BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

APRIL, 1931.

General, Physical, and Inorganic Chemistry.

Excitation function of atomic hydrogen. L. S. Ornstein and H. Lindeman (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 1097—1100).—A preliminary account is given of a method of exciting atomic hydrogen by electrons of definite velocities. Intensity–exciting potential curves for the H_α and H_β lines between 15 and 60 volts are given.

O. J. Walker.

Relationships between the continuous and the many-lined spectrum of hydrogen. Y. Hukumoto (Sci. Rep. Tôhoku, 1930, **19**, 773—792).—A detailed account of work previously noted (A., 1930, 969).

W. E. Downey.

New band system of hydrogen and the conditions of its production. Z. Bay, W. Finkelnburg, and W. Steiner (Z. physikal. Chem., 1931, **B**, **11**, 351—362; cf. A., 1929, 111).—When a condensed discharge having a mean current strength of 50—200 amp. is passed through hydrogen at pressures between 0·5 and 5 mm., a group of fine lines of great intensity appears between λ 5836 and 5761 Å., accompanied by other lines distributed over the whole spectrum, whilst the remaining complex line spectrum almost disappears.

F. L. Usher.

High-frequency and direct-current discharges in helium. F. L. Jones (Phil. Mag., 1931, [vii], **11**, 163—173).—Measurements of high-frequency and direct-current discharges in helium over the pressure range 1—35 mm. indicate that the mean force in the high-frequency discharges is the same as in the uniform positive column of direct-current discharges. The effect of minute traces of impurities on the luminosity and force of the discharges is discussed.

F. G. Tryhorn.

Excitation probabilities of singlet and triplet states. H. S. W. Massey and C. B. O. Mohr (Nature, 1931, **127**, 234—235).—The probability of excitation of the 2^3P and 2^1P states of helium as a function of the velocity of the exciting electrons has been calculated.

L. S. Theobald.

Beryllium isotope of mass 8, and fine structure measurements in the beryllium hydride bands. W. W. Watson and A. E. Parker (Physical Rev., 1931, [ii], **37**, 167—175; cf. A., 1928, 1305).—With the object of investigating the possible presence of the theoretically predicted Be^8 isotope in beryllium minerals an intense spectrogram of the λ 4991 BeH band was obtained. Every *P* and *R* line of the (0,0) band was accompanied by a very weak line in the position calculated for Be^8H, except where a strong line of another branch prevented measurement. The relative intensities of the Be^8H and Be^9H lines were about 1 : 2000, favouring the presence of the Be^8 isotope.

N. M. Bligh.

Bands in the spectrum of boron hydride. W. Lochte-Holtgreven and E. S. van der Vleugel (Nature, 1931, **127**, 235—236).—The radiation emitted by a condensed discharge in boron trichloride shows widely-spaced bands near 4000 Å. which are ascribed to the molecule BH. The *P* and *R* lines of the strongest band are accompanied in certain cases by weak satellites due to the isotopic molecule $B^{10}H$. The moments of inertia found are I' $2·32\times10^{-40}$ g.-cm.^{2} and I'' $2·35\times10^{-40}$ g.-cm.^{2}, and the internuclear distances $r_0'=r_0''=1·23\times10^{-8}$ cm.

L. S. Theobald.

Rotation temperatures of band spectra in discharge tubes. II. W. Lochte-Holtgreven (Z. Physik, 1931, **67**. 590—600; cf. A., 1930, 1331).—From quantitative intensity determinations of the rotation structure of the C_2 and CH bands for the electric discharge through different hydrocarbons, very high rotation temperatures are deduced. New results for acetylene and ethylene and rotation temperatures are discussed in connexion with the process of disintegration of hydrocarbons.

A. J. Mee.

Dispersion of internal energy in the quadruple and triple terms, 3*sP*, 3*pP*, 3*pD*, in the spectra of carbon, nitrogen, oxygen, and fluorine at various degrees of ionisation. J. Gilles (Compt. rend., 1931, **192**, 350—352).—Relations are shown to exist between the intervals of certain terms of the same and different multiplicities in the spectra of B I, C I and II, N I—III, O I—IV, and F I and III.

C. A. Silberrad.

High-frequency discharge in nitrogen in presence of mercury. R. Zouckermann (Compt. rend., 1931, **192**, 409—411).—The spectra obtained on passing discharges of frequencies 3×10^7 and $10^7\times1/19$ through nitrogen at a pressure of 0·4 mm. in presence of mercury in an electrodeless tube show between 2400 and 4800 Å., the bands of N_2, N_2^+, and CN, several mercury lines. Previous results are discussed, and it is suggested that the bands of N_2^+ are due to collisions of the second kind.

C. A. Silberrad.

Discharge in gases. III. Changes in sparking potential of nitrogen. E. Badareu (Bul. Fac. Stiinte Cernauti, 1930, **4**, 32—49; Chem. Zentr., 1930,

ii, 2613).—A study of the changes in the sparking potential of nitrogen between 0·05 and 2·85 mm. pressure as a function of the interval between two successive discharges, and of the previous discharge.
A. A. Eldridge.

Energy levels of molecular oxygen. J. C. McLennan, H. D. Smith, and J. O. Wilhelm (Trans. Roy. Soc. Canada, 1930, [iii], **24**, III, 65—86).—The absorption spectrum of liquid oxygen has been investigated from λ 2200 to 10,600 Å. Seven new bands between 3000 and 10,600 Å. were observed. A comparative study of the absorption spectra of gaseous, liquid, and solid oxygen seems to show that in their normal state the molecules of oxygen have the same electronic configurations and energy states whether the substance is in the gaseous, liquid, or solid form. W. Good.

Revised values of (0,1) terms, nebular and coronal lines of oxygen. J. J. Hopfield (Physical Rev., 1931, [ii], **37**, 160—166; cf. A., 1928, 1296).—The chief triplet of oxygen λ 1302, measured in the third order of a vacuum grating spectrum having a dispersion of 1·7 Å. per mm. gave the values 109837·1, 109679·17, and 109610·52 for the ground triplet term of oxygen: the ionisation potential of oxygen is 13·55 volts. Experimental details for the production, for the first time in the laboratory, of nebulium lines are described. The previously unidentified coronal line λ 6374 is shown to be identical with the oxygen line λ 6374·29, indicating the presence of oxygen in the solar corona. Complete revised values of the (0,1) terms of oxygen are tabulated.
N. M. Bligh.

Selective excitation of the OH band in the air afterglow. M. Kaczyńska (Z. Physik, 1931, **67**, 601—604).—If the air in which the afterglow is to be produced is mixed with water vapour, the spectrum so obtained not only consists of the already known continuous spectrum, but also contains the OH band at 3064 Å. The intensity of this band increases with the amount of water vapour present. A. J. Mee.

Determination of natural width of the sodium *D* lines by means of a compensation method. M. Weingeroff (Z. Physik, 1931, **67**, 679—698).—The method depends on a combination of magnetic rotation of the plane of polarisation, and light absorption. The mean experimental value is in good agreement with theory, *i.e.*, $0{\cdot}62 \times 10^8$ sec.$^{-1}$ A. J. Mee.

Resonance series in diatomic sulphur vapour. J. Genard (Bull. Acad. roy. Belg., 1931, [v], **16**, 1369—1377).—A continuation of previous work (this vol., 6). Higher dispersion has revealed two further series excited by the lines 3308 and 3349 Cu I. Fluorescence spectra were excited by the lines 2897, 2929, 2934, 3281, 3382, and 3502 Ag at 570°/1 mm.
C. W. Gibby.

The temperature and heat generation in the positive column in argon. W. Pupp (Z. Physik, 1931, **67**, 297—310).—The mean temperature of the positive column in argon at constant pressure for varying current densities has been determined from volume changes for columns of different lengths.
R. W. Lunt.

Intensity measurements of some Cd I hyperfine structures and relation to nuclear angular momentum and isotope ratio. H. Schüler and J. E. Keyston (Z. Physik, 1931, **67**, 433—439).—Apparent contradictions of the experimentally observed intensity distribution in hyperfine structure of the Cd I triplet lines ${}^3P_{0,1,2}$—${}^2S_1$, with theory, when assuming isotopes of nuclear angular momentum 0 and ½ (cf. A, 1929, 967), are explained by discharge tube conditions: these intensity anomalies appear simultaneously with displacements of term levels. 23% of Cd atoms have nuclear angular momentum ½.
A. B. D. Cassie.

Infra-red region of xenon and iron. J. C. McLennan and F. M. Quinlan (Trans. Roy. Soc. Canada, 1930, [iii], **24**, III, 47—52).—Interferometer measurements of the wave-lengths of lines in the infra-red region of the xenon spectrum show that reproduction of the spectrum is difficult, thus making the gas unsuitable as a source of accurate standard wave-lengths. W. Good.

Arc spectrum of rhenium. H. Schober and J. Birke (Naturwiss., 1931, **19**, 211—212).—The rhenium arc spectrum has been investigated over the wave-length range 2000—7000 Å. by introducing rhenium salt solutions into a carbon arc. The lines measured are tabulated and relative intensities indicated. Strong lines occur at 3452·02, 3460·61, and 3464·87 Å. J. W. Smith.

Recombination in mercury vapour. H. W. Webb and D. Sinclair (Physical Rev., 1931, [ii], **37**, 182—193).—Using an apparatus previously described (cf. A., 1929, 480), the afterglow in ionised mercury vapour was studied as a recombination phenomenon. Empirical relations for the results were found, with corresponding critical energies of 1·15 and 1·35 volts.
N. M. Bligh.

Persistence of molecular rotation and vibration in collision. O. Oldenberg (Physical Rev., 1931, [ii], **37**, 194—201).—Theoretical. Some observed exchanges of vibrational and rotational energy of molecules are discussed on the basis of the classical laws of impact in conjunction with the postulate of quantisation. The persistence of rotation of HgH molecules in an excess of nitrogen (cf. Beutler and Rabinovitsch, A., 1930, 1083) is considered, and is related to some chemical activations produced by hydrogen molecules only (cf. Hinshelwood, A., 1927, 630, 1036); the failure of helium to cause a similar effect is accounted for. N. M. Bligh.

Origin of the Fraunhofer lines in the solar spectrum. M. Minnaert (Naturwiss., 1931, **19**, 211).—Measurements have been made of the "total intensity" of a number of Fraunhofer lines.
J. W. Smith.

Stark effect in band spectra. W. G. Penney (Phil. Mag., 1931, [vii], **11**, 602—609).—A theoretical investigation of the effect of an electric field on molecular spectra. The Stark effect is calculated up to terms in E^2 for the first few rotational levels of a rigid body with three different moments of inertia and an electric moment. An expression is derived, which is valid for all rotational states in the case where two

moments of inertia are equal or nearly equal. The Stark effect in diatomic molecules is discussed.
E. S. HEDGES.

Radiation of multipoles. K. F. HERZFELD (Physical Rev., 1931, [ii], 37, 253—259).—Mathematical.

[Light emission, atomic structure, and electron behaviour.] A. SOMMERFELD (Ann. Physik, 1930, [v], 7, 889—891).—Polemical against Stark (cf. A., 1930, 654, 1333, 1493). A. B. D. CASSIE.

Distribution of space-potential in high-frequency glow discharge. D. BANERJI and R. GANGULI (Phil. Mag., 1931, [vii], 11, 410—422).

Radiation emitted by compressed crystalline substances under high potentials. I. A. BALINKIN (Phil. Mag., 1931, [vii], 11, 315—322).

Optical investigation by means of the Kerr effect of spark ignition in air. L. VON HÁMOS (Ann. Physik, 1930, [v], 7, 857—888).

Absorption power of black and white substances used for radiation measurements. E. HASCHÉ (Ann. Physik, 1931, [v], 8, 47—88).—Two methods are described for determination of the reflecting power of diffusely reflecting substances, such as are used in solar pyrometers, between 0·36 and 8 μ. The results confirm Ångström's theory of the pyrometer. Conditions governing an absolute thermopile are discussed. A. B. D. CASSIE.

Evaluation of prism spectrograms by means of Hartmann's formula. P. GRASSMANN (Physikal. Z., 1931, 32, 148—149).—A simple apparatus is described for the evaluation of prism spectrograms, *e.g.*, Raman spectra photographs. A. J. MEE.

Quantitative analysis of emission spectra in any percentage without standard curves. G. SCHEIBE and O. SCHNETTLER (Naturwiss., 1931, 19, 134; cf. A., 1930, 1391).—There is a linear relationship between the blackening and the logarithm of the percentage. The slope of this curve depends not only on the blackening curve, but also on the curve between the percentage and the intensity of the line of the added substance, which need not be linear, as was formerly supposed. A. J. MEE.

Selection rules in the absorption spectra of *X*-rays. M. SIEGBAHN (Z. Physik, 1931, 67, 567—571).—It is shown that selection rules hold for absorption edge frequencies as well as for emission lines. A. J. MEE.

Fine structure of *X*-ray absorption edges. J. PALACIOS and M. VELASCO (Anal. Fís. Quím., 1931, 29, 126—130).—Theoretical. It is shown from measurements with nickel, copper, and iron that for all substances so far investigated the fine structure of the absorption edge can be observed only if the thickness of the absorption layer corresponds with the maximum difference of the intensities transmitted by the two sides of the edge. H. F. GILLBE.

Fine structure of the *K*-absorption spectrum of selenium. S. IDEI (Sci. Rep. Tôhoku, 1930, 19, 653—658).—The fine structure was found and measured; chemical combination has no effect.
W. E. DOWNEY.

Fine structure of the Moseley curves for the *M*-absorption edges in the heavier elements. S. IDEI (Sci. Rep. Tôhoku, 1930, 19, 651—652).—Theoretical. W. E. DOWNEY.

Fine structure of the Moseley curves for the energy levels in the lower elements. S. IDEI (Sci. Rep. Tôhoku, 1930, 19, 641—649).—Theoretical.
W. E. DOWNEY.

Precise measurements of the *L*-group of the *X*-rays from heavy elements. S. IDEI (Sci. Rep. Tôhoku, 1930, 19, 559—639).—Precise measurements have been made for tantalum, tungsten, iridium, platinum, gold, thallium, lead, bismuth, thorium, and uranium. W. E. DOWNEY.

Regularities of *X*-ray spark spectra. S. IDEI (Sci. Rep. Tôhoku, 1930, 19, 551—558).—Theoretical.
W. E. DOWNEY.

Effects of cathode-ray diffusion on intensities in *X*-ray spectra. D. L. WEBSTER, H. CLARK, and W. W. HANSEN (Physical Rev., 1931, [ii], 37, 115—135).—Theoretical. Rediffusion data necessary for the calculation of effects on *X*-ray emission intensities are reviewed. Recent results for the intensity of *K* lines from very thin silver targets (cf. A., 1928, 1294) are corrected for the opposing effects of the diffusion of cathode rays within the target and rediffusion from the support, the error not exceeding 2%; other possible sources of error are shown to be small.
N. M. BLIGH.

Electron velocities as the cause of Compton line breadth. J. W. M. DU MOND and H. A. KIRKPATRICK (Physical Rev., 1931, [ii], 37, 136—159).—The theory that the greater breadth of the Compton shifted line compared with the unshifted or with the primary line is due to the initial velocities of electrons in the scattering body (cf. 1929, 747; Wentzel, A., 1927, 804) was investigated.
N. M. BLIGH.

Thermal theory of cathodic disintegration. H. P. WARAN (Phil. Mag., 1931, [vii], 11, 397—404).—It is suggested that the sputtering of a metal cathode in a discharge tube is due to evaporation of small masses of metal at the points of impact of protons on the electrode in consequence of the localised heat of bombardment. R. CUTHILL.

Apparatus for demonstrating cathode-ray interference. F. KIRCHNER (Physikal. Z., 31, 772—773).—A simple form of apparatus is described which can be easily constructed and is suitable for lecture demonstration and qualitative work.
R. W. LUNT.

Measurement of ionisation current by means of the Zeleny electroscope. R. BARTON (Rev. Sci. Instr., 1931, 2, 118—124).—In the Zeleny electroscope the gold leaf is automatically recharged as it falls, by striking a charged plate. It is shown how the ionisation current may be calculated. The experimental procedure is described. C. W. GIBBY.

Photo-ionisation of cæsium vapour by absorption of principal series wave-lengths. K. FREUDENBERG (Z. Physik, 1931, 67, 417—432).—The photo-ionisation of cæsium vapour was studied by measuring the disturbance by positive ions of the

ii, 2613).—A study of the changes in the sparking potential of nitrogen between 0·05 and 2·85 mm. pressure as a function of the interval between two successive discharges, and of the previous discharge.
A. A. Eldridge.

Energy levels of molecular oxygen. J. C. McLennan, H. D. Smith, and J. O. Wilhelm (Trans. Roy. Soc. Canada, 1930, [iii], 24, III, 65—86).—The absorption spectrum of liquid oxygen has been investigated from λ 2200 to 10,600 Å. Seven new bands between 3000 and 10,600 Å. were observed. A comparative study of the absorption spectra of gaseous, liquid, and solid oxygen seems to show that in their normal state the molecules of oxygen have the same electronic configurations and energy states whether the substance is in the gaseous, liquid, or solid form.
W. Good.

Revised values of (0,1) terms, nebular and coronal lines of oxygen. J. J. Hopfield (Physical Rev., 1931, [ii], 37, 160—166; cf. A., 1928, 1296).—The chief triplet of oxygen λ 1302, measured in the third order of a vacuum grating spectrum having a dispersion of 1·7 Å. per mm. gave the values 109837·1, 109679·17, and 109610·52 for the ground triplet term of oxygen; the ionisation potential of oxygen is 13·55 volts. Experimental details for the production, for the first time in the laboratory, of nebulium lines are described. The previously unidentified coronal line λ 6374 is shown to be identical with the oxygen line λ 6374·29, indicating the presence of oxygen in the solar corona. Complete revised values of the (0,1) terms of oxygen are tabulated.
N. M. Bligh.

Selective excitation of the OH band in the air afterglow. M. Kaczyńska (Z. Physik, 1931, 67, 601—604).—If the air in which the afterglow is to be produced is mixed with water vapour, the spectrum so obtained not only consists of the already known continuous spectrum, but also contains the OH band at 3064 Å. The intensity of this band increases with the amount of water vapour present.
A. J. Mee.

Determination of natural width of the sodium *D* lines by means of a compensation method. M. Weingeroff (Z. Physik, 1931, 67, 679—698).—The method depends on a combination of magnetic rotation of the plane of polarisation, and light absorption. The mean experimental value is in good agreement with theory, *i.e.*, $0{\cdot}62\times10^8$ sec.$^{-1}$
A. J. Mee.

Resonance series in diatomic sulphur vapour. J. Genard (Bull. Acad. roy. Belg., 1931, [v], 16, 1369—1377).—A continuation of previous work (this vol., 6). Higher dispersion has revealed two further series excited by the lines 3308 and 3349 Cu I. Fluorescence spectra were excited by the lines 2897, 2929, 2934, 3281, 3382, and 3502 Ag at 570°/1 mm.
C. W. Gibby.

The temperature and heat generation in the positive column in argon. W. Pupp (Z. Physik, 1931, 67, 297—310).—The mean temperature of the positive column in argon at constant pressure for varying current densities has been determined from volume changes for columns of different lengths.
R. W. Lunt.

