_1 from rice-polishings. I. A. Simpson (Bull. Inst. Med. Res. Fed. Malay States, 1931, no. 2, 1—10).—Active acid clay prepared according to Jansen and Donath had a pigeon-curative day-dose of 14 mg. Further concentration by the same authors' methods yielded a Pt compound from which a semi-cryst. material was obtained with a curative day-dose of 0·01 mg. R. K. Callow.

Determination of vitamin-B_1. E. F. Chase and H. C. Sherman (J. Amer. Chem. Soc., 1931, 53, 3506—3510).—The rate of growth of rats is determined during 4—8 weeks on a vitamin-*B*-free diet supplemented by autoclaved yeast (for vitamin-B_2) and the material under investigation. H. Burton.

Chemical nature of vitamin-B_1 from evidence afforded by its electrical transference. T. W. Birch and B. C. Guha (Biochem. J., 1931, 25, 1391—1396).—Crude and purified extracts of vitamin-B_1 behave as a base even at p_H 8·5 when electrodialysed at different [H$^•$]. Vitamin-B_1 can be conc. in appreciable quantities free from vitamin-B_2 at the cathode by electrolysing crude yeast extracts. S. S. Zilva.

Physiological function of vitamin-B_1. B. C. Guha (Biochem. J., 1931, 25, 1367—1384).—The requirement of vitamin-B_1 for young growing rats receiving a sub-optimum dose is independent of the protein/carbohydrate ratio of the diet and of the nature of the carbohydrate. With galactose and lactose as sole sources of carbohydrate in the diet the animals decline in wt. Palm-kernel oil and olive oil have little sparing action on vitamin-B_1, whilst lard has a definite effect. The ingestion of Na lactate does not hasten the appearance of symptoms of vitamin-B_1-deficiency in rats, and raises the p_H of the urine of animals on a vitamin-*B*-free diet. The lethal dose of injected Na lactate is lower for deficient than for normal animals. The cytochrome content of the liver, kidney, brain, and heart-muscle tissues of rats is not diminished in vitamin-B_1 deficiency. Lactic acid is oxidised fairly efficiently by the liver and brain tissues of deficient rats. S. S. Zilva.

Galactose as dietary carbohydrate. B. C. Guha (Biochem. J., 1931, 25, 1385—1390).—When galactose is the sole carbohydrate of the diet, mice and rats decline in wt. and die. The animals develop typical "beriberi" symptoms although receiving ample quantities of the vitamin-*B* complex.

S. S. Zilva.

Biochemical lesions in vitamin-*B* deficiency. N. Gavrilescu and R. A. Peters (Biochem. J., 1931, 25, 1397—1409).—Brain tissue from polyneuritic pigeons shows *in vitro* a lowered power of O_2 uptake in the presence of dextrose as substrate. This is the case, when symptoms are prolonged, in all parts of the brain except the cerebellum. The phenomenon is an expression of vitamin-B_1 deficiency. The symptoms of opisthotonus are associated with chemical changes in certain parts of the brain. S. S. Zilva.

Carbohydrate metabolism in birds. III. Effects of rest and exercise on lactic acid content of the organs of normal and rice-fed pigeons. R. B. Fisher (Biochem. J., 1931, 25, 1410—1418).—There are marked differences between the normal and the polyneuritic pigeon in the responses of the lactic acid contents of the heart, liver, and muscle to exercise and rest. These are probably due to the fact that in normal birds lactic acid formed in exercise is removed much more rapidly from the tissues than in polyneuritic birds. S. S. Zilva.

Determination of vitamin-*G* (B_2). A. Bourquin and H. C. Sherman (J. Amer. Chem. Soc., 1931, 53, 3501—3505).—The rate of growth of rats is determined during 4—8 weeks on a vitamin-*B*-free diet to which is added the residue from an 80% EtOH extract of ground whole wheat (*i.e.*, vitamin-B_1) and the material under investigation. H. Burton.