Intensity measurements of some Cd I hyperfine structures and relation to nuclear angular momentum and isotope ratio. H. Schüler and J. E. Keyston (Z. Physik, 1931, 67, 433—439).—Apparent contradictions of the experimentally observed intensity distribution in hyperfine structure of the Cd I triplet lines $^3P_{0,1,2}$—$^2S_1$, with theory, when assuming isotopes of nuclear angular momentum 0 and ½ (cf. A, 1929, 967), are explained by discharge tube conditions: these intensity anomalies appear simultaneously with displacements of term levels. 23% of Cd atoms have nuclear angular momentum ½.
A. B. D. Cassie.

Infra-red region of xenon and iron. J. C. McLennan and F. M. Quinlan (Trans. Roy. Soc. Canada, 1930, [iii], 24, III, 47—52).—Interferometer measurements of the wave-lengths of lines in the infra-red region of the xenon spectrum show that reproduction of the spectrum is difficult, thus making the gas unsuitable as a source of accurate standard wave-lengths.
W. Good.

Arc spectrum of rhenium. H. Schober and J. Birke (Naturwiss., 1931, 19, 211—212).—The rhenium arc spectrum has been investigated over the wave-length range 2000—7000 Å. by introducing rhenium salt solutions into a carbon arc. The lines measured are tabulated and relative intensities indicated. Strong lines occur at 3452·02, 3460·61, and 3464·87 Å.
J. W. Smith.

Recombination in mercury vapour. H. W. Webb and D. Sinclair (Physical Rev., 1931, [ii], 37, 182—193).—Using an apparatus previously described (cf. A., 1929, 480), the afterglow in ionised mercury vapour was studied as a recombination phenomenon. Empirical relations for the results were found, with corresponding critical energies of 1·15 and 1·35 volts.
N. M. Bligh.

Persistence of molecular rotation and vibration in collision. O. Oldenberg (Physical Rev., 1931, [ii], 37, 194—201).—Theoretical. Some observed exchanges of vibrational and rotational energy of molecules are discussed on the basis of the classical laws of impact in conjunction with the postulate of quantisation. The persistence of rotation of HgH molecules in an excess of nitrogen (cf. Beutler and Rabinovitsch, A., 1930, 1083) is considered, and is related to some chemical activations produced by hydrogen molecules only (cf. Hinshelwood, A., 1927, 630, 1036); the failure of helium to cause a similar effect is accounted for.
N. M. Bligh.

Origin of the Fraunhofer lines in the solar spectrum. M. Minnaert (Naturwiss., 1931, 19, 211).—Measurements have been made of the "total intensity" of a number of Fraunhofer lines.
J. W. Smith.

Stark effect in band spectra. W. G. Penney (Phil. Mag., 1931, [vii], 11, 602—609).—A theoretical investigation of the effect of an electric field on molecular spectra. The Stark effect is calculated up to terms in E^2 for the first few rotational levels of a rigid body with three different moments of inertia and an electric moment. An expression is derived, which is valid for all rotational states in the case where two

moments of inertia are equal or nearly equal. The Stark effect in diatomic molecules is discussed.
E. S. HEDGES.

Radiation of multipoles. K. F. HERZFELD (Physical Rev., 1931, [ii], 37, 253—259).—Mathematical.

[Light emission, atomic structure, and electron behaviour.] A. SOMMERFELD (Ann. Physik, 1930, [v], 7, 889—891).—Polemical against Stark (cf. A., 1930, 654, 1333, 1493). A. B. D. CASSIE.

Distribution of space-potential in high-frequency glow discharge. D. BANERJI and R. GANGULI (Phil. Mag., 1931, [vii], 11, 410—422).

Radiation emitted by compressed crystalline substances under high potentials. I. A. BALINKIN (Phil. Mag., 1931, [vii], 11, 315—322).

Optical investigation by means of the Kerr effect of spark ignition in air. L. VON HÁMOS (Ann. Physik, 1930, [v], 7, 857—888).

Absorption power of black and white substances used for radiation measurements. E. HASCHÉ (Ann. Physik, 1931, [v], 8, 47—88).—Two methods are described for determination of the reflecting power of diffusely reflecting substances, such as are used in solar pyrometers, between 0·36 and 8 μ. The results confirm Ångström's theory of the pyrometer. Conditions governing an absolute thermopile are discussed. A. B. D. CASSIE.

Evaluation of prism spectrograms by means of Hartmann's formula. P. GRASSMANN (Physikal. Z., 1931, 32, 148—149).—A simple apparatus is described for the evaluation of prism spectrograms, *e.g.*, Raman spectra photographs. A. J. MEE.

Quantitative analysis of emission spectra in any percentage without standard curves. G. SCHEIBE and O. SCHNETTLER (Naturwiss., 1931, 19, 134; cf. A., 1930, 1391).—There is a linear relationship between the blackening and the logarithm of the percentage. The slope of this curve depends not only on the blackening curve, but also on the curve between the percentage and the intensity of the line of the added substance, which need not be linear, as was formerly supposed. A. J. MEE.

Selection rules in the absorption spectra of *X*-rays. M. SIEGBAHN (Z. Physik, 1931, 67, 567—571).—It is shown that selection rules hold for absorption edge frequencies as well as for emission lines. A. J. MEE.

Fine structure of *X*-ray absorption edges. J. PALACIOS and M. VELASCO (Anal. Fís. Quím., 1931, 29, 126—130).—Theoretical. It is shown from measurements with nickel, copper, and iron that for all substances so far investigated the fine structure of the absorption edge can be observed only if the thickness of the absorption layer corresponds with the maximum difference of the intensities transmitted by the two sides of the edge. H. F. GILLBE.

Fine structure of the *K*-absorption spectrum of selenium. S. IDEI (Sci. Rep. Tôhoku, 1930, 19, 653—658).—The fine structure was found and measured; chemical combination has no effect. W. E. DOWNEY.

Fine structure of the Moseley curves for the *M*-absorption edges in the heavier elements. S. IDEI (Sci. Rep. Tôhoku, 1930, 19, 651—652).—Theoretical. W. E. DOWNEY.

Fine structure of the Moseley curves for the energy levels in the lower elements. S. IDEI (Sci. Rep. Tôhoku, 1930, 19, 641—649).—Theoretical. W. E. DOWNEY.

Precise measurements of the *L*-group of the *X*-rays from heavy elements. S. IDEI (Sci. Rep. Tôhoku, 1930, 19, 559—639).—Precise measurements have been made for tantalum, tungsten, iridium, platinum, gold, thallium, lead, bismuth, thorium, and uranium. W. E. DOWNEY.

Regularities of *X*-ray spark spectra. S. IDEI (Sci. Rep. Tôhoku, 1930, 19, 551—558).—Theoretical. W. E. DOWNEY.

Effects of cathode-ray diffusion on intensities in *X*-ray spectra. D. L. WEBSTER, H. CLARK, and W. W. HANSEN (Physical Rev., 1931, [ii], 37, 115—135).—Theoretical. Rediffusion data necessary for the calculation of effects on *X*-ray emission intensities are reviewed. Recent results for the intensity of *K* lines from very thin silver targets (cf. A., 1928, 1294) are corrected for the opposing effects of the diffusion of cathode rays within the target and rediffusion from the support, the error not exceeding 2%; other possible sources of error are shown to be small. N. M. BLIGH.

Electron velocities as the cause of Compton line breadth. J. W. M. DU MOND and H. A. KIRKPATRICK (Physical Rev., 1931, [ii], 37, 136—159).—The theory that the greater breadth of the Compton shifted line compared with the unshifted or with the primary line is due to the initial velocities of electrons in the scattering body (cf. 1929, 747; Wentzel, A., 1927, 804) was investigated. N. M. BLIGH.

Thermal theory of cathodic disintegration. H. P. WARAN (Phil. Mag., 1931, [vii], 11, 397—404).—It is suggested that the sputtering of a metal cathode in a discharge tube is due to evaporation of small masses of metal at the points of impact of protons on the electrode in consequence of the localised heat of bombardment. R. CUTHILL.

Apparatus for demonstrating cathode-ray interference. F. KIRCHNER (Physikal. Z., 31, 772—773).—A simple form of apparatus is described which can be easily constructed and is suitable for lecture demonstration and qualitative work. R. W. LUNT.

Measurement of ionisation current by means of the Zeleny electroscope. R. BARTON (Rev. Sci. Instr., 1931, 2, 118—124).—In the Zeleny electroscope the gold leaf is automatically recharged as it falls, by striking a charged plate. It is shown how the ionisation current may be calculated. The experimental procedure is described. C. W. GIBBY.

Photo-ionisation of cæsium vapour by absorption of principal series wave-lengths. K. FREUDENBERG (Z. Physik, 1931, 67, 417—432).—The photo-ionisation of cæsium vapour was studied by measuring the disturbance by positive ions of the emission of electrons from a heated filament. This magnifies the positive ion current by 10^6. Both the blue $1s$—$3p$ and red $1s$—$2p$ cæsium lines ionised the vapour. The results fit Mohler and Boeckner's conclusion (A., 1930, 1079) that the ions are molecular, and are formed on collision of an excited cæsium atom with an unexcited one. A. B. D. Cassie.

Photo-electric effect with lead and mercury at low temperatures. J. C. McLennan, R. G. Hunter, and J. H. McLeod (Trans. Roy. Soc. Canada, 1930, [iii], **24**, III, 3—23).—Photo-electric currents from lead and mercury have been measured at temperatures down to that of liquid helium. No abrupt change in the photo-electric emission of electrons from lead as the latter was cooled through the temperature range of superconductivity was found. W. Good.

Photo-emission from potassium sensitised by sulphur, selenium, and tellurium. W. Kluge (Z. Physik, 1931, **67**, 497—506).—Experiments are described showing that there exists an optimum layer thickness for sensitising photo-emission from potassium by sulphur, selenium, and tellurium: increased emission is due to a shift of the long wave-length limit, and to selective maxima at 410, 425, and 430 mμ, respectively. A. B. D. Cassie.

Photo-electric electron emission from thin potassium and cæsium layers. R. Fleischer (Physikal. Z., 1931, **32**, 217—218).—For potassium there was a maximum sharing at 436 mμ of $37{\cdot}9\times10^{-2}$ coul./g.-cal., quantum equivalent 1·48 coul./g.-cal., efficiency 25·7%. For cæsium at 492 mμ, the sharing is $17{\cdot}1\times10^{-2}$ coul./g.-cal., quantum equivalent 1·66 coul./g.-cal., and efficiency 10·3%. A. J. Mee.

Electronic interference at organic liquids, especially oils. A. Bühl and E. Rupp (Z. Physik, 1931, **67**, 572—581).—Definite interference can be obtained at oil surfaces by reflexion of electrons of 100—400 volts. Orientation of molecules can be determined. The position of the interference spots can be used to give the plane distances by Bragg's method. For triolein, d=12·3 Å., oleic acid, d=12 Å. (approx.), paraffin oil, d=4—5 Å. The method is suitable for surface analysis, inasmuch as vapour pressure has no effect on electronic reflexion. A. J. Mee.

Dependence of intensity of emission on the velocity of exciting electrons, and the relative intensities of electronically excited Cd and Zn lines. K. Larché (Z. Physik, 1931, **67**, 440—477).—The excitation functions for 42 cadmium and 72 zinc lines were determined between 3·8 and 500 volts. All lines showed one maximum, except those originating in $^1S_0$ levels, which have two (cf. A., 1930, 830). Relative intensities of cadmium and zinc lines between 6500 and 2300 Å. showed 7 triplets and 2 spark doublets which fit the Ornstein–Burger intensity relation. A. B. D. Cassie.

Wave mechanics and the specific charge of the electron. F. Sauter (Naturwiss., 1931, **19**, 165—166).

Effective cross-section of argon and hydrogen towards electrons of 0·2—6 volts. H. Gaertner (Ann. Physik, 1931, [v], **8**, 135—161).—The method of Rusch (A., 1926, 989) for determining the effective cross-section towards slow electrons in a longitudinal field was so modified that it was possible to measure this value for electrons of 0·1 volt. The minimum value found for argon by Rusch at 0·4 volt was corrected and shows good agreement with the work of Townsend and Bailey and of Ramsauer and Kollath (A., 1929, 1123). A. J. Mee.

Ideal gas equation and the properties of the electron and proton. R. D. Kleeman (Z. Elektrochem., 1931, **37**, 77—80).—Mathematical. The ideal gas equation is expressed in a form such that the kinetic energy of the molecules is approximately independent of the volume within certain limits and becomes zero at infinite volume. Interaction of radiation and gas molecules is considered. It is shown that the potential energy of a proton or an electron resulting from its electric field can be converted into internal energy and *vice versa*; as a result of motion radiant energy can be absorbed and converted into internal energy, and can be re-emitted wholly or in part as radiation. H. F. Gillbe.

Discharge by electron impact in hydrogen. S. Vencov (Ann. Physique, 1931, [x], **15**, 131—266).—The electronic discharge in hydrogen was investigated electrically and spectroscopically with the object of correlating critical potentials and the appearance of different spectra. Using a double-grid tube and three methods of potential determination serving as a check on each other, critical potentials were found at 11·5, 16·5, 29·7, and 13·5 volts. The form of the current–potential curves showed that the influence of secondary processes was negligible. The atomic spectrum of hydrogen under electronic bombardment was very weak below 18 volts and increased in intensity to a maximum at 30 volts. The Richardson triplet series of bands decreased in intensity with rise of potential, whilst the singlet system intensity reached a marked maximum and then decreased. The appearance of the continuous resembled, in general, that of the atomic spectrum. N. M. Bligh.

Motion of electrons in argon. H. B. Wahlin (Physical Rev., 1931, [ii], **37**, 260—262; cf. A., 1930, 1082).—The motion of electrons in argon was investigated by the alternating-potential method and results are shown to be in agreement with calculations based on Compton's theory. For low fields the mobility is a constant, but rises rapidly with the field. N. M. Bligh.

Effect of water vapour on the mobilities of negative ions in air. J. J. Nolan (Proc. Roy. Irish Acad., 1930, **39**, **A**, 82—99; cf. A., 1930, 658).—An apparatus for the measurement of mobilities of ions by the Rutherford–Franck alternating-field method is described. Negative ions in moist air favour certain sizes, with corresponding mobilities ranging from 1·5 to 2·4 cm./sec., and increasing with decrease of water vapour pressure. The maximum negative-ion mobility in air dried by contact with sulphuric acid was 2·4 cm./sec. Ions of mobility about 12 cm./sec. have about 0·1% concentration in air containing 0·87 mm. pressure of water vapour. N. M. Bligh.

Production of an intense beam of hydrogen positive ions. L. R. Maxwell (Rev. Sci. Instr., 1931, [ii], 2, 129—140).—An intense beam of hydrogen positive ions is obtained by placing a discharge chamber in a strong magnetic field parallel to the direction of motion of the ions. Beams corresponding with currents up to 3 milliamp. can be produced.
C. W. Gibby.

Charging effect by passage of protons through helium. R. Döpel (Naturwiss., 1931, **19**, 179—180).—An effect analogous to the Ramsauer effect but due to protons has been observed on passing *H*-canal rays through helium. W. E. Downey.

Capture of electrons by positive ions. J. L. Destouches (Compt. rend., 1931, **192**, 345—348).—The author shows that his theory of the Davis–Barnes effect is in agreement with the results obtained by other workers (cf. Barnes etc., A., 1929, 971; 1930, 393; Henderson, A., 1925, ii, 922; Rutherford, A., 1924, ii, 225; Stetter, A., 1927, 494).
C. A. Silberrad.

Trapping of atoms in a magneto-cathodic or cathodic beam. E. Henriot, O. Goche, and (Mlle.) F. Dony-Hénault (J. Phys. Radium, 1931, [vii], 2, 1—11).—An apparatus is described by which it is shown that atoms of tungsten, carbon, platinum, sodium, and sulphur vaporised from a small electrically heated furnace can be trapped in a cathodic or magneto-cathodic beam. N. M. Bligh.

Theory and construction of the spherical mass spectrograph. H. Murawkin (Ann. Physik, 1931, [v], **8**, 203—260).—It is shown that the principal radius is not in general the mean radius, and a correction is therefore necessary in the at. wt. formula. The effect of horizontal and vertical scattering on the resolving power is discussed and a new formula for the resolving power is given. The intensity is directly proportional to the slit width and inversely proportional to the cube of the mean radius. The resolving power of the instrument is almost independent of the apparatus constant, and can be increased with better indicating instruments. A. J. Mee.

Frequency of occurrence of elements. M. F. Soonawala (Indian J. Physics, 1930, **5**, 681—684; cf. A., 1929, 973).—From considerations previously discussed the value of the energy liberated in the nuclear synthesis of isotopes from rare gas nuclei is calculated for ten typical elements and groups, and considered in connexion with the atomic percentage of elements composing the earth. N. M. Bligh.

At. wt. of nitrogen and silver. I. Ratio of ammonia to silver. G. P. Baxter and C. H. Greene (J. Amer. Chem. Soc., 1931, **53**, 604—613; cf. Hönigschmid, Zintl, and Thilo, A., 1927, 806).—The ratio Ag : NH_3 is 6·33420, determined by way of the chlorides and bromides; hence the ratio NO_3 : NH_3 is 3·64083, and the at. wts. of nitrogen and silver are 14·0078 and 107·879, respectively.
J. G. A. Griffiths.

Anomalous scattering of α-particles by light atoms. T. Sexl (Z. Physik, 1931, **67**, 766—779).—A detailed account of work already noted (A., 1930, 516).

Ionisation by α-rays passing through the thin walls of a small sphere. W. Mund (Bull. Soc. chim. Belg., 1930, **39**, 518—528; cf. A., 1925, ii, 732; Glockler, A., 1927, 1003).—The equation expressing the ionisation produced in a spherical vessel by the α-ray emission of radon and of its disintegration products contained in a small sphere enclosed therein is deduced in a modified form. J. W. Smith.

Scattering of hard γ-rays. II. L. H. Gray (Proc. Roy. Soc., 1931, **A**, **130**, 524—541; cf. A., 1930, 372).—The validity of the Klein–Nishina formulæ for heavy elements has been tested by comparing the intensity of the radiation scattered in the forward direction by heavy and light elements, using an ionisation chamber containing oxygen at 85 atm. pressure. The elements compared were magnesium, aluminium, copper, zinc, cadmium, tin, and lead, using radium-*C* γ-rays filtered through 4 cm. of lead, and thorium-*C''* γ-rays filtered through 3 cm. of lead. No variations in the scattering power of different elements have been found beyond such as might be attributed to experimental error (of the order of 1%), and it is concluded that the binding forces are without sensible influence on the scattering power of the extranuclear electrons. Not more than one third of the difference between the absorption coefficients of the thorium-*C''* γ-rays in heavy and light elements can be due to nuclear absorption resulting in the re-emission of approximately isotropic radiation.
L. L. Bircumshaw.

Rate of decay of polonium in various places. L. Bogoiavlenski (J. Phys. Radium, 1931, [vii], 2, 12—19; cf. A., 1929, 737, 1358).—The period of polonium kept from 4 to 5 months at 63 places in Russia varied from 135·5 to 141·1 days. N. M. Bligh.

Groupings of radioactive atoms. E. L. Harrington (Compt. rend., 1931, **192**, 414—415; cf. Jedrzejovski, also Chamié, A., 1929, 620).—Previous results are confirmed, but impurities are not necessary for the formation of the groupings. These are found predominantly at such points as scratches, leaflets, or edges of a mica plate. C. A. Silberrad.

Radiometer effect. E. Brüche and W. Littwin (Z. Physik, 1931, **67**, 333—361).—The radiometer consisted of a platinum leaf 0·01 mm. thick hung between two platinum plates 0·01 mm. thick, one of which could be heated electrically. The radiometer effect was proportional to the excess temperature of the heated surface. At low pressures variation with pressure agreed with Knudsen's theoretical results (cf. A., 1930, 1246) for all gases except hydrogen and helium; at high pressures (0·01 mm.) the effect was inversely proportional to the pressure. At high pressures the effect is proportional to the square of the mean free path of the gas. A. B. D. Cassie.

Dynamics of the atomic nucleus. P. Fadda (Nuovo Cim., 1930, 7, clxiii—clxxxv; Chem. Zentr., 1930, ii, 2993).—A summary and discussion.
A. A. Eldridge.

Quantum mechanics of electrons in crystal lattices. R. de L. Kronig and W. G. Penney (Proc. Roy. Soc., 1931, **A**, **130**, 499—513).—An investigation has been made of the mechanics of electrons in periodic fields of potential such that the energy values and eigenfunctions of the wave-equation can be computed. The spectrum of permissible energy values is found to consist of continuous regions separated by finite intervals.

L. L. Bircumshaw.

Modification of quanta by photo-ionisation. S. Bhargava and J. B. Mukerjie (Nature, 1931, **127**, 273, 305).—Experiments are described indicating that the quantum can impart energy varying from $h\nu$ to $h\nu_k$ to the bound electron and can be modified to any frequency less than $\nu-\nu_k$.

L. S. Theobald.

Spectrum of cosmic rays. E. Regener (Nature, 1931, **127**, 233—234).—Details of absorption of cosmic rays in Lake Constance to a depth of 236·5 m. are given. Four components of different penetrating powers are distinguished.

L. S. Theobald.

Cosmic-ray ionisation–depth curve, and the present evidence for atom building. R. A. Millikan and G. H. Cameron (Physical Rev., 1931, [ii], **37**, 235—252).—Measurements previously reported (cf. A., 1928, 1303) on the relation between cosmic-ray ionisation and depth have been corrected and extended in both directions. Evidence indicates that the strongest and most absorbable band arises from the formation of helium from hydrogen, and the next three bands from the formation of oxygen, silicon, and iron. Proofs are given that the cosmic rays enter the earth's atmosphere as photons, indicating that they must originate in interstellar space rather than in the atmosphere of the stars.

N. M. Bligh.

Transmitted structural blue in microscopic objects. C. W. Mason (J. Physical Chem., 1931, **35**, 73—81).—Particle size or size of structure is correlated with the colours exhibited. Transmitted blue is apparent to the unaided eye with particles or structures coarser than 0·4 μ, and is due to greater deviation of red than blue either by diffraction or scattering. L. S. Theobald.

Absorption spectra of rare-earth double nitrates. D. W. Pearce and J. A. Harris (Trans. Roy. Soc. Canada, 1930, [iii], **24**, III, 145—151).—Double nitrates of bivalent metals with cerium group rare earths were crystallised under identical conditions. From a comparative study of the relative intensity of the most characteristic absorption band of each element the relative efficiencies of the double nitrates as means of separation of the rare elements of this group were determined. W. Good.

Absorption of the carbonyl chromophore in the ultra-violet of short wave-length. H. Ley and B. Arends (Z. physikal. Chem., 1931, **B**, **12**, 132—138).—In hexane solution the maximum of the absorption band of acetone in the ultra-violet is at 187 mμ, and in aqueous solution at a shorter wave-length. Since the maximum of the band in the ultra-violet of long wave-length is displaced in the same direction, Scheibe's theory that the band in the ultra-violet of short wave-length originates in the electrons of the carbon atom of the carbonyl group (A., 1926, 774) is untenable. R. Cuthill.

Application of the resonance radiometer to the reflexion spectrum of quartz. J. D. Hardy and S. Silverman (Physical Rev., 1931, [ii], **37**, 176—181).—The reflexion spectrum of quartz was examined in the region 8—9·5 μ, using light from a Nernst glower and magnesium oxide filtration (cf. Pfund, A., 1930, 1235); high dispersion was obtained by an echelette grating spectrometer. N. M. Bligh.

Behaviour of water with change of temperature and with addition of electrolytes as studied by the Raman effect. I. R. Rao (Proc. Roy. Soc., 1931, **A**, **130**, 489—499; cf. A., 1930, 662; Ganesan and Venkateswaran, A., 1929, 1215).—Accurate wave-length measurements of the bands in the visible and ultra-violet regions of the spectrum have been made. The maximum of the water band lies at about 2·92 μ, with the two extremes at 2·75 and 3·24 μ. In solutions of electrolytes (nitric acid, sodium nitrate and chlorate) the band becomes sharper with increase in concentration and the maximum shifts towards 2·70 μ, a second maximum appearing at 2·79 μ with 76% of nitric acid. A similar effect is found on rise of temperature. It is suggested that these results are due to changes in the proportions of single, double, and triple water molecules. L. L. Bircumshaw.

Raman effect in salt solutions. II. H. Braune and G. Engelbrecht (Z. physikal. Chem., 1931, **B**, **11**, 409—419; cf. A., 1930, 1344).—Mercuric iodide in alcohol shows a strong line, 150 cm.$^{-1}$ The values of $\Delta\nu$ for the bromide and iodide calculated from that in the chloride from heats of dissociation agree with the observed values, supporting the view that the observed frequency is due to symmetrical linear oscillation of the halogen atoms with respect to the mercury atom. The complex halides K_2HgCl_4, K_2HgBr_4, K_2HgI_4 give a Raman spectrum similar to that of the simple halides. Potassium cadmium chloride, like cadmium chloride, shows no Raman effect, but the complex iodide gives a strong line, 118 cm.$^{-1}$ A very weak line of the same frequency can be observed in concentrated solutions of cadmium iodide, and the effect is therefore attributed to the complex anion. Of complex cyanides, potassium argenticyanide alone has a Raman line corresponding with an oscillation of the CN radical with respect to the central atom. F. L. Usher.

Polarisation experiments with the Raman effect with liquids. G. Placzek and W. R. van Wijk (Z. Physik, 1931, **67**, 582—589).—The application of Wood's arrangement for polarisation experiments is possible, and is of advantage because of the short time of exposure necessary. The method was used for the investigation of the polarisation at the critical point of the continuum. A. J. Mee.

Raman effect in certain substances with a new apparatus. B. Venkatesachar and L. Sibaiya (Indian J. Physics, 1930, **5**, 747—754).—An apparatus for the study of the Raman effect for substances in the inner of two coaxial tubes, surrounded by the exciting arc, is described. Results are tabulated for calcite, aragonite, and acetylene; halite, fluorite, and chalk gave negative results. Acetylene gave lines corresponding with the infra-red absorption bands at 2·45 and 7·5 μ; the strong absorption band at 13·7 μ gave no corresponding Raman line. The temperature effect on the continuous wings accompanying unmodified lines in the scattered spectrum was studied, and their origin suggested (cf. Raman and Krishnan, A., 1929, 240). N. M. Bligh.

Raman spectra of organic sulphides. V. N. Thatte and A. S. Ganesan (Nature, 1931, **127**, 306).—Details of the Raman spectra of ethyl and allyl sulphides are recorded and discussed. The former is simple, whilst the latter is rich in lines. L. S. Theobald.

Raman effects with liquid and gaseous nitrous oxide. J. C. McLennan, H. D. Smith, and J. O. Wilhelm (Trans. Roy. Soc. Canada, 1930, [iii], **24**, III, 197—205).—Two frequency shifts, 1282 and 2223 cm.$^{-1}$, were observed in a study of the Raman effect in liquid nitrous oxide. They are shown to correspond respectively with the inactive fundamental vibration of the nitrous oxide molecule and with the fundamental vibration of the central oxygen atom of the molecule along the line of centres of the two nitrogen atoms. W. Good.

Raman effect with acetylene. E. Segrè (Atti R. Accad. Lincei, 1930, [vi], **12**, 226—228).—Details are given of a method of measuring the Raman effect in gases in the visible region. For acetylene, five fine lines of frequencies 25,417, 25,377, 25,318, 22,725, and 20,950 were observed. A diffuse line at a frequency of approximately 21,930 was also noted, of which the interpretation is uncertain. F. G. Tryhorn.

Raman effect. X. Raman spectra of organic substances. A. Dadieu and K. W. F. Kohlrausch (Monatsh., 1931, **57**, 225—240; cf. this vol., 21).—Raman spectra of the following substances have been examined: propylamine, ethylenediamine, aniline, formamide, dicyanodiamide, diethylamine, diphenylamine, trimethylamine, triethylamine, methylnitroamine, chloral, ethyl chloroformate, chloroacetyl chloride, dimethyl ether, and diphenyl ether. The results are discussed. The third frequency characteristic of the oscillating point system $-NH_2$ has not yet been discovered. F. L. Usher.

Ultra-violet absorption spectrum of acetylene. G. B. Kistiakowsky (Physical Rev., 1931, [ii], **37**, 276—278).—Photographs of the ultra-violet bands of carefully purified acetylene in absorption tubes illuminated by a hydrogen discharge tube showed no trace of bands between 3157 and 2236 Å. reported by Henri and Landau (A., 1913, ii, 267), which are attributed to impurities. Bands are observed only below 2400 Å., and are tabulated. The bands are arranged in three progressions and interpreted from infra-red absorption data (cf. Mecke, A., 1930, 1236). N. M. Bligh.

Rational classification of light-scattering media. M. Gurevič (Physikal. Z., 1930, **31**, 753—763).—A general theory of the reflexion and transmission of light at a surface consisting of light-scattering particles is developed which involves two constants characteristic of the medium of which the surface is composed. Experiments are described in which the predictions of the theory are fulfilled. R. W. Lunt.

Fluorescence dissociation of silver iodide vapour. A. Terenin (Physica, 1930, **10**, 209—212; Chem. Zentr., 1930, ii, 2872).—The lines 3383 and 3281 Å. are emitted on photo-dissociation of silver iodide with different intensities dependent on the excitant wave-length. The absorption spectrum of the silver iodide molecule must possess maxima at 2100 and 2060 Å. The dissociation energy of silver iodide is 2·20 volts or 51 kg.-cal. per mol. A. A. Eldridge.

Photo-electric behaviour of salts, particularly of the action of longer wave-lengths on salts previously irradiated with shorter wave-lengths. J. Klaphecke (Z. Physik, 1931, **67**, 478—496; cf. A., 1929, 1217).—The photo-electric effect was studied for sublimed, recrystallised, and dehydrated lead chloride and cadmium iodide. Photo-emission due to long wave-lengths increases rapidly with the number of water molecules present. The results indicate that photo-emission, inner electrical conductivity, phosphorescence, and colouring of the first kind are closely related. A. B. D. Cassie.

Effect of space charge in a gas at low pressures. E. W. B. Gill (Phil. Mag., 1931, [vii], **11**, 95—98).—It is found that, as with a three-electrode valve, so with a two-electrode valve under certain conditions when definite potentials are applied to the electrodes the current passing from the filament to the anode may have two or three different values. F. G. Tryhorn.

Influence of thermal treatment on the characteristics of copper oxide rectifiers. L. Dubar (Compt. rend., 1931, **192**, 484—485).—By comparing the current passing from the oxide to copper with a *P.D.* of 4 volts the best method of treating the copper plate has been ascertained. C. A. Silberrad.

Copper oxide rectifiers. L. Dubar (Compt. rend., 1931, **192**, 341—343).—The explanation of the action of the copper oxide rectifier as stated by Pélabon (cf. B., 1930, 565) is supported by the separate preparation of the semi-conducting layer of mixed cuprous and cupric oxides, and of the semi-insulating layer of pure cuprous oxide. C. A. Silberrad.

Uni-directional conductors (detectors). G. Siemens and W. Demberg (Z. Physik, 1931, **67**, 375—387).—Experiments are described relating to the mechanism of the detector action of lead sulphide in dry and moist gases. R. W. Lunt.

Properties of cuprous oxide. O. von Auwers (Naturwiss., 1931, **19**, 133—134).—The specific resistance of cuprous oxide artificially prepared varies between wide limits. To discover the cause of this, experiments were carried out with outgassed cuprous oxide. In the case of air and hydrogen, with decreasing pressure, the specific resistance decreases; with oxygen, decrease of pressure involves increase of specific resistance, but with nitrogen and neon there was no effect. The resistance increases with the amount of outgassing. Cuprous oxide has a transition point at 56°, above which the transparent oxide becomes opaque. Freshly prepared cuprous oxide has practically no coefficient of expansion up to 56°; above this, there is a measurable coefficient. For the oxide which has been outgassed in a high vacuum there is a measurable coefficient which becomes smaller above 56°. The cuprous oxide lattice depends to a great extent on dissolved substances, and on those adsorbed at its surface. This appears to be general for metallic oxides, *e.g.*, the oxides of nickel, tin, and zinc. A. J. MEE.

Significance of electro- and magneto-photophoresis. F. EHRENHAFT, M. REISS, and E. WASSER (Z. Physik, 1931, **67**, 519—522). Electro- and magneto-photophoresis can be explained by assuming the accommodation coefficient dependent on the electric and magnetic fields. A. B. D. CASSIE.

Super-conductivity. W. MEISSNER (Z. ges. Kälteind., 1930, **37**, 174—177; Chem. Zentr., 1930, ii, 2876).—A summary and discussion.
A. A. ELDRIDGE.

Conductivity of insulating oils. K. F. HERZFELD (Physical Rev., 1931, [ii], **37**, 287—291).—Theoretical. Methods developed in the study of conduction of electricity through gases (cf. *ibid.*, 1929, [ii], **34**, 791) are applied to the measurements of the space charge set up in insulating oils by a steady electric field, in order to determine the nature of the ions present. N. M. BLIGH.

Passage of continuous current through acetone. G. REBOUL and J. SAMBUSSY (Compt. rend., 1931, **192**, 490—491).—The variations in the current observed by Garrigue (cf. A., 1930, 1126) are traced to the presence of light. They disappear in darkness, the current then diminishing regularly and exponentially with time, as found by Lafond.
C. A. SILBERRAD.

Theory of dielectrics. G. GUÉBEN (Phil. Mag., 1931, [vii], **11**, 405—410).—A general expression for the current in a solid dielectric has been deduced, assuming that both ions and dipoles take part in the conduction of the current. R. CUTHILL.

Dielectric constant and conductivity of ionised gases. T. V. IONESCU and C. MIHUL (Compt. rend., 1931, **192**, 343—345).—A curve showing the variations with wave-length of the oscillator (cf. this vol., 285) is given, the results being some 30 times those calculated, which is attributed to resonance. This is supported by the fact that by modifying the method of experiment results have been obtained indicating that in certain circumstances the electrons are associated with molecules of the gas, in which case they possess a definite period of vibration.
C. A. SILBERRAD.

Dielectric constants of liquefied gases. J. C. MCLENNAN, R. C. JACOBSEN, and J. O. WILHELM (Trans. Roy. Soc. Canada, 1930, [iii], **24**, III, 37—46).—The method and results of measurements of the dielectric constants of liquid nitrogen, argon, methane, and nitrous oxide are given. W. GOOD.

Electric moment and molecular structure. I. Ethyl esters of mono- and di-carboxylic acids. C. P. SMYTH and W. S. WALLS. **II. *tert.*-Butyl and triphenylmethyl chlorides and alcohols.** C. P. SMYTH and R. W. DORNTE (J. Amer. Chem. Soc., 1931, **53**, 527—539, 545—555).—I. Dielectric constants and densities of benzene solutions of the esters at 25° and 50° are tabulated. The electric moments at 25° and 50°, respectively, are: ethyl formate, 1·94, 1·93; acetate, 1·86, 1·82; propionate, 1·81, 1·78; maleate, 2·54, 2·56; fumarate, 2·38, 2·40; oxalate, 2·49, 2·52; malonate, 2·54, 2·57; succinate, 2·14, 2·21; glutarate, 2·41, 2·42; adipate, 2·40, 2·42; sebacate, 2·49, 2·50, and hexadecamethylenedicarboxylate, 2·49, $2·48\pm0·02\times10^{-18}$ e.s.u. (cf. A., 1925, ii, 846). It is concluded that long-chain molecules have extended structures which do not bend appreciably in small external electric fields. Owing to free rotation, the relative positions of the carbethoxyl groups in the molecule have only small effects in the electric moment.

II. The dielectric constants and densities of heptane or benzene solutions of the substances have been determined at temperatures between —70° and 70°, and the following electric moments are recorded: *tert.*-butyl chloride, $2·14\times10^{-18}$ e.s.u.; *tert.*-butyl alcohol, 1·65; triphenylchloromethane, 1·95; triphenylcarbinol, 2·11. The polarisation–concentration curves for *tert.*-butyl alcohol in heptane each exhibit a maximum and a minimum. The solutions in benzene conform approximately to the Debye equation. The polarisations indicate that the triphenylmethyl group, unlike the *tert.*-butyl, has a greater screening effect on the field of the dipole than has the *n*-butyl group. The moments of the butyl compounds (A., 1930, 135, 1093; Parts, *ibid.*, 667) are in harmony with the view that the inductive influence of the principal dipole is exerted along a carbon chain to a distance not greater than the second carbon atom.
J. G. A. GRIFFITHS.

Electric moments of organic molecules. VI. "*Ortho* effect" in derivatives of *p*-dichlorobenzene and of *s*-trichloro- and tribromo-benzene. O. HASSEL and E. NÆSHAGEN (Z. physikal. Chem., 1931, **B**, **12**, 79—88; cf. A., 1930, 1348).—Measurement of the dipole moments of the above compounds has yielded further examples of the "*ortho* effect." It seems possible that the *ortho* effect may be of value in determining the configuration of benzene derivatives with three or four substituents.
R. CUTHILL.

Intramolecular field and the dielectric constant. F. G. KEYES and J. G. KIRKWOOD (Physical Rev., 1931, [ii], **37**, 202—215).—Mathematical. A statistical calculation of the average internal field in a dielectric is made, and a relation is obtained between the dielectric constant, the molecular polarisability, the molal volume, and the density; the expression becomes identical with the Clausius–Mosotti relation at zero density, and is applied to dielectric constant measurements on air, nitrogen, hydrogen, carbon dioxide, and ammonia. N. M. BLIGH.

Pleochroic "giant" haloes in cordierite. M. S. KRISHNAN and C. MAHADEVAN (Indian J. Physics, 1930, **5**, 669—680; cf. A., 1927, 956).—More than 200 haloes in 20 thin sections of cordierite gneiss from South India were found to include a few "giant" haloes, having dimensions larger than for normal ranges of α-particles in the uranium and thorium series. They are shown to correspond with the ranges 9·3 cm. for radium-*C'* (cf. Philipp, A., 1929, 371) and 11·5 cm. for thorium-C' (cf. Nimmo, *ibid.*). N. M. Bligh.

Birefringence of safrole. Pauthenier and Bart (Compt. rend., 1931, **192**, 352—353).—In contradiction to Leiser's statement (cf. A., 1911, ii, 563), safrole shows no residual birefringence. Its Kerr constant is $0{\cdot}82\times10^{-7}$ for λ 5460 Å. No hysteresis occurs when the electrostatic field is varied. C. A. Silberrad.