Biological assay of water-soluble antineuritic and antipellagric vitamins. H. T. Graber and R. A. Cowles (J. Amer. Pharm. Assoc., 1931, 20, 876—881).—A review of present methods. Autoclaved yeast and EtOH extract of whole wheat are favoured for antineuritic and antipellagric concentrates, respectively. H. Davson.

Vitamin-*C* content of Japan green tea. H. S. Mitchell (J. Amer. Dietet. Assoc., 1929, 5, no. 1, 28—31).—No demonstrable amount is present.

Chemical Abstracts.

Antiscorbutic vitamin of apples. IV. M. B. Crane and S. S. Zilva (J. Pomology, 1931, 9, 228—231; cf. this vol., 531).—The antiscorbutic potency of Belle de Boskoop equals that of Bramley's Seedling, whilst that of Blenheim Orange and of Lane's Prince Albert is a little lower. The first three varieties are "triploid," and a connexion between high vitamin-*C* content and high chromosome no. is possible.

R. K. Callow.

Antiscorbutic fractions of cabbage and their biological value. N. Bezssonoff (Bull. Soc. Chim. biol., 1931, 13, 950—961).—Addition of neutral $Pb(OAc)_2$ to cabbage juice ppts. the impurities and leaves the vitamin-*C* content unimpaired. On making the filtrate alkaline the vitamin itself is precipitated, but its properties, after removal of Pb, are modified so that it cannot preserve the original wt. of a guinea-pig for 80 days, during which time it is free from scurvy. This is additional evidence of the existence of a C_2 factor. P. G. Marshall.

Standardisation of vitamin-*D* preparations. J. W. R. Everse and J. van Niekerk (Nederl. Tijdschr. Geneeskunde, 1931, 75, I, 1101—1107; Chem. Zentr., 1931, i, 2781).—A graphic method of comparison of the absorption spectrum with the antirachitic activity is described. A. A. Eldridge.

Relation of calcium and phosphorus intake to the hypercalcæmia and hyperphosphatæmia induced by irradiated ergosterol. J. H. Jones and M. Rapoport (J. Biol. Chem., 1931, 93, 153—166).—Normal or thyroparathyroidectomised dogs fed on Ca-poor diet experience an increase in blood-Ca on administration of irradiated ergosterol (4500 *D* units per kg. body-wt.). Administration of Ca gluconate by stomach tube results in a slight rise of serum-Ca and occasionally in serum-P. Simultaneous administration of vitamin-D results in a more pronounced increase in the Ca, whilst the P level is unchanged. Similarly, administration of Na_2HPO_4 produces a slightly greater degree of hyperphosphatæmia after than before administration of irradiated ergosterol, the serum-Ca decreasing in both cases. Aq. suspensions of $CaHPO_4$ normally induce a slight fall in the blood-Ca and practically no change in the P, whereas after vitamin-D administration there is no change in the P, but an increase in the Ca. Vitamin-D appears to function by increasing absorption of Ca and possibly of P from the intestinal tract. F. O. Howitt.

Avitaminosis. XV. Basal metabolism of rats in *E*-avitaminosis with and without administration of the hormone of the anterior lobe of the pituitary. F. Verzár, A. von Árvay, and E. von Kokas (Biochem. Z., 1931, **240**, 19—27).—Changes of the texture of the hair of male rats occur when they receive a diet free from vitamin-E, and complete recovery is obtained either when the vitamin is administered or when the hormone of the anterior lobe of the pituitary is injected. The basal metabolism of rats on a vitamin-E-free diet and of castrated animals is 18% below normal and in both cases is restored to normal by injection of the pituitary hormone. Formation of the hormone normally occurs only when vitamin-E is present in the diet.

P. W. Clutterbuck.

Temperature characteristics for the production of carbon dioxide by germinating seeds of *Lupinus albus* and *Zea Mays*. P. Tang (J. Gen. Physiol., 1931, **15**, 87—95).—The rates of production of CO_2 by germinating seeds of *L. albus* at various temp. below 20° lie on a smooth curve corresponding with a temp. characteristic of 16,100 g.-cal.; the rates above 20° lie on another curve and give a temp. characteristic of 24,000 g.-cal. With germinating seeds of *Zea Mays* there is no point at which discontinuity occurs, the temp. characteristic in this case being 20,750 g.-cal. over the range of temp. employed (12·5—25°). W. O. Kermack.