Magneto-optical dispersion of organic liquids in the ultra-violet region of the spectrum. II. Magneto-optical dispersion of methyl propionate, ethyl propionate, and ethyl formate. I. Jenkins and E. J. Evans (Phil. Mag., 1931, [vii], **11**, 377—396; cf. this vol., 24).—The magneto-optical dispersion of the above liquids over the spectral range 0·30—0·45 μ can be represented by equations of the type $n\delta=K_1\lambda^2/(\lambda^2-\lambda_1^2)^2$, where δ and n are the values of Verdet's constant and the refractive index for a wave-length λ, K_1 is a constant which varies from liquid to liquid, and λ_1 is the wave-length of the absorption band. The natural dispersion over the range 0·2700—0·6678 μ is given by the equation $n^2-1=b_0+b_1/(\lambda^2-\lambda_1^2)$, where b_0 and b_1 are constants which increase with the mol. wt. of the liquid. For methyl propionate, ethyl propionate, and ethyl formate the values of λ_1 are 0·1066, 0·1075, and 0·1061 μ, respectively, and the values of e/m calculated from the rotatory power are $0{\cdot}96\times10^7$, $0{\cdot}99\times10^7$, and $0{\cdot}99\times10^7$ e.m.u., respectively. R. Cuthill.

Change in specific magnetic rotation in passing from the liquid to the gaseous state. R. de Malleman and P. Gabiano (Compt. rend., 1931, **192**, 487—489).—The specific magnetic rotations for the gaseous (Λ_g) and liquid (Λ_l) states of eleven paraffins or halogen derivatives thereof, benzene, and carbon disulphide are tabulated, and the values of Λ_g/Λ_l and of $9n\Lambda_l/(n^2+2)^2$ shown to agree respectively with those of $9n/(n^2+2)^2$ (as required by Lorentz' law), and Λ_g, with differences rarely as much as 5%. C. A. Silberrad.

Diamagnetism of free electrons. E. Teller (Z. Physik, 1931, **67**, 311—319).—Theoretical (cf. Landau, A., 1930, 1355).—Boundary conditions are taken into account, but the expression for diamagnetism of free electrons remains unchanged. A. B. D. Cassie.

Paramagnetism of polychromates. F. W. Gray and J. Dakers (Phil. Mag., 1931, [vii], **11**, 297—314).—The magnetic susceptibilities of chromium trioxide and potassium chromate, dichromate, trichromate, and tetrachromate have been measured. The best interpretation of the results is obtained by supposing that the structures of these molecules are similar to those previously postulated for halogenates and perhalogenates (A., 1930, 1101). In the addition of solid chromium trioxide to potassium chromate and the polychromates it appears that the first step is the depolymerisation of the trioxide, which has a deparamagnetising effect, then the single molecules of trioxide combine with single molecules of chromate, the rise in complexity having a paramagnetising effect. R. Cuthill.

Dependence of the susceptibility of diamagnetic metals on the field. W. J. de Haas and P. M. van Alphen (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 1106—1118; cf. this vol., 28).—As in the case of long single crystals of bismuth previously investigated, the susceptibility of a small single crystal (5×5×5 mm.) of bismuth is a periodic function of the field at 20·4° and 14·2° Abs. O. J. Walker.

Magnetic susceptibilities and ionic moments in the palladium and platinum groups. A. N. Guthrie and L. T. Bourland (Physical Rev., 1931, [ii], **37**, 303—308; cf. Bose, A., 1928, 823; Cabrera, A., 1927, 926).—Predictions by Hund's method from spectroscopic theory were investigated by means of an improved Curie balance. Palladium and platinum followed approximately a Curie–Weiss law; ruthenium, rhodium, osmium, and iridium had paramagnetic susceptibilities which increased with rise of temperature. The compounds $RuCl_3$ and IrO_2 followed a Curie–Weiss law which gave for the ions Ru^{III} and Ir^{IV} moments of 9·8 and 13·8 Weiss magnetons per mol. respectively. The paramagnetic susceptibility of Rh_2O_3 was independent of, and that of RuO_2 increased rapidly with, temperature; $IrCl_3$ and $PtCl_2$ are diamagnetic with susceptibilities independent of temperature. N. M. Bligh.

Susceptibility of cupric sulphate pentahydrate at low temperatures; magneton numbers in the iron group. W. J. de Haas and C. J. Gorter (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 1101—1105).—The susceptibility of cupric sulphate pentahydrate between 290° and 14·29° Abs. has been measured. This substance obeys the Curie–Weiss law, with $\theta=-0{\cdot}70°$ and $p=9{\cdot}51$ Weiss magnetons. A comparison of the experimental magneton numbers in the iron group with those calculated from various theories shows that the best agreement is found in the case of the Bose–Stoner theory (cf. A., 1929, 1371). O. J. Walker.

Magnetic susceptibilities of the polyoxymethylenes and formaldehyde solutions. W. Good (J. Roy. Tech. Coll. Glasgow, 1931, **2**, 401—409).—The magnetic susceptibilities (κ) of the four polyoxymethylenes were measured in a Curie balance (error ±1·5%). The values found (α $-0{\cdot}503\times10^{-6}$, β $-0{\cdot}501\times10^{-6}$, γ $-0{\cdot}467\times10^{-6}$, δ $-0{\cdot}417\times10^{-6}$, ordinary trioxymethylene, which is probably a mixture of the β- and γ-compounds, $-0{\cdot}447\times10^{-6}$) are not in agreement with the theoretical values calculated by the law of additivity from the formulæ previously proposed. The results suggest that the polyoxymethylenes are mixtures of substances having the formula $CH_3\cdot[O\cdot CH_2]_n\cdot O\cdot CHO$. J. Grant.

Diamagnetism of polyhalides. F. W. Gray and J. Dakers (Phil. Mag., 1931, [vii], **11**, 81—95).—Measurements have been made of the diamagnetism of numerous halides, and of simple and mixed polyhalides, chiefly derived from tetramethyl-, tetraethyl-, and phenyltrimethyl-ammonium hydroxide. The diamagnetism of these compounds is discussed from the the point of view previously stated (A., 1930, 1101). F. G. Tryhorn.

Stereochemistry of crystalline compounds. IV. Atomic distances in crystals. P. Niggli (Z.

Krist., 1930, 76, 235—251).—The distances between atoms in crystalline binary compounds and in the pure elements are tabulated, and the results discussed with reference to the positions of the elements in the periodic system. Certain regularities are deduced.

C. A. Silberrad.

Change of the magnetic moment of nitric oxide with temperature. E. C. Wiersma, W. J. de Haas, and W. H. Capel (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 1119—1124).—The magnetic moment of the nitric oxide molecule has been determined for the range 292·1—112·77° Abs. The values are in good agreement with those predicted by van Vleck (A., 1928, 572). O. J. Walker.

Thermo-magnetic investigation of certain anhydrous compounds of cobalt and nickel. B. Cabrera and A. Duperier (Anal. Fís. Quím., 1931, **29**, 5—14).—The variation with temperature of the magnetic susceptibility of nickel and cobalt halides and sulphates has been determined at temperatures up to 500—700° Abs. The Curie–Weiss law is valid for cobalt fluoride and sulphate. Nickel fluoride and bromide apparently conform also to the law, but the chloride and sulphate exhibit deviations at the higher temperatures which indicate a transformation of the nickel structure at about 550° Abs. H. F. Gillbe.

Theory of magnetism. K. Honda (Sci. Rep. Tôhoku, 1930, **19**, 745—759).—A modification of the author's earlier theory (cf. A., 1928, 454) enables the gyromagnetic effect as well as the magnetic deflexion of atomic rays in a strong field to be explained.

W. E. Downey.

Hydrates of the alkaline-earth oxides. C. Nogareda (Anal. Fís. Quím., 1931, **29**, 33—64).—The dehydration isotherms of two specimens of calcium hydroxide of the approximate compositions $CaO,3\cdot55H_2O$ and $CaO,4\cdot6H_2O$, prepared by different methods, afford no evidence for the existence of hydrates of the hydroxide. Specimens having the composition of a monohydrate had mol. vol. 47·5—48·6, and appear to be a definite, labile compound. By the vacuum evaporation of a solution of calcium hydroxide at 30° hard transparent crystals of the hydroxide have been obtained without the intermediate formation of a hydrate; the mol. vol. of the crystalline hydroxide is the same as that of the amorphous form. Dehydration isotherms of strontium and barium hydroxides indicate that only the very stable monohydrates and the feebly stable octohydrates exist. The densities are: $Sr(OH)_2,8H_2O$ 1·860 (lit. 1·396—1·90), $Sr(OH)_2,H_2O$ 2·862, $Sr(OH)_2$ 3·305 (lit. 3·625), $Ba(OH)_2,8H_2O$ 2·164 (lit. 1·656), $Ba(OH)_2,H_2O$ 3·743, and $Ba(OH)_2$ 4·463.

H. F. Gillbe.

Hydrates of the alkaline-earth peroxides. II. Constitution. C. Nogareda (Anal. Fís. Quím., 1931, **29**, 131—145).—Octohydrated calcium, strontium, and barium peroxides have *d* 1·700, 1·951, and 2·291, respectively, and the calculated mol. vol. of the anhydrous peroxides are 21·2, 28·3, and 30·0. The volume of the second oxygen atom is thus about 25% of the normal value, viz., 2·9—3·0. All the alkaline-earth peroxides react as true peroxides, *e.g.*, they liberate iodine from neutral iodide solutions and do not yield free hydrogen peroxide when extracted with ether. Isothermal dehydration of the octohydrates proceeds continuously, without any indication of the formation of lower hydrates, until 7·5 mols. of water have been evolved, when decomposition of the peroxides commences. Hydrated strontium peroxide is considerably more stable than the barium and calcium compounds. The dehydrated substances are deficient in oxygen, and the residual water is eliminated only at temperatures above 200°. It appears that the product of dehydration of the octohydrates at the ordinary temperature consists of anhydrous peroxide with about 20% of hydroxide resulting from partial hydrolysis. H. F. Gillbe.

Structure and properties of hydrated oxalic acid. M. A. Rakuzin (Chem.-Ztg., 1931, **55**, 128).—It is shown by discussion of previous work that the water present in crystallised oxalic acid must be regarded as water of crystallisation, and not of constitution. A specimen of the acid when exposed to the air for 29 days at 20° did not lose a trace of water.

H. F. Gillbe.

Stability relationships of complexes formed between metallic salts and organic molecules. Compounds of zinc halides with amines, and their heats of formation. W. Hieber and H. Appel (Z. anorg. Chem., 1931, **196**, 193—212).—The heats of formation of a number of complexes of (solid) zinc chloride, bromide, and iodide with (gaseous) pyridine, aniline, hydrazine, ethylenediamine, and *o*-phenylenediamine have been determined from measurements of the heats of dissolution of the complexes and their components and of the latent heats of evaporation of the organic constituents. The results, expressed as valency–affinity diagrams by plotting the heat of formation against the co-ordination valency, are similar to those obtained with cobalt complexes (A., 1930, 421); thus hydrazine and ethylenediamine behave co-ordinatively as bivalent compounds, and the complexes are of cyclic structure. The heats of formation of the amino-complexes exceed the values for the corresponding ammonia derivatives, and in general diminish in the order ethylenediamine, pyridine, aniline, ammonia, hydrazine. The anion has a specific influence on the stability of the complexes. Whereas the stability of the cobalt compounds diminishes in the order chloride, bromide, iodide, such an effect scarcely exists with the zinc compounds, and in certain series the bromides possess a maximum stability. In complexes of zinc chloride and bromide with from 1 to 3 mols. of *o*-phenylenediamine the latter functions co-ordinatively as a bivalent compound and the complex is therefore cyclic.

The latent heats of evaporation of pyridine, ethylenediamine, and hydrazine at 0° are 10·21±0·05, 16·14±0·08, and 11·50±0·06 kg.-cal. per mol., respectively. H. F. Gillbe.

Formation of molecular aggregates in radon-gas mixtures containing polar molecules. E. L. Harrington and O. A. Gratias (Phil. Mag., 1931, [vii], **11**, 285—296).—A continuation of the investigation previously described (A., 1928, 1301) has shown that the presence of polar molecules favours, and is perhaps necessary for, the formation of molecular aggregates in gas mixtures containing radon and its disintegration products. In no case was the formation of aggregates observed when only non-polar molecules were present. R. CUTHILL.

Scattering of *X*-rays by water and aqueous salt solutions. W. GOOD (Helv. phys. Acta, 1930, 3, 205—248; Chem. Zentr., 1930, ii, 2485—2486).—The application of a correction factor leads to results different from those of other investigators. With concentrated solutions of salts the two water maxima are weakened or absent; hence the formation of such "ice crystallites" is prevented by the marked hydration of the ions. A. A. ELDRIDGE.

Methods in crystal analysis. I. Fourier series and the interpretation of *X*-ray data. II. The enhancement principle and the Fourier series of certain types of functions. A. L. PATTERSON (Z. Krist., 1930, 76, 177—186, 187—200).—The direct application of Fourier analysis to crystal structure problems without the aid of parameter determination is attempted. C. A. SILBERRAD.

***X*-Ray examination of microscopic crystals. I, II.** O. KRATKY (Z. Krist., 1930, 73, 567—571; 76, 261—276).—A description of a suitable apparatus. C. A. SILBERRAD.

Interferometric determination of molecular form. I. H. MARK (Z. angew. Chem., 1931, 44, 125—130).—A survey of recent work on the application of the *X*-ray interferometer to the investigation of the molecular form of simple aliphatic compounds and vapours. H. F. GILLBE.

***X*-Ray interference at di- and tri-atomic molecules of light gases.** H. GAJEWSKI (Physikal. Z., 1931, 32, 219—221).—Scattering experiments were carried out with nitrogen, oxygen, carbon dioxide, ammonia, and the vapours of carbon disulphide and water. The results are used for the determination of the internal dimensions of molecules. A. J. MEE.

Raman lines in *X*-ray spectra. G. A. LINDSAY (Nature, 1931, 127, 305).—Modified lines of a copper radiation scattered by carbon, similar to those described by Ray (A., 1930, 1334), could not be observed. L. S. THEOBALD.

Determination of the thickness of thin transparent crystal layers. G. BAUER (Ann. Physik, 1931, [v], 8, 7—47).—Wiener's correction term (*ibid.*, 1887, 31, 632) determining the thickness of a thin parallel layer lying between two parallel plates is determined for any angle of incidence, and for multiple reflexions. Approximation formulæ are given for layers thin compared with the air thickness, and for layers of thickness comparable with this air space. These formulæ are applied to experimental observations on layers from 1 mμ to several μ in thickness. Experimental conditions necessary to obtain good interference fringes with white light are given in detail; the method is extended to the determination of the thickness of wedge-shaped layers, both thick and thin. The dispersion of lead chloride is between 270 and 650 mμ. This method is applicable to the determination of absolute absorption coefficients for layers such as those used by Hilsch and Pohl (A., 1928, 812). A. B. D. CASSIE.

Nature of a crystallisation centre. A. GLAZUNOV (Coll. Czech. Chem. Comm., 1931, 3, 76—80).—The process of crystallisation is discussed with reference to the structure of the nuclei. Crystallisation in absence of extraneous matter will commence when the temperature at any point falls below a certain level; the volume thus affected will be large compared with the dimension of the crystal lattice. All crystals which grow from one centre form a single grain (crystallite), usually of heterogeneous structure. H. F. GILLBE.

Artificial etched figures on α-sulphur. J. NOVÁK (Z. Krist., 1930, 76, 169—173).—Natural crystals of α-sulphur (from Girgenti) were etched very slowly by a mixture of 92% of ethyl ether and 8% of carbon disulphide. The resulting figures clearly indicate enantiomorphic hemihedry, confirming assignment of α-sulphur to the bisphenoidal class of the orthorhombic system. C. A. SILBERRAD.

Internal and surface structure of organic liquids. J. J. TRILLAT (J. Chim. phys., 1930, 27, 525—542).—Probable causes of error in the *X*-ray investigation of the internal structure of liquids are discussed and an improved photographic technique, whereby disturbances due to the continuous background and to the walls of the containing vessel are in part eliminated, is described; results are given for a series of fatty acids, alcohols, and triglycerides (cf. A., 1930, 672). H. F. GILLBE.

***X*-Ray examination of hydrides of titanium, zirconium, vanadium, and tantalum.** G. HÄGG (Z. physikal. Chem., 1931, B, 11, 433—454; cf. A., 1930, 147).—The products formed by heating some metals in hydrogen have been examined. Vanadium gave diagrams from which no definite information could be obtained. Titanium gives a product, homogeneous between 50 and 60 at.-% H, having face-centred cubic lattice, *a* 4·40 Å. Zirconium, 20—33 at.-% H, face-centred cubic, *a* 4·66 Å.; 33 at.-%, hexagonal close-packed, *a* 3·335, *c* 5·453 Å.; 50 at.-%, face-centred cubic, *a* 4·765 Å.; 67 at.-%, face-centred tetragonal, *a* 4·964, *c* 4·440 Å. Tantalum, 33 at.-% H, hexagonal close-packed, *a* 3·094, *c* 4·923 Å.; 50 at.-%, space-centred rhombic, *a* 4·811, *b* 4·781, *c* 3·434 Å. In the hydride phases with 50 at.-% H the effective radius of the hydrogen atom is 0·46 Å. F. L. USHER.

Crystal structure of lanthanum. J. C. McLENNAN and R. W. McKAY (Trans. Roy. Soc. Canada, 1930, [iii], 24, III, 33—35).—The crystal structure of metallic lanthanum was investigated by the *X*-ray powder method. Hexagonal close-packing was found, the side of the unit cell being equal to 3·72 Å. W. GOOD.

Crystal structure of uranium. J. C. McLENNAN and R. W. McKAY (Trans. Roy Soc. Canada, 1930, [iii], 24, III, 1—2).—The crystal structure of metallic uranium has been investigated by the *X*-ray powder method. The spacings were those of a body-centred cubic arrangement with the side of the unit cell equal to 3·43 Å. W. GOOD.

Atomic grouping and its properties. Experiments on the alloy $AuCu_3$. G. Sachs and J. Weerts (Z. Physik, 1931, 67, 507—515).—*X*-ray photographs showed that the alloy $AuCu_3$ solidified to a single crystal at 800° retains its face-centred cubic structure after annealing for 10 days at 350°. Variations in elastic and electrical properties which occurred during this annealing must therefore be due to subatomic changes. A. B. D. Cassie.

Lattice constants of copper–nickel mixed crystals. W. G. Burgers and J. C. M. Basart (Z. Krist., 1930, 75, 155—157; Chem. Zentr., 1930, ii, 2739).—The values deviate from those required by Vegard's additivity law. A. A. Eldridge.

***X*-Ray investigations of the crystal structure of the ε-phase in the Cu–Sn system.** J. O. Linde (Ann. Physik, 1931, [v], 8, 124—128).—*X*-Ray photographs of the alloy Cu_3Sn in the powdered state showed the two atoms regularly arranged in a grating structure, which could not be correlated with the simple hexagonal packing of spheres. A. B. D. Cassie.

***X*-Ray examination of the system sulphur–selenium. II. Space lattice of monoclinic selenium I.** F. Halla, F. X. Bosch, and E. Mehl (Z. physikal. Chem., 1931, B, 11, 455—463; cf. A., 1930, 1503).—The simplest unit cell has *a'* 11·50, *b'* 8·98, *c'* 8·98 Å., β 90° 57', and contains 32 atoms. Space-group C_{2h}^6. The crystal molecule is probably Se_8. F. L. Usher.

Regularities in the crystal structure of hydrides, borides, carbides, and nitrides of the transition elements. G. Hägg (Z. physikal. Chem., 1931, B, 12, 33—56; cf. A., 1930, 147).—In binary systems consisting of a transition element and hydrogen, boron, carbon, or nitrogen, the phases consist of simple metallic lattices with the metalloid atoms in the interstices, provided that the ratio of the radius of the metalloid atom to that of the metal atom does not exceed 0·59. Phases of this interstitial type are mostly homogeneous for compositions in the neighbourhood of those corresponding with the formulæ M_4X, M_2X, MX, and MX_2, where M is the metal. The metal lattice has usually the cubical closest spherical packing or the hexagonal closest spherical packing, the co-ordination number in both cases being 12. In a few instances, however, the lattice is the body-centred cubic or simple hexagonal with the axial ratio 1; in either case the co-ordination number is 8. R. Cuthill.

Crystal structure and polymorphism of hydrogen halides. G. Natta (Nature, 1931, 127, 235).—The cubic modification of hydrogen chloride has *a* 5·44±0·01 Å. at the transition temperature [98° ?]; the volume of the elementary cell is 161×10^{-24} c.c.; $d_{calc.}$ for a cell containing 4 mols. is 1·49. At 85° Abs. the second form of hydrogen chloride shows numerous lines of which only a certain number correspond with the tetragonal system for *c*/*a* 1·10 with *a* 5·27 Å. Hydrogen bromide is also dimorphous, the high-temperature modification showing at 100° Abs. a face-centred cubic structure, *a* 5·77 Å., $d_{calc.}$ for a cell of 4 mols. 2·78, and the volume of the elementary cell 192×10^{-24} c.c. The low-temperature modification shows tetragonal symmetry (or possibly pseudotetragonal) with *a* 5·55 Å., *c*/*a* 1·10, and the volume of the cell 188×10^{-24} c.c. at 90° Abs. Conclusions concerning the structure of hydrogen iodide (A., 1930, 1099) are revised. The structure is face-centred tetragonal and not face-centred cubic, with *c*/*a* 1·08, and *a* 6·10 Å. at 100° Abs., $d_{calc.}$ 3·45, and the volume of the cell is 245×10^{-24} c.c. The calculated ionic radii are Cl' 1·92, Br' 2·04, and I' 2·21.
L. S. Theobald.

[Crystal] structure of strontium bromide hexahydrate. Z. Herrmann (Z. anorg. Chem., 1931, 196, 79—84).—The orthohexagonal unit cell contains two molecules and has *a* 8·212, *c* 4·146, and *b* 14·23 Å. The space-group is C_{3i}^1. H. F. Gillbe.

Crystal structure of cadmium chloride. L. Pauling and J. L. Hoard (Z. Krist., 1930, 74, 546—551; Chem. Zentr., 1930, ii, 2103).—Cadmium chloride has *a* 6·23 Å., α 36° 2'; space-group C_{3v}^5, D_3^7, or D_{3d}^5. A. A. Eldridge.

Crystal structure of barium tungstate. II. J. Palacios and I. Navarro (Anal. Fís. Quím., 1931, 29, 21—32; cf. A., 1930, 279).—The positions of the oxygen atoms in the elementary prism have been determined and the results are in fair agreement with those derived theoretically from the positions of the barium and tungsten atoms. A microphotometric method for the determination of the relative reflexion intensities is described. H. F. Gillbe.

Habit-variation in crystals of barium and lead nitrates. H. E. Buckley (Z. Krist., 1930, 76, 147—168; cf. this vol., 151).—Crystallisation was effected in three ways. With barium nitrate the octahedral faces ordinarily predominate, but with very slow evaporation the cubic; a trace of carbonate has the same effect. Lead nitrate behaves similarly, but changes its habit more readily. The effect of minute additions of many substances on the habit is described. C. A. Silberrad.

Crystal structure of calcium chromate. J. H. Clouse (Z. Krist., 1930, 76, 285—286).—Calcium chromate, *d* 3·22, is tetragonal; the unit cell has *a* 7·10, *c* 6·19, and contains four molecules. The lattice is body-centred, space-group D_{4h}^{19}. It is isomorphous with zircon and yttrium phosphate and vanadate. Strontium chromate is monoclinic, and like lead chromate isomorphous with monazite.
C. A. Silberrad.

Structure of silver permanganate. W. Büssem and K. Herrmann (Z. Krist., 1930, 74, 458—468; Chem. Zentr., 1930, ii, 2102).—Silver permanganate has *a* 5·66, *b* 8·27, *c* 7·12 Å., with 4 mols. of $AgMnO_4$ in the unit cell; space-group C_{2h}^5.
A. A. Eldridge.

Structure of cubic modification of perchlorates. K. Herrmann and W. Ilge (Z. Krist., 1930, 75, 41—66; Chem. Zentr., 1930, ii, 2739).—The following values of *a* (Å.), *n* (number of mols. in the unit cube), and *d* are recorded for perchlorates: potassium (340°) 7·47, 4, 2·181; ammonium (270°) 7·63, 4, 1·732; thallous (280°) 7·61, —, 4·58; cæsium (250°) 7·96, —, 3·025; rubidium (320°) 7·65, —, 2·71; sodium (380°) 7·25, —, 2·11; silver (200°) 6·92, —, 4·10. The space-group is T^2 or T_d^2. The lattice is ionic of the rock-salt type. A. A. ELDRIDGE.

Fine structure of Tutton's salts. I. Space-group. W. HOFMANN (Z. Krist., 1930, **75**, 158—159; Chem. Zentr., 1930, ii, 2868—2869).—The following values for *a* (±0·02 Å.), *b* (±0·02 Å), *c* (±0·01 Å.), and β are recorded: $(NH_4)_2Mg(SO_4)_2,6H_2O$ 9·28, 12·57, 6·20, 107° 6′; $(NH_4)_2Fe(SO_4)_2,6H_2O$ 9·28, 12·58, 6·22, 106° 50′; $(NH_4)_2Zn(SO_4)_2,6H_2O$ 9·20, 12·47, 6·23, 106° 52′. The unit monoclinic-prismatic cell contains 2 mols.; space-group C_{2h}^5.

A. A. ELDRIDGE.

Crystal structure of cementite. S. B. HENDRICKS (Z. Krist., 1930, **74**, 534—545; Chem. Zentr., 1930, ii, 2103).—Cementite has *a* 4·518, *b* 5·069, *c* 6·736 Å., with 4 mols. of Fe_3C in the unit cell.

A. A. ELDRIDGE.

Crystal structure of Fe_2P, Fe_2N, Fe_3N, and FeB. S. B. HENDRICKS and P. B. KOSTING (Z. Krist., 1930, **74**, 511—533; Chem. Zentr., 1930, ii, 2103).—The compound Fe_3N has *a* 2·695√3; *c* 4·362 Å., closest packed hexagonal; space-group D_6^6. Fe_2N forms with Fe_3N a continuous series of mixed crystals; it has *a* 4·79, *c* 4·42 Å., space-group D_{3a}^1. FeB has *a* 4·053, *b* 5·495, *c* 2·946 Å., with 3·75 mols. in the unit cell; space-group V_h^{16}. Fe_2P has *a* 5·852, *c* 3·453 Å., with 3 mols. in the unit cell; space-group D_{3h}^3.

A. A. ELDRIDGE.

Crystal structure of martensite. E. ÖHMAN (Nature, 1931, **127**, 270—272).—*X*-Ray photograms of quenched steel have been obtained in which the line (101) of the tetragonal phase is separated from the (111) line of γ-iron. The curves showing axial dimensions (*a* and *c*) as a function of carbon content converge to a point corresponding with the edge of the elementary cube of pure α-iron (cf. Kurdjumov and Kaminsky, A., 1928, 1178), confirming the view that the tetragonal martensite is a supersaturated solution of carbon in α-iron. L. S. THEOBALD.

Crystal structure of columbite. J. H. STURDIVANT (Z. Krist., 1930, **75**, 88—108; Chem. Zentr., 1930, ii, 2757).—A specimen of columbotantalite, $(Fe,Mn)(Nb,Ta)_2O_6$, consisting chiefly of columbite, had *a* 5·082, *b* 14·238, *c* 5·730 Å., with 4 mols. in the unit cell: space-group V_h^{14}. A. A. ELDRIDGE.

Structure of enstatite, $MgSiO_3$. B. E. WARREN and D. I. MODELL (Z. Krist., 1930, **75**, 1—14; Chem. Zentr., 1930, ii, 2757—2758).—Hypersthene crystals were used: *a* 18·20, *b* 8·86, *c* 5·20 Å., the unit cell containing 16 mols. of $(Mg,Fe)SiO_3$; space-group V_h^{15}.

A. A. ELDRIDGE.

Structure of danburite. C. DUNBAR and F. MACHATSCHKI (Z. Krist., 1930, **76**, 133—146).—Danburite, $CaB_2Si_2O_8$, is orthorhombic, the unit cell has *a* 8·75, *b* 8·01, *c* 7·72 Å., and contains 4 molecules; space-group V_h^{16}. C. A. SILBERRAD.

Structure of chrysotile. B. E. WARREN and W. L. BRAGG (Z. Krist., 1930, **76**, 201—210).—Chrysotile, $H_4Mg_3Si_2O_9$, is monoclinic, the unit cell has *a* 14·66, *b* 18·5, *c* 5·33 Å., β 93° 16′; space-group probably C_{2h}^3. The structure indicates $(OH)_6Mg_6Si_4O_{11},H_2O$, four to the unit cell. C. A. SILBERRAD.

Crystal structure of muscovite. W. W. JACKSON and J. WEST (Z. Krist., 1930, **76**, 211—227).—Muscovite (from Hundholmen), $KH_2Al_3(SiO_4)_3$, is monoclinic; the unit cell has *a* 5·18, *b* 9·02, *c* 20·04 Å., β 95° 30′, and contains 4 molecules. The space-group is C_{2h}^6. C. A. SILBERRAD.

Crystal structure of bixbyite and the *C*-modification of the sesquioxides. L. PAULING and M. D. SHAPPELL (Z. Krist., 1930, **75**, 128—142; Chem. Zentr., 1930, ii, 2739).—Bixbyite has *a* 9·365 Å., with 16 mols. of $(Mn,Fe)_2O_3$ in the unit cube; space-group T_h^7. The *C*-modifications of the sesquioxides probably have the same structure as bixbyite.

A. A. ELDRIDGE.

[Crystal form of sodium cyanoplatinite.] O. MÜGGE (Z. Krist., 1930, **75**, 32—40; Chem. Zentr., 1930, ii, 2992—2993).—Sodium cyanoplatinite trihydrate, triclinic, has $a:b:c=1{\cdot}7108:1:0{\cdot}8139$, α 94° 57′, β 92° 17′, γ 89° 13·5′. A. A. ELDRIDGE.

Crystallographic relationships between epidote and zoisite. B. GOSSNER and F. MUSSGNUG (Zentr. Min. Geol., 1930, **A**, 369—371; Chem. Zentr., 1930, ii, 3125).—Epidote has *a* 8·96, *b* 5·63, *c* 10·20 Å., β 115° 24′; zoisite has *a* 16·21 (=2×8·10), *b* 5·63, *c* 10·08, β 90°. The unit cell of zoisite contains 4 mols. of $Al_2Ca_2(SiO_4)_3(AlOH)$; epidote has only 2 mols. in the unit cell. A. A. ELDRIDGE.

Comparison of the crystal structures of an additive and a substitution compound. E. HERTEL and K. SCHNEIDER (Z. physikal. Chem., 1931, **B**, **12**, 109—114).—The crystals of aniline picrate and 2 : 4 : 6-trinitrodiphenylamine both have the space-group C_{2h}^5 and two of the principal periods of identity have nearly the same value for each. The difference in the values of the third period of identity is ascribed to the space occupied by the additional molecule of water in the picrate and to a peculiar molecular arrangement in the substitution compound.

R. CUTHILL.

Crystallographic constants. II. G. GILTA (Bull. Soc. chim. Belg., 1930, **39**, 581—589).—The crystallography of a number of organic compounds has been examined. 1 : 4-Dihydroxy-1 : 4-dimethyl*cyclo*hexane, m. p. 193°, is monoclinic, whilst the form m. p. 166° is orthorhombic pseudoquadratic. 2-Acetoxy-*m*-toluic acid, αααββγγ-heptachloropropane, αββ-trichloroacrylamide, and calcium di-*s*-dichloro*iso*propyl phosphate all crystallise in monoclinic forms. The angles of orientation and the parameters are tabulated.

J. W. SMITH.

Silk fibroin. III. O. KRATKY and S. KURIYAMA (Z. physikal. Chem., 1931, **B**, **11**, 363—380; cf. A., 1929, 1222).—Considerable differences are apparent between the lattice structure of fibroin from *Bombyx mori* and from *Satonia*. In *Satonia* the lattice constants are: *a* 6·46, *b* 15·43, *c* 7·2 Å., α 90°, β 90°, γ 61° 10′. In *Bombyx* six possible lattice types are conformable with the measurements.

F. L. USHER.

***X*-Ray determination of the mol. wt. of methylbixin.** J. HENGSTENBURG and R. KUHN (Z. Krist., 1930, **76**, 174—175).—Methylbixin is pseudorhombic monoclinic, *d* 1·10; the unit cell has *a* 10·48, *b* 17·59, *c* 13·40 Å. The calculated mol. wt., 412±2·5%, agrees

better with $C_{26}H_{32}O_4$ (Kuhn, A., 1929, 1456) than with $C_{24}H_{30}O_4$ (Karrer, *ibid.*, 1075).
C. A. Silberrad.

Structure of cellulose nitrate. Desmaroux and Mathieu (Compt. rend., 1931, **192**, 354—355; cf. this vol., 290).—The *X*-ray diagrams previously described indicate the anisotropy of the structure. They are compared with the Debye–Scherrer diagrams of nitrated ramie obtained by Náray-Szabó and others (cf. A., 1928, 48, 818). C. A. Silberrad.

Changes in electrical resistance due to magnetism and hardness. S. R. Williams and R. A. Sanderson (Physical Rev., 1931, [ii], **37**, 309—314; cf. B., 1927, 604).—The increase of resistance of nickel rods due to the magnetic field varied largely with, but the specific resistance was independent of, the degree of hardness (cf. McKeehan, A., 1930, 1504).
N. M. Bligh.

Magnetostriction of overstrained [metallic] materials. J. S. Rankin (J. Roy. Tech. Coll. Glasgow, 1931, **2**, 385—395).—The author's experiments (B., 1930, 376) are extended to the effect produced by permanent stretch and by wire-drawing on the change in length observed when iron, steel, and nickel are magnetised. Recovery from overstrain was not observed with nickel. J. Grant.

Recrystallisation of single aluminium crystals. III. Connexion between deformation phenomena and recrystallisation texture for aluminium. W. G. Burgers and P. C. Louwerse (Z. Physik, 1931, **67**, 605—678).—In order to discover the connexion between a definite deformation and the recrystallisation texture in subsequent recrystallisation, the deformation and recrystallisation of externally, homogeneously strained single aluminium crystals were investigated. A. J. Mee.

Hardening of metals by rotating magnetic fields. E. G. Herbert (Proc. Roy. Soc., 1931, A, **130**, 514—523; cf. B., 1929, 818).—Metals super-hardened by the "cloud-burst" method become still harder by a process of ageing, probably due to atomic re-arrangement. It was proved that in a magnetic material this re-arrangement might be assisted by effecting an artificial atomic disturbance, such as might be caused by a magnetic polarity of changing direction.
L. L. Bircumshaw.

Production of single metal crystals. L. Graf (Z. Physik, 1931, **67**, 388—416).—A new method of making single crystals in an oven, using induction heating, is described. Single crystals were produced from copper, silver, gold, nickel, and gold–silver, gold–copper, and palladium–copper alloys. A simple procedure is given for determining the crystal axes by the *X*-ray rotating-crystal method.
A. B. D. Cassie.

Polishing of surfaces. J. M. Macaulay (J. Roy. Tech. Coll. Glasgow, 1931, **2**, 378—385).—The theory (A., 1926, 998) that the process of surface-polishing by friction involves raising the surface material to its m. p. is supported by the fact that red lead and lead dioxide are changed to litharge, and precipitated chalk to lime, when used as polishing agents on flint glass or cork under a pressure of 1 lb. per in.^{2} for 1—17 hrs. J. Grant.

Allotropic transformation of calcium. E. Rinck (Compt. rend., 1931, **192**, 421—423).—Cooling and resistance curves for metallic calcium show discontinuities near 450°, indicating two forms of calcium: Caα stable below, and Caβ stable above 450°. Attempts to obtain Caβ at the ordinary temperature by sudden cooling failed. C. A. Silberrad.

Degree of orientation in hard-drawn copper wires. W. A. Wood (Phil. Mag., 1931, [vii], **11**, 610—617).—A method is described whereby the degree of orientation may be determined with the aid of a photometer. A core effect is found to exist. A non-oriented layer encloses an oriented core, the line of demarcation being quite sharp. The results are discussed in connexion with the mechanical action of dies. E. S. Hedges.

Allotropy in liquids. I. A. Smits (Z. physikal. Chem., 1931, **153**, 287—298).—The theory of allotropy is re-stated and developed, especially in its application to liquid helium and ethyl ether.
H. F. Gillbe.

Determination of mol. wt. from dialysis coefficients. H. Brintzinger and W. Brintzinger (Z. anorg. Chem., 1931, **196**, 33—43).—Measurements with a large number of sugars and alcohols demonstrate the validity of the linear relationship between the dialysis coefficient and (mol. wt.)$^{\frac{1}{2}}$ (cf., A., 1930, 153), especially for cellophane diaphragms. The constants for different substances vary among themselves less than do those derived from diffusion coefficient measurements, and diminish only slowly with increase of concentration. The presence of other substances within reasonable concentration limits does not interfere with the determination of dialysis coefficients. A convenient form of apparatus is described. Measurements with purified tannin indicate that this substance is a mixture of compounds having different mol. wt., but after dialysis for 2 hrs. the mol. wt. assumes a steady value of 1790.
H. F. Gillbe.

Velocity of sound in substances in the solid and liquid states. M. Reich and O. Stierstadt (Physikal. Z., 1931, **32**, 124—130).—The directional effect in hearing was utilised for the determination of the velocity of sound and the compressibility. The change of velocity at the m. p. was determined for ice-water, mercury, lead, cadmium, tin, and bismuth. Except in the case of bismuth, the velocity of sound is almost twice as great in the solid as in the liquid state. A. J. Mee.

Dispersion and refractive index of nitrogen measured as functions of pressure by displacement interferometry. C. E. Bennett (Physical Rev., 1931, [ii], **37**, 263—275).—An apparatus for the simultaneous measurement of the dispersion and refractive index of nitrogen over a pressure range 1—7 atm. at 0° and 30° is described. The Lorentz–Lorenz relation is followed, and the dispersion is a linear function of the pressure. Values of *n* at *N.T.P.* for λ 4811, 5893, and 6362 Å. are 1·0002991, 1·0002969, and 1·0002967, respectively. Reduction to infinite wave-length leads to the value 1·000585 for the dielectric constant. N. M. Bligh.