Effect of certain hydrocarbon oils on the transpiration rate of some deciduous tree fruits. V. W. Kelley (Illinois Agric. Exp. Sta. Bull., 1930, no. 353, 581—600).—Petroleum oils, whether refined or not, reduced transpiration rates of all trees examined. The effect is confined to the under surface of the leaves and is greater in old than in young leaves. A. G. Pollard.

Lignin formation in plants during lignification. K. Sisido (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, **16**, 136—139).—Bamboo lignin is similar to lignin from wood. The OMe content of bamboo lignin increases with age. The pectin and hemicellulose show similar behaviour.

A. A. Levi.

Distribution of lignin in the cell wall of wood. H. E. Dadswell (J. Counc. Sci. Ind. Res. Australia, 1931, **4**, 185—186).—Sections of jarrah wood after destruction of the cellulose with 72% H_2SO_4 showed the lignin from cell walls to be arranged in numerous fine radial lines. Chemical combination of lignin and cellulose in the cell is unlikely. A. G. Pollard.

Chemical study of cranberries. F. W. Morse (Massachusetts Agric. Exp. Sta. Bull., 1930, no. 265, 102 pp.).—During the ripening of cranberries on the vines there is an increase in total sugar content, without appreciable change in the total acid present. During cold storage there is a decrease in sugar by respiration and a smaller decrease in total acid content. A. G. Pollard.

Distribution of the nitrogenous and mineral constituents in the oat plant at different stages of growth. T. W. Fagan and J. E. Watkin (Welsh J. Agric., 1931, **7**, 229—246).—With advancing growth the dry matter content of the whole oat plant rises steadily to the "under-ripe" stage and subsequently increases more rapidly. There is a progressive decrease in total ash, K, CaO, and Cl contents, whilst the PO_4''' content remains practically unchanged. The N content falls steadily to a min. at the "milky-ripe" stage, rising again to the "under-ripe" stage, and finally decreasing somewhat to maturity. In the leaf the % of total ash, P, and N decrease with growth, whilst that of Fe increases slightly. In comparison with other constituents, the proportion of the total CaO of the plant present in the leaf is high and that of PO_4 low. In the stem there is a continuous decrease in the P and N contents from the first appearance of the panicle to the ripe stage. Dry matter and K rise to a max. at the "milky" stage and subsequently decline, whilst the ash and Fe remain practically const. throughout. A high proportion of the total Cl of the plant exists in the leaf at all stages of growth. In the spikelet the % P and N remain const. throughout, but there is a decrease in K, Cl, and CaO with maturity. The migration of N and P from the straw to the spikelet is much more complete than that of the other constituents. The ratio N : P in the spikelet remains const. throughout growth, but in the straw the ratio decreases with maturity. In the spikelet the ratios N : CaO and H_3PO_4 : CaO increase during the ripening stages, but in the straw these ratios decrease from the beginning of panicle formation to the "milky-ripe" stage. A. G. Pollard.

Some carbohydrate and nitrogen constituents of alternate-bearing sugar prunes associated with fruit-bud formation. L. D. Davis (Hilgardia, 1931, 5, no. 6, 119—154).—In a comparison of bearing and disbudded trees the former were characterised by a higher content of reducing substances from about mid-season onward and a lower starch content. The roots of bearing trees had a low, and of disbudded trees a high, proportion of starch. In the aërial portions the starch and moisture contents showed an inverse relationship. The proportion of reducing substances per flower or fruit increased throughout the season, the sugar content rising very rapidly during the 3 weeks prior to maturity.

A. G. Pollard.

Influence of soil moisture on plant growth. K. Tsukunaga (Agric. Exp. Sta. S. Manchuria Rly. Co. Bull., 1930, no. 1, 31—44).—Soya bean and wheat grew best at 80% H_2O-absorbing capacity of the soil, but the seed yield was best at 70%. The H_2O

requirement for the production of 1 g. of dry matter is 1 kg. for soya beans and 0·7 kg. for wheat.