Thermal conductivity of gases. E. Brüche and W. Littwin (Z. Physik, 1931, 67, 362—374).—The resistance and temperature of a platinum foil with a constant current passing across it were determined with the foil surrounded by thirteen different gases at pressures between 10^{-5} and 1 mm. Krypton has an extremely low conductivity $(1\cdot9 \times 10^{-5})$ and xenon indicates a still lower one. A. B. D. Cassie.

Estimation of specific heats of gases from vapour-pressure curves. M. Trautz and W. Badstübner (Ann. Physik, 1931, [v], 8, 185—202).—By applying the Clausius equation to experimental vapour-pressure curves, the (negative) temperature coefficient of the mol. heat of evaporation was obtained. The approximate relationship $C_v=c_p-12$ is given, where C_v refers to the vapour, and c_p to the condensed phase. From this relationship, and a knowledge of the vapour-pressure curve and the determined mol. heat of the condensed phase, it is possible to obtain values of the gas-mol. heat.
A. J. Mee.

Methods and apparatus in use at the Bureau of Physico-Chemical Standards. III. F. B. Marti (Bull. Soc. chim. Belg., 1930, 39, 590—626).—Methods for the purification of several solid organic compounds are described. The technique employed for the accurate measurement of m. p., b. p., and of density, viscosity, and surface tension of the compounds in the fused state is detailed. Precision measurements of the rotatory power of mannitol have also been made. J. W. Smith.

Organic compounds proposed as temperature standards. F. Burriel (Anal. Fís. Quím., 1931, 29, 89—125).—The following redetermined m. p. and b. p. are recommended as standards of temperature: salol 41·68°, —, benzophenone 47·85°, 305·9°, naphthalene 80·06°, 217·96°, benzoic acid 122·45°, 250·0$_5$°, phthalic anhydride 131·60°, 285·1°, mannitol 166·00°, —, anthracene 216·0$_5$°, 339·9°, carbazole 240·3$_5$°, —, anthraquinone 284·8$_4$°, 376·8$_5$°. The values of $d_{\text{liq.}}$, viscosity, surface tension, rotatory power, and heat of combustion have also been accurately determined.
H. F. Gillbe.

Vapour pressures of some hydrocarbons. E. G. Linder (J. Physical Chem., 1931, 35, 531—535).—Vapour-pressure data, obtained near 0° by a modification of the Ramsay–Young method, are recorded for 39 hydrocarbons. Disagreements with previous values, notably in the case of mesitylene, *o*- and *p*-xylene, ethylbenzene, *n*- and *iso*-propylbenzene are noted. L. S. Theobald.

Properties of saturated vapours including steam. A. Press (Phil. Mag., 1931, [vii], 11, 111—118).—Two functional equations are derived from the first law of thermodynamics, of which the first represents the universal characteristic and includes Callender's fundamental equation as a special case applying to the mixture region, and the second gives a theoretical basis to all equations of state of the van der Waals type. F. G. Tryhorn.

Thermodynamics of supercooled phases. N. von Raschevsky (Z. Physik, 1931, 67, 531—532).—Entropy remains valid for supercooled phases.
A. B. D. Cassie.

Calculation of entropy and enthalpy of moist gases. G. van Lerberghe and P. Glansdorff (Bull. Acad. roy. Belg., 1931, [v], 17, 60—72).—Mathematical. The conception of affinity due to Donder is applied to the biphasic system formed by a volatile liquid in the presence of a permanent gas. The entropy values are derived as functions of experimental variables, thus rendering it possible to construct entropy diagrams. J. R. I. Hepburn.

Change of density of ethyl ether with temperature. J. Mazur (Nature, 1931, 127, 270).—The density of ethyl ether increases from 0·6964 at 35° to 0·8595 at −105·4°; at lower temperatures, the density still increases but at a much slower rate (cf. A., 1930, 1501, 1554; this vol., 148). At the f. p., −117·2°, the density is 0·8654. L. S. Theobald.

Compressibility isotherms of methane at pressures to 1000 atm. and at temperatures from −70° to 200°. H. M. Kvalnes and V. L. Gaddy (J. Amer. Chem. Soc., 1931, 53, 394—399).—In an extension of previous work, the results of Keyes and Burks (A., 1927, 719) are confirmed. The isotherms have considerable curvature except in the pressure range 500—1000 atm. at 100°. At about 533 atm., methane exhibits a constant deviation from the ideal gas law within the range 100° to 200° (cf. nitrogen and carbon monoxide, Bartlett and others, A., 1930, 678, 679). J. G. A. Griffiths.

Vapour pressure of pyridine. P. A. van der Meulen and R. F. Mann (J. Amer. Chem. Soc., 1931, 53, 451—453).—At temperatures between −20° and 120°, the vapour pressure of pyridine is given by the relation $\log p(\text{mm.})=6\cdot8827-1281\cdot3/(t^{\circ}+205)$.
J. G. A. Griffiths.

Relation between orthobaric volumes and temperature. J. Horiuti (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, 15, 89—104).—The equation already deduced (A., 1926, 1198) has been tested for sixteen substances. E is an additive quantity. The orthobaric densities of krypton are calculated.
C. W. Gibby.

Effect of temperature on the viscosity of air. A. O. Rankine (Phil. Mag., 1931, [vii], 11, 225—227).—A critical examination of the facts does not sustain the contention of Shilling and Laxton that there is a small but steady deviation from Sutherland's law in the case of air. F. G. Tryhorn.

Viscosity and inner friction in solids. B. Gutenberg and H. Schlechtweg (Physikal. Z., 1930, 31, 745—753).

Physical constants of the system methane–hydrogen. F. A. Freeth and T. T. H. Verschoyle (Proc. Roy. Soc., 1931, A, 130, 453—463).—Determinations of the isotherm of methane at 0° (Keyes and Burks, A., 1927, 719) have been extended to 215 atm. The isotherm at 20° has also been determined by the method previously described (Verschoyle, A., 1926, 894). The accuracy did not exceed 1 in 500, but it is evident that a pv_A minimum exists at 160—165 atm. for the isotherms at 0° and 20°. The results are in good agreement with those of Keyes and Burks (*loc. cit.*), but the isotherm for 0° derived from their equation of state begins to fail rapidly at pressures

above 125 atm. (corresponding with a specific volume of about 8·5 cm.^{3} per g.). Determinations of the triple point (temperature −182·46°, pressure 8·737 cm.) were made with samples of methane prepared by two different methods, the vapour pressures of the solid were measured down to −208°, and the m.-p. curve was followed to a pressure of 46 atm. In the system methane–hydrogen the upper portion of the three-phase curve is found to have the same form as in the binary systems carbon monoxide–hydrogen and nitrogen–hydrogen. From a $p-x$ isotherm measured at −182·5°, the critical point of contact appears to lie at about 60 atm., the corresponding proportion of methane in the vapour phase being about 1%.
L. L. BIRCUMSHAW.

Viscosity, heat conductivity, and diffusion in gas mixtures. XIII. Diffusion constants of dilute gas mixtures. M. TRAUTZ and W. RIES (Ann. Physik, 1931, [v], 8, 163—184).—The apparatus of Wuppermann was used to determine the diffusion constant of one gas in another, using benzene–hydrogen and carbon tetrachloride–hydrogen mixtures. The values obained were 0·363 and 0·342 c.c. per sec., respectively. The former value agrees with that obtained by the use of another apparatus. The square-root rule does not appear to apply to these two mixtures, whereas it holds very well for benzene–oxygen.
A. J. MEE.

Mixing contraction of liquids. N. GERASIMOV (Physikal. Z., 1931, 32, 226—229).—Mathematical. The analogy of the mixture of two kinds of lead shot varying in diameter is examined, and applied to the case of the mixture of two liquids. The results derived correspond closely with experiment.
A. J. MEE.

Hydrodynamics of systems of variable viscosity. IV. M. REINER (Kolloid-Z., 1931, 54, 175—181; cf. A., 1930, 145).—Theoretical. Mathematical formulæ are derived for the fluidity of non-Newtonian liquids.
E. S. HEDGES.

***X*-Ray investigations on copper–arsenic alloys.** N. KATOH (Z. Krist., 1930, 76, 228—234).—The α-phase alloys, *i.e.*, solid solutions of arsenic in copper containing up to 4%Cu, have the face-centred lattice of copper. The edge of the unit cube increases from 3·608 Å. for pure copper to 3·640 Å. for the saturated solution; $d_{\text{calc.}}$ 8·75. The β-phase, homogeneous from 28·6 to 29·6% As, and consisting of Cu_3As with small amounts of copper or arsenic in solid solution, has a hexagonal unit cell containing six molecules (cf. Machatschki, A., 1930, 1352). For maximum copper and arsenic content, respectively, a is 7·121 and 7·095; c 7·293 and 7·0267. A quenched alloy containing 38·7% As shows no β-phase.
C. A. SILBERRAD.

System Fe–C–Si. II. Section through the tridimensional diagram at 8% Si. A. KŘIŽ and F. POBOŘIL (Coll. Czech. Chem. Comm., 1931, 3, 61—72).—Previous work (B., 1930, 1031) has been extended to alloys containing Si 8% and C 0·14—2·7%. Increase of the silicon content from 6 to 8% causes the disappearance of the homogeneous γ phase, of the three-phase γ+carbon+liquid region, and of the γ+carbon and γ+liquid regions. The pearlitic transformation of alloys containing more than 0·48% C ceases when melting commences. An invariant point occurs at 1160°. The γ′ edge of the four-phase plane which touches the single-phase (γ) region lies between 6 and 8% Si, and the α′ edge, which touches the homogeneous α region, lies above 8% Si. The A2 transformation in alloys containing 8% Si occurs at 655° in the α+carbon region.
H. F. GILLBE.

Thermal analysis of the system lithium–silver. S. PASTORELLO (Gazzetta, 1931, 61, 47—51; cf. A., 1930, 1359).—Two compounds, AgLi (m. p. 955°) and $AgLi_3$ (m. p. 450°), are indicated as well as three eutectic points at 610°, 410°, and 180° corresponding with 30, 70, and 100 at.-% Li, respectively. No solid solutions are formed. *X*-Ray analysis shows the existence of AlLi, similar to AgLi, with a body-centred lattice, a 3·23 Å.
O. J. WALKER.

Molecular constitution of the α solid solutions of tin in copper and of the corresponding liquid solutions examined thermodynamically. F. H. JEFFERY (Trans. Faraday Soc., 1931, 27, 136—137).—Application of the equation previously derived (A., 1930, 406) to the data for the system copper–tin shows that the α-phase and also the liquid phase between 1083° and 800° consist of solutions of the compound Cu_4Sn in solid and liquid copper, respectively, the molecules of copper being monatomic in both cases.
O. J. WALKER.

Molecular constitution of the β solid solutions of tin in copper examined thermodynamically. F. H. JEFFERY (Trans. Faraday Soc., 1931, 27, 137—139; cf. preceding abstract).—The β-phase of the copper–tin system consists of solid solutions of monatomic tin in monatomic copper.
O. J. WALKER.

Structural analogies of binary alloys of the transition elements with zinc, cadmium, and aluminium. W. EKMAN (Z. physikal. Chem., 1931, B, 12, 57—78).—The *X*-ray diagrams of binary alloys of zinc with iron, cobalt, nickel, rhodium, palladium, and platinum and of alloys of nickel with cadmium show that in all these systems a phase with the structure of γ-brass is capable of existence. In each case the region of homogeneity extends on either side of a composition corresponding with an at. ratio of the transition element to the other component of 5 : 21. If the transition elements are assumed to possess zero valency, this composition represents a ratio of valency electrons to atoms of 21 : 13 (cf. Westgren and Phragmén, A., 1929, 987). The iron–zinc phase is homogeneous between 19 and 23 at.-% Fe, the cobalt–zinc phase between 15 and 22 at.-% Co, and the nickel–zinc phase between 15 and 19 at.-% Ni. In the system cobalt–zinc a phase having the structure of β-manganese may be present, and in the system cobalt–aluminium a phase similar to β-brass, the region of homogeneity of the latter phase including a mixture for which the ratio of valency electrons to atoms is 3 : 2. The formation of all the above phases from their constituent elements is accompanied by a considerable diminution in volume.
R. CUTHILL.

Solubilities in the system water–iodine to 200°. F. C. KRACEK (J. Physical Chem., 1931, 35, 417—

422).—Above 112·3°, the system water–iodine forms two liquid layers, the mutual solubility increasing with a rise in temperature. The solubility curves have been determined up to 200°. Below 112·3°, the solutions are saturated with solid iodine. The aqueous and iodine layers at the invariant temperature, 112·3°, contain 0·0517 and 98·3 mol.-% I, respectively. The m. p. of iodine is 113·7° and the critical solution temperature is estimated to be at approximately 300°. L. S. Theobald.

Determination of the solubilities of some fluosilicates. (Miss) K. K. Worthington and M. M. Haring (Ind. Eng. Chem. [Anal.], 1931, 3, 7—9).—The solubilities and densities of saturated solutions of sodium, magnesium, zinc, lead, and copper fluosilicates at 20° are 0·733%, 1·0054; 37·94%, 1·2395; 49·94%, 1·4336; 81·90%, 2·4314; and 59·08%, 1·6175, respectively. Methods for the analysis of these compounds are critically examined; volumetric methods are untrustworthy if the compound is readily hydrolysed or if it is derived from an amphoteric base. The most trustworthy process for the heavy metal fluosilicates consists in converting into sulphate by heating to vigorous fuming with sulphuric acid containing a little nitric acid. The heavy metal salts are efflorescent and decompose slowly; lead fluosilicate is particularly unstable, and both the solid and its solutions are therefore highly corrosive. H. F. Gillbe.

Solubilities of alkali chlorides and sulphates in anhydrous alcohols. E. R. Kirn and H. L. Dunlap (J. Amer. Chem. Soc., 1931, 53, 391—394).—The data refer to anhydrous sodium and potassium salts in methyl, ethyl, *n*-propyl, *iso*propyl, *n*-butyl, and *iso*butyl alcohols between 20° and 50°. Potassium sulphate is insoluble in these liquids. The solubility of sodium sulphate in methyl alcohol decreases with rise of temperature, whilst in ethyl and *iso*propyl alcohol it passes through a maximum. This salt is insoluble in the other alcohols. The solubilities of the chlorides in methyl alcohol decrease and in the butyl alcohols increase with rise of temperature. The solubilities in the other solvents pass through maxima. J. G. A. Griffiths.

Solubility of thallous iodate in ethyl alcohol–water mixtures. V. K. LaMer and F. H. Goldman (J. Amer. Chem. Soc., 1931, 53, 473—476; cf. A., 1929, 1387).—Solvents containing 0—47 wt.-% of ethyl alcohol have been used at 25°. The average ionic radii calculated from Born's equation for the electrostatic work of transfer are 0·78 and 0·9 Å., which compares with values of *a* ranging from 1·05 to 1·6 given by the data for the solubility in salt solutions. J. G. A. Griffiths.

Dissolution of carbon dioxide in fused tellurium. A. Šimek and J. Šmída (Coll. Czech. Chem. Comm., 1931, 3, 93—95).—A preliminary determination gave for the solubility of carbon dioxide in tellurium at 485° the value 0·16 c.c. per c.c. This is about one third of the value calculated from the observed lowering of the m. p. of tellurium in an atmosphere of carbon dioxide. H. F. Gillbe.

Concentration currents and the cause of stratification of solutions. A. K. Boldyrev (Z. Krist., 1930, 74, 552—553; Chem. Zentr., 1930, ii, 2101).—The direction of concentration currents produced when a crystal is suspended in a solution differentiates between supersaturated (upwards) and unsaturated (downwards) solutions. "Stratification" of supersaturated solutions (observed by Semjatschenski) containing three crystals suspended at different heights, wherein the weight of the lowest crystal and the density of the lower portion of the solution increase at the expense of the upper, is discussed; stratification takes place only when the crystals are present. A. A. Eldridge.

Absorption of gas from a current of air. II. M. M. Dubinin, S. I. Parschin, and A. A. Pupirev. **III.** M. M. Dubinin, L. A. Soloviev, and G. K. Schilin (J. Russ. Phys. Chem. Soc., 1930, 62, 1947—1951, 1953—1956; cf. A., 1930, 989).—II. The protective action of adsorbent charcoal, measured by the time, θ, during which it is able to remove completely small quantities of chlorine from a current of air, is incomplete below a certain critical thickness of layer; above this thickness θ is proportional to the thickness of layer. The value of the critical thickness as determined experimentally differs from that calculated from Mecklenburg and Kubelka's formula (Z. Elektrochem., 1925, 31, 488).

III. Traces of chlorine in air may be detected by passing the gas over a filter-paper moistened in a starch–potassium iodide solution. The sensitivity of this reaction depends on adsorption of chlorine on the filter-paper. R. Truszkowski.

Adsorption. H. Schlüter (Z. physikal. Chem., 1931, 153, 68—82).—Measurements of the adsorption of pentane and carbon disulphide vapours on powdered glass and silver have given results which are contradictory to the unimolecular layer theory. The adsorption was followed up to the production of adsorption layers having a thickness of 50 mols., and the fact that silver powder behaves similarly to glass disposes of the view that the apparently high degree of adsorption on glass is due to dissolution of the vapour by swelling of the outer film of glass. The results can be expressed in the form $N=ab^P$, where N is the number of molecular layers, P the pressure, and a and b are constants. E. S. Hedges.

Adsorption of ethylene by wood charcoal, silicic acid gel, and aluminium oxide. A. Magnus and H. Windeck (Z. physikal. Chem., 1931, 153, 113—126).—The adsorption isotherms of ethylene, using wood charcoal, silica gel, and aluminium oxide as adsorbents, have been determined over the pressure range 0·02—600 mm. A marked difference was observed between the behaviour of charcoal on the one hand and the oxide adsorbents on the other. The initial portion of the curve for charcoal rises relatively steeply. The heats of adsorption are less for silica gel and aluminium oxide than for wood charcoal. E. S. Hedges.

Vapour-adsorption capacity of silica gels as affected by the extent of drying before wet-heat treatment and by the temperature of acid treatment and activation. H. N. Holmes and A. L. Elder (J. Physical Chem., 1931, 35, 82—92; cf. B., 1926, 438).—Eleven silica gels showed a decreased

(2—34%) adsorption capacity for benzene after ageing for 3—6 years. With four of the gels, activation temperatures up to 800° do not greatly affect the adsorption capacity for benzene, but a large decrease results if the activation temperature rises to 1000°. A rise in the temperature in the acid treatment of a gel from 30° to 100° increases its porosity, and a gel capable of adsorbing 156% of its own weight of benzene from an air stream saturated with benzene at 30° has been prepared. The most porous gels which still possess a firm structure have been made from gels dried to 50—60% moisture content before acid treatment. Such gels have large capacities for adsorbing benzene under high partial pressures, but are not efficient at lower partial pressures. Vitreous gels and Patrick's glassy gel are equally efficient under low partial pressures of benzene and the most efficient removal of vapour is obtained by a combination of the two types of gel. L. S. THEOBALD.