CHEMICAL ABSTRACTS.

Effect of the p_H of the reservoir on the acid–base balance of peat. I. A. SMORODINCEV and A. N. ADOVA (Bull. Soc. Chim. biol., 1931, **13**, 943—949).—If sufficient Na_2CO_3 is added to a suspension of peat (p_H 7·29) to change the p_H immediately to 10·91, a fixation of alkali rapidly occurs which reduces the p_H to 9·71. Penetration varies with the amount of alkali added. Additions of NaCl, $CaCl_2$, or HCl (0·003*N*) have scarcely any effect on the acid–base balance of peat. P. G. MARSHALL.

Effects of Shive's three-salt nutrients on rice seedlings. S. K. MITRA and L. PHUKAN (Proc. XV Indian Sci. Cong., 1928, 167).—Max. root development was associated with a culture in which 0·5 of the total osmotic concentration was due to KH_2PO_4, 0·2 to $MgSO_4$, and 0·3 to $Ca(NO_3)_2$, and min. root development with 0·3, 0·2, and 0·5, respectively.

CHEMICAL ABSTRACTS.

Injection experiments with special reference to the production of alkaloids etc. and general metabolism in plants. S. KRISHNA and H. CHAUDHURI (Proc. XV Indian Sci. Cong., 1928, 224).—Injection of colloidal Fe into the opium poppy diminished the berberine content, but produced berberine when injected into the red poppy.

CHEMICAL ABSTRACTS.

Biochemistry and physiology of organic phosphorus compounds in plants and animals. V. Influence of light and temperature on the occurrence of water-soluble phosphatides in plants. VI. Influence of salts, acids, and alkalis on the occurrence of water-soluble phosphatide in plants. H. MAGISTRIS and P. SCHÄFER (Beitr. Biol. Pflanz., 1930, **18**, 116—140, 141—160; Bied. Zentr., 1931, [ii], **1A**, 367, 368).—I. The extent of exosmosis of phosphates is a direct measure of the permeability of the outer cell-walls. The latter is increased by exposure to light, either before or during dialysis, the shorter waves being particularly effective. Changes in permeability so induced are due to chemical changes in labile mols. rather than to altered physical conditions in the cell-wall. The elimination of H_2O-sol. phosphatides and of phosphates and carbohydrates is increased by rising temp. These changes are reversible.

II. The elimination of phosphatides is increased by the presence of the alkali metal and Mg ions, is arrested by the alkaline earths, and reduced by metallic salts. Acids and alkalis increase permeability in proportion to the concentrations used. CO_2 and H_2S increase exosmosis, the effect being reversible. In their effect on P osmosis cations are arranged in the series, K (greatest), Na, NH_4, . . . Sr.

A. G. POLLARD.

Importance of sulphur and phosphorus in plant nutrition. G. BERTRAND and L. SILBERSTEIN (Ann. sci. agric. franç., 1930, **47**, 324; Bied. Zentr., 1931, [ii], **1A**, 370).—The ratio of S : P in numerous types of plants varied between 0·3 and 1·7, and was greater in leaves than in roots. During flowering the ratio ranged from 0·44 to 1·56. In numerous soils the proportion of S in an assimilable form is insufficient for the normal growth of plants.

A. G. POLLARD.

Anatomical and physiological changes in citrus produced by boron deficiency. A. R. C. HAAS and L. J. KLOTZ (Hilgardia, 1931, **5**, no. 8, 175—197).—B is essential for cell division in the meristematic tissue of the growing points of citrus. B-deficiency is marked by a gradual reduction in the size of buds, a disintegration of the cambium and portions of the phloem, gum formation, and an abnormal accumulation of carbohydrate in the leaves.

A. G. POLLARD.

Formation of chlorophyll and yellow plant pigments. K. SJÖBERG (Biochem. Z., 1931, **240**, 156—186).—The formation of chlorophyll and carotenoids by *Vicia faba* and *Tropæolum majus* was investigated under natural conditions in July—Sept. The amounts of these pigments vary only within narrow limits and the variations can be correlated with changes in daylight. Electric light in addition to daylight in February and March causes an increase in the chlorophyll content of the leaves of *Phaseolus vulgaris*. Short-wave light (Hg lamp) increased the chlorophyll content of young plants in February more than did long-wave light (W lamp). The chlorophyll and carotenoid contents of *Rubus idæus* leaves decrease in autumn but may be brought back almost to the summer vals. by irradiation with electric light. With leaves of *Brassica rapa*, irradiation with light of feebler intensity for a longer time caused quicker and greater pigment formation than irradiation for a shorter time and greater intensity. Both carotene and xanthophyll, but not chlorophyll, are present in the leaves of plants grown in the dark. P. W. CLUTTERBUCK.

Effect of chlorates on the catalase activity of the roots of bindweed. J. R. NELLER (J. Agric. Res., 1931, **43**, 183—189).—Spraying with $NaClO_3$ solution reduced the catalase activity of bindweed roots, the depth of root affected increasing with the concentration of spray used. For the eradication of the plant, the spray strength must be sufficient to lower the catalase activity of the roots to 2 ft. Apparatus for determining catalase activity is described.

A. G. POLLARD.

Chemical investigations of the tobacco plant. I. The non-volatile organic acids of tobacco leaves. II. Changes which occur during the curing of Connecticut shade-grown tobacco. H. B. VICKERY and G. W. PUCHER (Connecticut Agric. Exp. Sta. Bulls., 1931, nos. 323—324, 155—202, 207—240).—I. The org. acids of tobacco leaves are precipitated by $Ba(OH)_2$ in presence of EtOH, and subsequently esterified and fractionated. Malic acid predominates and there is a considerable proportion of citric and small quantities of fumaric, succinic, oxalic, and other acids. Citric is the principal acid of the seed, and malic and fumaric acids occur in small amounts. The $H_2C_2O_4$ content decreases but does not entirely disappear with the development of the plant. Malic acid reaches its max. concentration in the young plant and the proportion does not change appreciably in the mature leaf. Citric acid decreases in maturing green leaf but increases again during curing.

II. During the curing of tobacco the loss in org. solids falls mainly on the protein and the originally insol. carbohydrate of the leaf. Considerable amounts of these constituents are probably transformed into a sol. condition and on subsequent decomp. yield CO_2, H_2O, NH_3, and other volatile substances. About 22% of the nicotine evaporates from the tissues and more than 80% of the sol. carbohydrates of the fresh leaf disappear as such. The crude fibre of the leaves remains unchanged. Much of the leaf protein is hydrolysed to NH_2-acids, which are subsequently involved in the production of amides and NH_3. There is a loss of 14% of the total N, of which only a small proportion is represented by nicotine evaporation. Amides less sol. than asparagine (*e.g.*, those of glutamic or hydroxyaspartic acids) probably exist in curing tobacco. The nitrate-N is not affected by curing. A. G. Pollard.

Resistance to poisons of *Elodea* leaves of different ages. W. A. Collins (Protoplasma, 1931, **12**, 549—553).—The injurious effects of solutions of EtOH, $H_2C_2O_4$, $BaCl_2$, $MgSO_4$, and $AgNO_3$ of similar concentrations, acting for similar times, were greater on old leaves than on young. A. G. Pollard.

Edible cellulose. I. Recovery of crude fibre from raw and cooked potato cellulose. S. Woodruff and E. F. Miller (J. Amer. Dietet. Assoc., 1929, **5**, no. 1, 23—27).—Crude fibre was recovered in fæces of rats in greater amounts when uncooked than when cooked potato was fed.

Chemical Abstracts.

Occurrence of dulcitol in a red seaweed. P. Haas and T. G. Hill (Nature, 1931, **128**, 378).—Dulcitol has been isolated from *Bostryschia scorpioides*.