Adsorption of gas mixtures by silica. E. C. MARKHAM and A. F. BENTON (J. Amer. Chem. Soc., 1931, **53**, 497—507).—The adsorption on silica (silicic acid dried at 250°) of oxygen, carbon monoxide, and carbon dioxide, and of each gas in the binary mixtures at 1 atm. has been determined at 100°, and for the first two gases at 0°. By an extension of Langmuir's theory it is shown the adsorption of a gas from a mixture should be less than that from the pure gas at the same partial pressure. The equation is supported by data for mixtures of oxygen and carbon monoxide, but the anomalous results with mixtures containing carbon dioxide may be caused by mutual interaction of the adsorbed molecules.
J. G. A. GRIFFITHS.

Specific adsorptive properties of active charcoals. II. Sugar charcoal. M. M. DUBININ (J. Russ. Phys. Chem. Soc., 1930, **62**, 1829—1846).—Ordinary sugar charcoal possesses feeble adsorptive power; inorganic acids are adsorbed in the order of diminishing basicity and organic acids in the order of diminishing mol. wt., whilst alkalis are not adsorbed. The order of adsorption of these acids is reversed when the charcoal is activated by heating in air or carbon dioxide at 600—1000°; the product adsorbs alkali when activated in the presence of oxygen, but not in its absence. These effects are ascribed to the formation of different suboxides of carbon, according to the temperature of activation, and to the inversion of the charge present on the surface of the grains of charcoal on immersion in aqueous solutions.
R. TRUSZKOWSKI.

Adsorption of organic acids by platinum-black. II. M. S. PLATONOV, J. A. BORGMAN, and G. J. SALMAN (J. Russ. Phys. Chem. Soc., 1930, **62**, 1975—1989; cf. A., 1930, 28).—The adsorption of organic acids on platinum-black depends chiefly on their structure, and only to a smaller extent on their mol. wt. and solubility. Traube's rule is followed by saturated monobasic but not by dibasic acids. Acids possessing a normal chain are more strongly adsorbed than are *iso*-acids. *cis*-Isomerides and unsaturated acids are more strongly adsorbed than *trans*-isomerides and saturated acids, respectively. *o*-Nitrobenzoic acid is adsorbed to a smaller extent than is the *m*-isomeride, whilst the contrary is the case with hydroxybenzoic acids. In general, the introduction of substituents into the benzene ring increases adsorption. The velocity of hydrogenation of citraconic, itaconic, mesaconic, and the isomeric crotonic acids is proportional to their adsorption by platinum-black. This rule applies to all substances yielding the same product of hydrogenation; in other cases no parallelism is found. The adsorptive qualities of platinum-black may be considerably modified without markedly affecting its catalytic properties, and the reverse is also the case. R. TRUSZKOWSKI.

Oxide hydrates. XXXV. Crystalline oxides and oxide hydrates of aluminium as adsorbents for organic dyes. G. F. HÜTTIG and A. PETER (Kolloid-Z., 1931, **54**, 140—147).—The adsorption of methyl-violet, methylene-blue, Congo-red, eosin, and Bordeaux-red R by various crystalline forms of aluminium oxide and hydrated oxide has been measured. The results can be expressed by the Freundlich adsorption isotherm. The general adsorption capacity of the substances examined decreases in the order böhmite$>\gamma$-aluminium oxide$>$diaspore$>$hydrargillite$>$corundum, but the selectivity of the adsorbents varies in the reverse direction. The adsorptive power of a given crystalline form is altered by the presence of impurities. With increasing hydrogen-ion concentration greater amounts of the acid dyes eosin and Bordeaux-red R and smaller amounts of the basic dyes methyl-violet and methylene-blue are adsorbed. E. S. HEDGES.

Adsorption of chromate ions by colloidal aluminium hydroxide. B. H. PETERSON and K. H. STORKS (J. Physical Chem., 1931, **35**, 649—652).—The adsorption of potassium chromate by colloidal aluminium hydroxide has been determined at concentrations above and below that required for coagulation. Three distinct types of adsorption occur; these are represented by (i) neutralisation of the charge on the sol particle, (iii) surface adsorption, not electrical in type, and (ii) a combination of (i) and (iii).
L. S. THEOBALD.

Acid adsorption and stability of cellulose nitrate. D. R. WIGGAM (J. Physical Chem., 1931, **35**, 536—539).—Nitric and sulphuric acids ($0{\cdot}01N$) are adsorbed to the same extent by cellulose nitrate; adsorption of hydrochloric acid is slightly less. Adsorption of bases apparently does not take place. Acid retained by the fibre lowers the resistance to heat of a given sample of cellulose nitrate and equal amounts of the three above-mentioned acids lower the heat-resistance to approximately the same extent. Acid adsorption plotted against stability (methyl-violet test) gives a smooth curve. For cellulose nitrate of high nitrogen content the effect on stability of the acid adsorbed is not serious when this is of the order of 3×10^{-6} g.-mol. per g. or less.
L. S. THEOBALD.

Adsorption. J. TERWELLEN (Z. physikal. Chem., 1931, **153**, 52—67).—Ageing phenomena do not take place in sols of methyl-violet and methylene-blue so long as the substances are pure and oxygen and light are excluded. The adsorption of these two dyes by silver and nickel wire has been measured by a spectrophotometric method, the surface of the adsorbent being determined by direct measurement. The results are not in accordance with Langmuir's unimolecular film theory. The amount adsorbed increases with the concentration of the solution beyond the value required for a saturated unimolecular layer and at the highest concentrations the molecular thickness of the adsorbed film of methyl-violet on silver is 4, and on nickel 5, methylene-blue on silver 11, and on nickel 5. Van der Waals forces are probably involved in the formation of these multimolecular layers. The results given above show that the amount adsorbed at saturation depends on both the adsorbent and the dye, and it is not therefore permissible to compare the surface areas of two different materials by measuring the ratio of their adsorbent capacities for a dye. The adsorbing power of the metal wire is reduced by previous heating, suggesting that adsorption takes place at certain active spots on the wire, probably indicating a distortion of the crystal space lattice.

E. S. Hedges.

Activation energy of adsorption processes. H. S. Taylor (J. Amer. Chem. Soc., 1931, **53**, 578—597).—The adsorption process *per se* is not necessarily rapid, and may be immeasurably slow; for each process there is a characteristic velocity which is determined by the same factors which affect the velocity of chemical reactions, viz., temperature, pressure, concentration, and nature of adsorbing surface. The effect of these has been examined on the assumption that there are two types of adsorption for the same gas. One of these is characterised by a low or negligible energy of activation and, in general, a low heat of adsorption ("secondary" or "reversible" adsorption) and the other by a large energy of activation and frequently with a high heat of adsorption ("primary" or "irreversible" adsorption). The theory receives support from the data for the adsorption of hydrogen, oxygen, carbon monoxide, nitrogen, water vapour, and sulphur dioxide on various substances. Certain abnormalities are explained.

J. G. A. Griffiths.

Velocity of adsorption processes and promoter action. H. S. Taylor and A. T. Williamson (J. Amer. Chem. Soc., 1931, **53**, 813—814; cf. preceding abstract).—Hydrogen is adsorbed immeasurably slowly by an active manganous oxide catalyst at 0° and 100°, but at 305° the velocity of adsorption rises to a value 10-fold that at 184°, corresponding with an energy of activation of about 10,000 g.-cal. Manganous oxide promoted with chromium oxide adsorbs hydrogen very slowly at 0°, but at 184° the adsorption is about 700 times as fast as with the unpromoted catalyst. The adsorptive capacity per g. is also much greater. In all of these cases, the adsorption is reversible.

J. G. A. Griffiths.

Kinetics of surface processes at crystal lattices. I. Adsorption system barium sulphate–electrolyte solution. L. Imre (Z. physikal. Chem., 1931, **153**, 262—286).—The time course of the adsorption of actinium and lead on barium sulphate surfaces under a variety of conditions has been investigated quantitatively. The time–adsorption curves for any given system are characteristic of the adsorbed ion, but are influenced by the quantity and nature of the adsorbent, the composition of the solution, and the temperature. The results are capable of interpretation if it is assumed that the process takes place in a series of stages, of which the earlier, relatively rapid, stages are determined by the valency of the adsorbed ion, and the later by the specific affinity of the ion for the lattice ions of the adsorbent. By taking into consideration the valency of the ions, the solubility of the adsorption complex, and the recrystallisation processes in the adsorbent, a mathematical expression has been derived for the kinetics of the adsorption. In conformity with this, the adsorption of actinium is shown to be the resultant of two effects, each of which obeys an exponential law; in the case of lead the later stages at least are more complex. H. F. Gillbe.

Adsorption of ions on a surface film. R. S. Bradley (Phil. Mag., 1931, [vii], **11**, 449—453).—An expression has been deduced for the potential due to a uniform plane array of dipoles oriented perpendicularly to the surface and this is used to calculate the magnitude of the layer of ions adsorbed in the film on the surface of a liquid (cf. Lyons and Rideal, A., 1929, 875). R. Cuthill.

Inner adsorption in crystalline salts. I. N. Stranski (Kolloidchem. Beih., 1931, **32**, 197—204).—Objections are raised against the theory of adsorption and crystal growth developed by Balarev (A., 1930, 684) on the ground that the considerations involved are based largely on a misunderstanding of the Gibbs relation. E. S. Hedges.

Nature of the specific property of molecular surface fields. Structure of active carbon and inversion effect of adsorption and heat of wetting. B. Iljin and J. Simanov (Z. Physik, 1930, **66**, 613—618).—Debye photographs of hydrophobic and quasi-hydrophilic carbon revealed no difference in their structure, although there is an inversion of adsorption from aqueous solutions of fatty acids, and heats of wetting of the homologous alcohol series. Inversion of adsorption effects cannot therefore be ascribed to a difference in the molecular surface fields.

A. B. D. Cassie.

Adsorptive binding. H. Cassel and F. Salditt (Naturwiss., 1931, **19**, 110—111).—The surface tension σ of pure mercury has been measured by the method of maximum drop pressure, in the absence of air, in contact with its own vapour and the vapours of various substances at different temperatures and pressures. According to the method of Gibbs, the σ–p isotherms permit the calculation of the amount of adsorption. In agreement with the conclusions of London and Polányi (this vol., 161), the magnitude of the dipole moment plays only a secondary rôle in adsorption. Within the experimental accuracy (0·1%) water vapour causes no change in the surface tension of mercury over the temperature range 0—50° and at pressures up to 62 mm. Below the saturation pressure water is generally not adsorbed on mercury. On the other hand, ethyl ether, with a much smaller dipole moment, shows large adsorption, and this is greater still with hexane, *cyclo*hexane, and benzene, which possess no dipole moments. In the series methyl, ethyl, and propyl alcohols the adsorption increases with increasing length of the hydrocarbon chain, independently of the magnitudes of their dipole moments. From the S form of their σ—p curves it is deduced that these compounds exist only as associated molecules in the adsorbed state. The same behaviour is shown by nitromethane, which has almost double the dipole moment of water. J. W. Smith.

Surface tension of crystals. D. Balarev (Kolloidchem. Beih., 1931, **32**, 205—211).—It is shown theoretically that the relation found by Ostwald and Freundlich between solubility, particle size, and surface tension cannot hold for homogeneous surfaces, but is valid when the surface tension is greater at the edges and solid angles of the crystal. The increase of surface tension with decreasing particle size begins to be apparent when colloidal dimensions are reached. E. S. Hedges.

Matter in the film state. A. V. Blom (Kolloid-Z., 1931, **54**, 210—220).—The conception of a film as a particular state of matter intermediate in properties between dispersoids and compact solid matter is developed. Films are considered as (1) unimolecular films, (2) Hardy films, having a thickness of not more than 10^{-4} cm., and (3) zone films, where the thickness is greater than 10^{-4} cm. and the forces acting between the molecules are not entirely of a surface character. Films may be formed by either physical or chemical processes. For film formation by evaporation two relations are derived: (1) the amount of evaporation per unit time is constant; (2) the velocity of film formation at any given time is proportional to the amount of the volatile portion remaining. The adhesion of films can be measured by determining the weight required to remove a surface brought into contact with the film, and some experimental results on these lines are briefly described. With continuous drying of films of resin in amyl alcohol the stickiness at first increases, passes through a maximum, and later decreases. The adhesive properties are not entirely connected with the rate of evaporation of the solvent, however, for the stickiness of oil varnish alters very considerably on exposure to ultra-violet light, whilst the rate of evaporation is unchanged thereby. E. S. Hedges.

Thermoelastic effect in cellulose ester films. J. G. McNally and S. E. Sheppard (J. Physical Chem., 1931, **35**, 100—114).—The heat changes associated with the stretching of films of cellulose nitrate and acetate have been investigated, and the coefficients of thermal expansion at different temperatures and stresses have been measured. The nitrate film cools on stretching up to the yield point, after which it warms until it breaks. The amount of heat evolved is greater than that absorbed. The acetate film behaves in a similar manner. The inversion of the thermal effect is not due to the increased rate of extension after the yield point is reached. When the structure of the film is altered by drying under a large stress, the region of strain corresponding with the exothermic reaction disappears. The thermoelastic properties of coagulated films are independent of their content of volatile solvent. The thermal coefficient of expansion of cellulose nitrate is a poorly-defined quantity which depends on stress, previous mechancial and thermal history, and temperature. At low temperatures and moderate stresses, a negative thermal expansion, analogous to the Joule effect in caoutchouc, has been observed. L. S. Theobald.

Cohesion. I. H. Tertsch (Z. Krist., 1930, **74**, 476—500; Chem. Zentr., 1930, ii, 2101).—Cleavage by drawing, pressure, and shock are differentiated and means for determination are described. Experiments were performed on the cleavage by tension of rock salt. A. A. Eldridge.

Surface processes in coagulating precipitates. II. Mechanism of adsorption in electrolyte solutions. L. Imre (Z. physikal. Chem., 1931, **153**, 127—142; cf. A., 1930, 287).—The time-course of the adsorption of ions at the surface of ageing suspensions of the silver halides has been followed by a radioactive-indicator method. The effect varies with the nature of the adsorption compound formed between the ion and the oppositely charged ionic component of the adsorbing particle. In cases where a sparingly soluble compound is produced the adsorption increases very slowly or remains constant, but where the compound is readily soluble more or less strong desorption occurs. During the ageing the structure of the particles is supposed to open up in consequence of the crystallisation tendency, thus enabling an exchange reaction to take place with the ions adsorbed in the vicinity of the space lattice. The adsorptive capacity of the silver halides for readily soluble electrolytes increases in the order chloride$<$bromide$<$iodide.

E. S. Hedges.

System electrolyte–water. Partition of the ions of a salt pair during diffusion through a membrane. H. Brintzinger and W. Brintzinger (Z. anorg. Chem., 1931, **196**, 61—64).—Measurement of the dialysis coefficient of the ions present in solutions containing lithium chloride and potassium iodide or lithium chloride and potassium sulphate indicate that the more rapidly moving cation tends to diffuse in company with the more rapid anion. Thus the potassium ion, which has the smaller surface electric field, diffuses principally with the iodide ion in the first solution and with the chloride ion in the second.

H. F. Gillbe.

Membrane and osmosis. I. F. A. H. Schreinemakers (Rec. trav. chim., 1931, **50**, 221—229).—The osmotic system consisting of an "inactive" membrane permeable only to water and placed between two liquids is treated theoretically.

O. J. Walker.

Measurements with the aid of the dialysis method. Enzymic decomposition of starch and thermal decomposition of dextrin in presence of acid. H. Brintzinger and W. Brintzinger (Z. anorg. Chem., 1931, **196**, 50—54).—Measurements of the dialysis coefficients of starch solutions to which diastase has been added show that the first stage of the hydrolysis is very rapid, but that after the mol. wt. has fallen to about 800 the reaction proceeds very slowly to completion. The process appears to take place in four stages, with the production of intermediate compounds of mol. wt. 22,800, 3700, and 600, in accordance with Biltz' results from viscosity measurements. Hydrolysis of a dextrin of mol. wt. 10,460 by acid proceeds continuously, with no evidence of the formation of intermediate compounds of definite composition. H. F. GILLBE.

Disturbance of neutrality of solutions in electrodialysis. S. OKA (J. Soc. Chem. Ind. Japan, 1931, **34**, 4—9B).—The electrolysis of 0·005N-potassium chloride solutions has been carried out using a constant voltage in a cell divided into three compartments by diaphragms of the same material. In different experiments parchment-paper, filter-paper impregnated with collodion and also with chromated gelatin were used as diaphragms. During the electrolysis the p_H of the solution fell to a low, nearly constant value, which, however, showed a tendency to rise slightly as electrolysis was further continued. It appears that the development of acidity or basicity is conditioned by the relative amounts of hydrogen and hydroxyl ions which enter the middle chamber. The mobilities of the ions as they pass through the pores of the diaphragms seem to be different from those in the bulk of the solution and the difference is probably occasioned by the electrokinetic potential of the diaphragms. This theory provides qualitative explanations of other observations made in the experiments. H. INGLESON.

Blocking effect of membranes. G. H. BISHOP, F. URBAN, and H. L. WHITE (J. Physical Chem., 1931, **35**, 137—143).—The flow of dilute solutions of potassium chloride through glass capillaries has been investigated and the results are discussed in relation to the blocking effect of membranes. The streaming potential of a given capillary varies from time to time and capillaries from the same piece of glass when treated in the same way and used under identical conditions show significant differences in streaming potential. With cellophane membranes, the gradual decrease in the rate of filtration and the absence of a measurable streaming potential may be associated with the electrical phenomena taking place in the various pores of the membrane. L. S. THEOBALD.

Viscosity and density of rubidium nitrate solutions. H. G. SMITH, J. H. WOLFENDEN, and (SIR) H. HARTLEY (J.C.S., 1931, 403—409).—The relative viscosity and the relative density of aqueous solutions of rubidium nitrate have been measured at 18° and 25° over the concentration range 0·092—1·786N. The relative viscosity of rubidium nitrate solutions can be represented by the Jones–Dole equation (A., 1929, 1385) at concentrations below 0·2N and the coefficient A of those authors is shown to have the negative value and negative temperature coefficient which they postulate. The molecular solution volume of rubidium nitrate at various concentrations has been calculated and is shown to fall in the normal periodic sequence of the alkali nitrates. E. S. HEDGES.

Specific heat of solutions of sodium sulphate. M. AUMÉRAS (Compt. rend., 1931, **192**, 359—361).—The specific heat at 20° of solutions containing 80 to 550 mols. of water per mol. of decahydrate has been determined. The results generally are slightly higher than those previously obtained. C. A. SILBERRAD.

Absorption of aqueous solutions of tartaric acid. G. BRUHAT (Compt. rend., 1931, **192**, 489—490).—The results of Lucas and Schwob (this vol., 302) are more directly opposed to the existence of two forms of tartaric acid in solution than those of the author (cf. A., 1930, 1341). C. A. SILBERRAD.

Variation of extinction coefficient of solutions with temperature. II. A. K. BHATTACHARYA and N. R. DHAR (J. Physical Chem., 1931, **35**, 653—655; cf. A., 1930, 120).—The extinction coefficients of solutions of neocyanine, ferric thiocyanate, sodium cobaltinitrite, and mixtures of solutions of sodium malonate and iodine, sodium tartrate and iodine, citric and chromic acids, lactic and chromic acids, citric acid and potassium permanganate, tartaric acid and potassium permanganate increase with a rise in temperature. This increase is attributed to a diminution in hydration of the solutes which partly explains the increase in quantum yield with rise in temperature. L. S. THEOBALD.