L. S. Theobald.

Change in composition of soya-beans and iodine values of the oil during periods of maturity. K. Tsukunaga and T. Nishino (Agric. Exp. Sta. S. Manchuria Railway Co., Res. Bull., 1931, no. 2, 21—48).—The N-free extract, crude fibre, and ash contents decrease, whilst the crude protein and Et_2O extract increase, as maturity is approached. The I val. of the oil is max. at 53—54 days after blooming. Oil from soya-beans grown in arid regions or kept long in storage had low I vals.

Chemical Abstracts.

Relation between composition of Manchurian soya-beans and colours of seed-coat and hilum. K. Tsukunaga, H. Ohara, and T. Nishino (Agric. Exp. Sta. S. Manchuria Railway Co., Res. Bull., 1931, no 2, 1—20).—The relation of the colours to the crude protein, N-free extract, crude fibre, and ash contents is recorded. Chemical Abstracts.

Tea-seed oil. A. Heiduschka and C. Shu-Sheng (Arch. Pharm., 1931, **269**, 456—468).—Hydrolysis of the oil obtained either by expressing or extracting the air-dried seeds (containing H_2O 5·49%, saponin 2·73%, and oil 46·89%) gives 95·86% of its wt. of fatty acids. The saturated acids (5·69% of oil) are mainly palmitic and stearic, whilst the unsaturated acids (88·79% of oil) consist of oleic (96—98%) and linoleic (2—4%). Fractional crystallisation of the oil from light petroleum or Et_2O at $-20°$ to $-25°$ affords palmitostearo-olein, m. p. 30·5°; the liquid glycerides present are mainly triolein. The unsaponifiable matter (0·72% of oil) contains 19·7% of phytosterol. Numerous colour reactions of the oil are given. H. Burton.

Unsaponifiable lipins of lettuce. II. Fractionation. III. Antioxidant. H. S. Olcott and H. A. Mattill (J. Biol. Chem., 1931, **93**, 59—64, 65—70).—II. The unsaponifiable fraction of the EtOH extract of dried lettuce leaves was fractionated by the use of org. solvents. Alcohols of high mol. wt. ($COMe_2$-insol. fraction), resins and a substance of m. p. 240—247° (petrol-sol. fraction), carotene and a mixture of sterols (MeOH-insol. fraction), vitamin-*E* and an antioxidant concentrate (92% MeOH-sol. fraction) were isolated. Thus the antioxidant and vitamin-*E* are two distinct entities.

III. Fractional distillation of the antioxidant concentrate yields a fraction, b. p. 165—185°/0·1—0·2 mm., which contains the greatest amount of activity. From this separate active crystals, m. p. 143° (corr.), of probable formula $C_{13}H_{14}O_5$ and yielding an Ac derivative, m. p. 72°, possessing no activity. F. O. Howitt.

Non-nitrogenous constituents of corn-silk. K. Tsukunaga (Agric. Exp. Sta. S. Manchuria Railway Co., Res. Bull., 1931, no. 2, 59—68).—Dry corn-silk contained 52·09% of N-free extract (Et_2O extract 2·20, total N 3·24, non-protein-N 0·66, crude fibre 20·26, ash 0·41%). The carbohydrate is chiefly dextrose, xylan, and galactan. The Et_2O extract contains phytosterol. Chemical Abstracts.

Constituents of the dried rind of the fruit of *Garcinia Gambogia*. K. I. Kuriyan and K. C. Pandya (J. Indian Chem. Soc., 1931, **8**, 469—470).—The aq. extract of the dried rind ("Kadumpuli") contains tartaric acid (10—13·6% of rind), H_3PO_4 (1·52%), reducing sugars (as dextrose) (7·4%), citrate, Fe, Ca, Mg, Na, and K. H. Burton.

Biochemistry of *Salix*. IV. Constitution of salipurposide. C. Charaux and J. Rabaté (Bull. Soc. Chim. biol., 1931, **13**, 814—820).—Hydrolysis of salipurposide yields dextrose and salipurpol, which when treated with $Ba(OH)_2$ or dil. KOH gives phloroglucinol and *p*-coumaric acid. Salipurposide has a marked glycosuric action. C. C. N. Vass.

Comparison of proteins from representatives of the family *Malvaceæ*. A. N. Belozerski (Bull. Univ. Asie Centr., 1929, no. 18, 1—4).—An albumin and two globulins were obtained from the seeds of *Hibiscus cannabinus*, *H. esculentus*, *Abutilon avicennæ*, and *Althæa nudiflora*. Analytical results for histidine-, arginine-, tyrosine-, lysine-N, total N, and S are recorded. Chemical Abstracts.

Potassium atractylate. H. Wunschendorff and P. Brandel (Bull. Soc. Chim. biol., 1931, **13**, 758—763, 764—770).—The aq. extract of the ground root of *Atractylis gummifera*, L., is neutralised with $CaCO_3$, kept at 60° for 20 min., filtered, and left for 24 hr., when inulin is precipitated. The inulin is dissolved in H_2O at 0° and mixed with the supernatant fluid. The solution is treated with CO_2 and filtered. The filtrate is evaporated under reduced pressure to a brown solid which is extracted with 85% EtOH. The alcoholic extract, on evaporation under reduced pressure, yields a syrup which is freed from fats and colouring matter and crystallises on keeping under Et_2O. K atractylate, $C_{25}H_{50}O_{18}S_2K_2$, m. p. 172°, $[\alpha]_D$ −64·39°, sol. in hot EtOH and H_2O giving an acid solution, is a non-reducing glucoside which on acid hydrolysis yields 1 mol. of dextrose, 2 mols. of $KHSO_4$, 1 mol. of valeric acid, and a resin, $C_{19}H_{34}O_6$. C. C. N. VASS.

Ipomœin, a globulin from sweet potatoes, *Ipomœa batatas*. Secondary protein derived from ipomœin by enzymic action. D. B. JONES and C. E. F. GERSDORFF (J. Biol. Chem., 1931, **93**, 119—126).—Sweet potatoes were extracted by 5% aq. NaCl and the extract was treated with AcOH, yielding a ppt. which was dissolved in NaOH and salted out by $(NH_4)_2SO_4$. The crude globulin was purified by re-precipitation and heat-coagulation at 82°. Storage of sweet potatoes at room temp. or the action of proteolytic enzymes on ipomœin results in formation of a secondary protein which was isolated by removal of the ipomœin by acidification and heating the filtrate to 68°. The percentage of NH_2-acids and the N-distribution of the protein and its fission product are given and compared with those of tuberin. F. O. HOWITT.

Change of barley protein in storage and germination. E. TAKAHASHI and K. SHIRAHAMA (J. Fac. Agric. Hokkaido Imp. Univ., 1931, **30**, II, 119—161).—Storage for 1 year increased the 70% EtOH-sol. and decreased the -insol. and H_2O-sol. N; storage for 2—3 years increased the 0·2% NaOH-sol. and decreased the -insol. and H_2O-sol. N. Germination for 72 hr. increased the H_2O-sol. and -insol. and decreased the NaOH- and EtOH-sol. N; that for 120 hr. increased the NaOH-sol. and decreased the -insol. and H_2O-sol. N. No change in 10% NaCl-sol. protein was observed. It appears that the EtOH-sol. and NaOH-sol. and -insol. proteins are synthesised from the H_2O-sol. and NaCl-sol. proteins. Bynin is an EtOH-sol., denatured hordein. CHEMICAL ABSTRACTS.

Characteristic chemical reactions of *Cannabis indica*. L. HÉBERT (Bull. Biol. Pharm., 1931, **2**, 189—190).—Froehde's reaction, which consists of the production of a red coloration when an amyl alcohol extract of *C. indica* is treated with a drop of 0·01% $NaWoO_4$ in H_2SO_4, whilst not sp., is given with all the preps. of the drug, whereas Beam's reaction, in which the residue of a petroleum extract is treated with 5% EtOH solution of KOH to give a violet coloration, is not sp., and is given only by fresh preps. of the drug. Tcherski's reaction is unsuitable. C. C. N. VASS.

Enzymes of *Gibberella Saubinetii*. G. SPITZER and M. M. DIEHM (J. Agric. Res., 1931, **43**, 223—229).—The presence of glucosidase, invertase, catalase, lipase, trypsin, and erepsin is indicated. A. G. POLLARD.

Hydrocyanic acid in sorghum. K. TSUKUNAGA (Agric. Exp. Sta. S. Manchuria Railway Co., Res. Bull., 1931, no. 2, 49—58).—Leaves of *Andropogon sorghum*, Broth., contain 0·0358—0·1066 (dry) % HCN. Variations associated with differences in seed colour and consistency are recorded. Kafir and Sudan grass contain much less HCN. CHEMICAL ABSTRACTS.

Concentration of potassium isotopes in plants. K. HELLER and C. L. WAGNER [with K. LANGER] (Z. anorg. Chem., 1931, **200**, 105—112).—No concentration of K^{41} could be detected in the crude potash from sugar-beet vinasse or leaves. O. J. WALKER.

Sap analysis. I. Carbohydrates. M. SREENIVASAYA and H. N. SASTRY (Proc. XV Indian Sci. Cong., 1928, 163—164).—The dextrins and the greater part of the proteins are removed by addition of 10 vols. of 95% EtOH containing a little NH_3. The alcoholic filtrate is concentrated, tannins etc. are eliminated with dialysed Fe, and the clear filtrate is used for the determination of sugar. Alternatively, the sap can be absorbed on fat-free filter-paper and extracted with alcoholic NH_3. CHEMICAL ABSTRACTS.

Biochemical determination of starch in plants. C. BOURDOUIL (Bull. Soc. Chim. biol., 1931, **13**, 809—813).—After extraction with EtOH, the finely powdered residue is hydrolysed by powdered pancreas at 40° for 4 days and the quantity of reducing sugars determined. The error does not exceed 2%. C. C. N. VASS.

Water hemlock, *Cicuta virosa*. I. Determination of cicutoxin. J. Z. SCHNEIDER (Chem. Obzor, 1931, **6**, 90—94).—Švagr's spectroscopic method is invalid. CHEMICAL ABSTRACTS.

Determination of calcium by alkalimetric titration. II. Precipitation of calcium. C. H. FISKE and M. A. LOGAN (J. Biol. Chem., 1931, **93**, 211—226).—The separation of Ca in presence of large amounts of PO_4''', SO_4'', and $Mg^{\cdot\cdot}$ is effected by precipitation by 1% $H_2C_2O_4$ at p_H 5 when the concentration of Ca is 0·001—0·003% and the solution is 0·5*N* in NH_4Cl or NH_4NO_3, which increase the solubility of MgC_2O_4. The ppt. is washed, dissolved in HNO_3, reconverted into CaC_2O_4 and ignited, the residue being dissolved in excess of 0·02*N*-HCl and titrated with 0·02*N*-NaOH. The application of the method to various types of urine is described. F. O. HOWITT.

Application of the uranyl zinc acetate method for determination of sodium in biological material. A. M. BUTLER and E. TUTHILL (J. Biol. Chem., 1931, **93**, 171—180).—The method of Barber and Kolthoff (A., 1928, 859; 1930, 52) is modified and adapted for analysis of tissue, urine, and fæces. With urine (6 c.c.) PO_4''' is removed by powdered $Ca(OH)_2$ and proteins by solid $HgCl_2$, Na then being precipitated by the U Zn acetate reagent, the ppt. washed with EtOH, dried, and weighed. Fæces and tissue are ashed and extracted with HCl whilst serum is digested with H_2SO_4–HNO_3 and H_2O_2 to remove org. matter. F. O. HOWITT.

F.-p. determination of small quantities of solutions with a thermocouple. T. MINOSIMA (Pflüger's Archiv, 1931, **226**, 794—798; Chem. Zentr., 1931, i, 2789).—The method, employing 0·5—1 c.c. of biological fluids (*e.g.*, toad's blood), is subject to an error of 2%. A. A. ELDRIDGE.