Hydrotropy. C. NEUBERG and F. WEINMANN (Biochem. Z., 1930, **229**, 467—479).—When solutions of salts of optically active acids are mixed with optically active non-conducting liquids which also exhibit surface activity and the optical rotation of the mixtures is measured an alteration of the rotation additional to that caused by the simple superposition of the rotations of the constituents is always observed. This alteration is not due to physical causes. Hydrotropy is probably a chemical phenomenon involving the formation of loose additive compounds of some kind. W. MCCARTNEY.

Porous disc method of measuring osmotic pressure. F. T. MARTIN and L. H. SCHULTZ (J. Physical Chem., 1931, **35**, 638—648).—Measurements of the osmotic pressure of dilute solutions of potassium chloride by the method of Townend (A., 1929, 134), considerably modified, show that the porous disc method offers promising possibilities. Slight inequalities of temperature within the apparatus are a source of error. L. S. THEOBALD.

Use of acetamide as solvent for cryoscopy. E. CHERBULIEZ and G. DE MANDROT (Helv. Chim. Acta, 1931, **14**, 183—186).—Acetamide is a suitable solvent for the determination of the mol. wts. of the decomposition products of caseinogen, although the cryoscopic constant, K, varies with the concentration. Values of K are given for solutions of acetanilide, hippuric acid, and diketopiperazine in acetamide. O. J. WALKER.

Ebullioscopic studies of the cadmium alkali halides. (MLLE.) C. HUN (Compt. rend., 1931, **192**, 355—356).—From b. p. observations (cf. Bourion, Rouyer, etc., A., 1927, 841; 1930, 853, 1120) the existence of the complexes $(NH_4)_2[CdCl_4]$, $(NH_4)_2[CdBr_4]$, and $(NH_4)_2[CdI_4]$ is inferred. Equilibrium constants for the potassium, ammonium, and sodium complexes corresponding with $2MX + CdX_2 \rightleftharpoons M_2[CdX_4]$ are, respectively, for the chlorides 0·605, 0·796, 1·12; for the bromides 0·0832, 0·208, 0·156; and for the iodides 0·006, 0·0576, 0·585. C. A. SILBERRAD.

Preparation of colloidal silver sols using alkaloids. M. O. CHARMANDARIAN and A. V. SAMOĬLOVA (J. Russ. Phys. Chem. Soc., 1930, **62**, 1915—1918).—Yellow to orange silver sols are obtained by the action of brucine, nicotine, opium, or atropine on solutions of silver nitrate. In the case of nicotine, small concentrations of alkaloid yield a yellow sol, which is flocculated by higher concentrations, whilst at still higher concentrations stable orange-coloured sols are obtained.

R. Truszkowski.

Mechanism of formation of colloidal silver. H. Q. Woodard (J. Physical Chem., 1931, **35**, 425—431).—The formation of silver sols by the method previously used (A., 1930, 289) has been investigated in solutions of different electrolytes. Attention has been directed to the composition of the liquid remaining after precipitation of the sol by prolonged arcing, whilst the fate of the cation of the original solution has been followed by titration or by determinations of p_H. Sol formation is favoured by a rise in temperature. The results support the view that the formation of colloidal silver by the Bredig method involves a reaction between the silver and the electrolyte simultaneously with the formation of a metal–anion complex. L. S. Theobald.

Preparation of colloidal metallic lead and lead phosphate. V. Cofman (Rev. gén. Colloid., 1930, **8**, 337—357).—Colloidal lead may be prepared conveniently by placing granulated lead under water and agitating the granules with two lead electrodes which are connected to a supply of 110 volts. Up to a certain point the concentration of the sol increases with the duration of sparking, but a considerable amount of lead sponge forms also and the containing vessel should be kept in ice. The sol is stabilised by small quantities of gelatin, sodium thiosulphate, and potassium and calcium chlorides, whether added before or immediately after the preparation. Determinations of particle size by the centrifugal method gave values between 0·5 and 0·1 μ. Colloidal lead phosphate is prepared in a form suitable for the treatment of cancer by adding a 1·028% solution of trisodium phosphate drop by drop to an equal volume of solution containing 1·46% of lead acetate, both solutions being kept at 60°. The sol is stabilised by gelatin and by gum arabic. The effects of temperature of mixing, hydrogen-ion concentration, and excess of reagent have been studied. Experiments with the ultracentrifuge indicate a particle radius of 16·2 μμ for colloidal lead phosphate prepared in the presence of gelatin. E. S. Hedges.

Colloidal nature of cuprammonium solution. A. J. Stamm (J. Physical Chem., 1931, **35**, 659—660).—Ultracentrifuging shows that cuprammonium solutions contain a colloidally dispersed material. This is regarded as a copper hydroxide sol.

L. S. Theobald.

Dispersoidal investigations on selenium. I. K. Juna (Bull. Chem. Soc. Japan, 1931, **6**, 23—24).—The formation of colloidal solutions of selenium when solutions of the element in hydrazine hydrate are poured into water, alcohol, or glycerol is due to atmospheric carbon dioxide and oxygen and does not occur in an atmosphere of nitrogen. O. J. Walker.

Photometric measurement of concentration and dispersity in colloidal solutions. III. T. Teorell (Kolloid-Z., 1931, **54**, 150—156; cf. this vol., 164).—Measurements carried out in the Zeiss nephelometer show that the weakening in the intensity of light passing through a mastic sol is due mainly to scattering. The results also indicate that only in sols of low concentration is the intensity of scattered light proportional to the concentration; at higher concentrations the relative scattering becomes less and the amount of scattered light passes through a maximum, after which it falls. The use of red light is recommended for nephelometric observations with colourless sols. E. S. Hedges.

Application of a photo-element to the determination of the relation between the dispersion of light and the number and dimensions of particles in disperse systems. N. N. Andreev, N. A. Kudrjavzev, and T. A. Schtessel (J. Russ. Phys. Chem. Soc., 1930, **62**, 2091—2099).—The expression $K=I/ns$ is derived, in which K is a constant ($5{\cdot}32\times 10^{-18}$), and I is the dispersion of light given by a suspension containing n particles each of surface s. This expression is verified for suspensions of *Staphylococcus albus*, and of spores of *Trichophyton asteroides* and *Penicillium glaucum*. R. Truszkowski.

Dielectric behaviour of disperse systems. R. Fricke and L. Havestadt (Z. anorg. Chem., 1931, **196**, 120—128).—The effect on the dielectric constant of the addition of acid or alkali to thorium hydroxide and aluminium hydroxide suspensions is described. When dilute hydrochloric acid is added to a stannic acid sol the viscosity of the latter increases until the sol becomes strongly thixotropic, and the dielectric constant simultaneously diminishes; immediately prior to flocculation the sol becomes mobile and no longer thixotropic, whilst after flocculation the dielectric constant falls very rapidly. The appearance of thixotropy appears to counteract the fall of dielectric constant due to diminution of the surface charge, whilst coagulation causes a fall of the dielectric constant as a result of the disappearance of the polarisable surface. This view is apparently contradicted by the fall of the dielectric constant of gelatin sols on ageing. Possibly the dielectric constant is influenced by the occurrence of thixotropy only when the sol particles are of an elongated form.

H. F. Gillbe.

Effect of radiations on colloids. III. Effect of ultra-violet light on emulsions. P. C. Sinha and P. B. Ganguli (Kolloid-Z., 1931, **54**, 147—150).—Further evidence is adduced to show that the coagulating effect of radiations on colloids is due to a photochemical influence of the radiation on the stabilising electrolyte. Various oil-in-water emulsions were prepared, using sodium oleate as the emulsifier, and magnesium oleate was used to emulsify water in benzene. When irradiated by ultra-violet light, the emulsions of benzene, light petroleum, coconut oil, and olive oil were coagulated, whilst emulsions of sperm oil, poppy-seed oil, and carbon disulphide remained unchanged. Aqueous solutions of sodium oleate alone gave a precipitate of acid soap with simultaneous increase in alkalinity and electrical conductivity when irradiated under similar conditions.

E. S. Hedges.

Ion interchanges in aluminium oxychloride hydrosols. A. W. Thomas and T. H. Whitehead (J. Physical Chem., 1931, **35**, 27—47).—The ageing of aluminium oxychloride sols at 20° is accompanied by an increase in the p_H of the sol, whilst heating at 80° for 4 days lowers the p_H, which does not return to the original value at 25°. Heating for only 3 hrs. has no measurable effect. Hydrolysis does not account for these changes. The addition of neutral salts produces an increase in the p_H of the positively-charged sols, the effect increasing in the order nitrate, halide, sulphate, acetate, and oxalate. The results and the constitution of sols are explained in accordance with the extension of the Werner theory by Bjerrum and by Stiasny. L. S. Theobald.

Mechanism of the coagulation of sols by electrolytes. I. Ferric oxide sol. H. B. Wieser (J. Physical Chem., 1931, **35**, 1—26).—The change in chloride concentration accompanying the stepwise addition of various electrolytes to three different ferric oxide sols containing a slight excess of hydrochloric acid or ferric chloride as stabilising electrolyte has been determined by a potentiometric method. Only a part of the chloride which is found in the supernatant liquid after coagulation can be detected potentiometrically in the original sol before the electrolyte is added, and the chloride determined after stepwise addition of the electrolyte consists of that originally present in the sol together with an additional amount which is displaced when the added anion is taken up. Curves showing the increase in chloride ion on adding potassium sulphate, nitrate, chromate, ferricyanide, oxalate, and citrate to three different ferric oxide sols are given and discussed. At concentrations up to and including that of precipitation, the multivalent anions are practically completely taken up by the sol, and the chloride displaced is less than half the amount equivalent to the multivalent anion taken up. At the precipitation concentration, the chloride in the supernatant solution is equivalent to or slightly greater than the amount of multivalent ion added. The curves showing the chloride displaced are practically linear at the commencement of the stepwise addition of multivalent anions, but as the precipitating concentration is approached the amount of chloride displaced for a given increment of precipitating ion becomes greater. Above the precipitation concentration, the curves have the form of an adsorption isotherm. The chloride displacement curves and the precipitating power of the bivalent anions are similar, but the ferricyanide ion coagulates the sol at a lower concentration with less displacement of chloride at the precipitation value. The curve for the nitrate follows a lower course than those for the multivalent anions. The micelle of the ferric oxide sols, exclusive of the outer layer, can be represented by the formula $x\mathrm{Fe_2O_3},y\mathrm{HCl},z\mathrm{H_2O}$, which corresponds with the observed facts that the micelle contains some chloride which is not displaced by electrolyte, and that the composition varies with the conditions of preparation and subsequent history. The outer layer, which largely determines colloidal properties, consists of an ionic double layer, the inner portion consisting of adsorbed hydrogen or ferric ions and the outer portion a diffuse layer of chloride ions. An adsorption mechanism which accounts for the change in composition, the nature of the double layer, and the decreased charge on the micelle when electrolytes are added to the sol is outlined and discussed in relation to Pauli's solubility theory. L. S. Theobald.

Coagulation of ferric oxide hydrosols. C. H. Sorum (J. Amer. Chem. Soc., 1931, **53**, 812).—A reply to Dhar (A., 1930, 1517).

J. G. A. Griffiths.

Polyhydroxy-compounds in the synthesis of electro-negative sols. VI. Hydrophilic properties of ferric hydroxide sols obtained in the presence of mannitol. A. Dumanski and T. A. Granskaya (J. Russ. Phys. Chem. Soc., 1930, **62**, 1879—1884).—Coagulation in the system ferric hydroxide sol–ether–alcohol is represented graphically using triangular co-ordinates. The hydrophilic properties of this sol, prepared by the addition of sodium hydroxide to ferric chloride in the presence of mannitol, are most pronounced at the isoelectric point.

R. Truszkowski.

Influence of light on the flocculation of colloidal solutions in a fluorescent medium. Action of antioxygenic substances. A. Boutaric and J. Bouchard (Compt. rend., 1931, **192**, 357—358; cf. this vol., 305).—The reduction of the time required for coagulation when a colloidal sol (*e.g.*, of arsenious sulphide) to which fluorescein has been added is illuminated by ultra-violet light, as compared with the time required for this in darkness, diminishes more or less logarithmically with the fluorescing power. If the latter is diminished by the addition of an antioxygenic substance (*e.g.*, a phenol, *p*-phenylenediamine, or tannin) the photosensitising power of the fluorescent material is also diminished. The possible value of the presence of fluorescent substances and of the absence of antioxygenic material in the agglutination of microbes is pointed out. C. A. Silberrad.

Kinetics of the coagulation of suspensoids. I. K. Jabłczyński (Kolloid-Z., 1931, **54**, 164—169).—Von Smoluchovski's equation has been applied to systems in which coagulation tends to an equilibrium and where all the particles are charged. The following equation is given: $k=1/t\,.\log[n(n_0-z)/n_0(n-z)]$, where n is the total number of particles after time t, n_0 the original total number, and z the number of charged particles. The equation is in agreement with experimental data. The measurement of coagulation velocity by the spectrophotometric method is also examined mathematically and the equations developed are supported by experiments. E. S. Hedges.

Hæmoglobin coagulation. II. S. L. Pupko (Kolloid-Z., 1931, **54**, 170—175).—The coagulation of hæmoglobin by potassium, calcium, and ferric chlorides in the presence of methyl and ethyl alcohols has been studied by making viscosity measurements, varying the concentration of alcohol and electrolyte and keeping a constant concentration of hæmoglobin. In the presence of methyl alcohol the viscosity either remains constant or decreases during coagulation, whilst in the presence of ethyl alcohol the viscosity either remains constant or increases. The valency of the cation has scarcely any effect on the viscosity change. The system is stabilised by high concentrations of calcium chloride and ethyl alcohol. Ferric chloride at concentrations between 0·1 and $2N$ stabilises hæmoglobin when ethyl alcohol is also present, but coagulation occurs at higher concentrations.

E. S. HEDGES.

Formation of Liesegang rings. (MISS) S. ROY (Kolloid-Z., 1931, **54**, 190—193).—Directions are given for obtaining periodic structures by precipitation in the following systems: mercuric iodide in gels of vanadium pentoxide, ceric hydroxide, zinc and manganese arsenates; thallous iodide in gels of starch, agar, zinc and manganese arsenates; cuprous iodide in agar; silver iodide in starch; silver chromate in ceric hydroxide; barium and thallous chromates and silver iodide in silicic acid. The influence of light in a number of cases of periodic precipitation has also been examined and the conclusion has been reached that the periodicity is in general more marked when diffusion takes place in the light than in the dark. The most notable difference was found with mercuric iodide; in the dark, alternating layers of yellow colloidal mercuric iodide and red crystals were formed, whilst in the light red crystals of mercuric iodide alternated with clear spaces devoid of precipitate. It is maintained that the influence of light is an acceleration of the process of coagulation. The peptising influence of agar, starch, gelatin, and silicic acid on the precipitates has been studied.

E. S. HEDGES.

Influence of electrolytes on the syneresis and clotting of [goat's] blood. S. PRAKASH and N. R. DHAR (J. Physical Chem., 1931, **35**, 629—637).—Syneresis decreases with an increase in concentration of added electrolyte; it may even be inhibited and in a few cases clotting of blood may be prevented by electrolytes. The results obtained are explained by the tendency of the blood to adsorb ions of a similar charge and thus to increase its stability. The stabilising effect is in the order sodium citrate > potassium oxalate > sodium hydroxide > potassium fluoride > calcium chloride > potassium chloride > ammonium sulphate. The stabilising effect of fluorides, citrates, or oxalates is not due to removal of calcium ions from the blood but to the adsorbed anions.

L. S. THEOBALD.

Reversibility of protein coagulation. M. L. ANSON and A. E. MIRSKY (J. Physical Chem., 1931, **35**, 185—193).—A discussion. With hæmoglobin, globin, or serum-albumin, coagulation appears to be reversible.

L. S. THEOBALD.

Ageing of aqueous ferric chloride solutions. A. LOTTERMOSER and E. LESCHE (Kolloidchem. Beih., 1931, **32**, 157—168).—The ageing of very dilute solutions (10^{-3}—$10^{-6}M$) and of ferric hydroxide sols has been followed by determinations of electrical conductivity and by colorimetric measurements. The more concentrated solutions of ferric chloride increase continuously in conductivity, whilst the more dilute solutions undergo an initial increase, which is followed by a continuous decrease. In no case is a constant end-value obtained. Both ferric chloride solutions and ferric hydroxide sols are temperature-irreversible systems.

E. S. HEDGES.

Dye sols. II. Dissolution of Congo acid by neutral salts. R. TANAKA (Kolloid-Z., 1931, **54**, 156—164; cf. this vol., 37).—The addition of neutral salts to Congo acid sol produces a colour change to red. Small amounts of potassium chloride dissolve the substance, but coagulation occurs when higher concentrations are used. Medium concentrations give the maximum red coloration and such sols have a stronger acid reaction than the original sol. Potassium iodide produces a more intense red coloration. With calcium chloride the amount of dye dissolved is greatest for medium concentrations of the electrolyte, and the position of this maximum is independent of the hydrogen-ion concentration of the solution, the effect clearly depending on the concentration of salt. Increasing hydrogen-ion concentration has the effect of diminishing the intensity of the red coloration and alters the concentration range of the change. Measurements of hydrogen-ion concentration show that the colour change cannot be traced to the initial presence of some free alkali, but is a true peptising effect of the neutral salt. The possibility of the formation of an additive compound between the neutral salt and the acid dye is discussed.

E. S. HEDGES.

Molecular dispersion of dissolved silicic and titanic acids. H. BRINTZINGER and W. BRINTZINGER (Z. anorg. Chem., 1931, **196**, 44—49).—The process of ageing of silicic acid solutions, prepared by hydrolysis of the tetraethyl ester, has been studied by means of dialysis coefficient measurements. In presence of $0{\cdot}002N$-hydrochloric acid a disilicic acid, $2SiO_2,2H_2O$, is first formed and polymerises completely within 1 day to $4SiO_2,3H_2O$; after 2 days an octosilicic acid, $8SiO_2,4H_2O$, is formed, and after 4 days an acid of mol. wt. 862. Further aggregation results in the production of a mixture of acids until an acid of mol. wt. 8260 is formed (45 days). After 110 days the dialysis coefficient falls to zero. In $0{\cdot}001N$-hydrochloric acid solution even the first product is a mixture of complexes, and aggregation proceeds more rapidly than in the more strongly acid solutions; a definite complex of mol. wt. 8260 is again produced, and there is evidence of the formation of an acid of mol. wt. 32,870. True solutions of titanic acid are extremely unstable; within a few hours the solute is completely converted into colloidally dispersed hydrated titanium dioxide. The results obtained demonstrate the value of the dialysis method for studying the gradual conversion from the molecular into the colloidal state.

H. F. GILLBE.

Sorption phenomena and chemical processes. VI. Composition of alkali-cellulose and imbibition by cellulose. S. M. LIEPATOV [with N. M. SOKOLOVA] (J. Russ. Phys. Chem. Soc., 1930, **62**, 1785—1793).—Cellulose forms a compound, $(C_6H_{10}O_5,3NaOH)_n$, when treated with aqueous alkali. The imbibition of cellulose films in water is due to entry of water within the pores of the membrane, whilst in alkaline solutions the cellulose molecules are covered by a unimolecular layer of water.

R. TRUSZKOWSKI.

Depolarisation and light absorption by alkaline protein solutions. G. ETTISCH, H. SACHSSE, and B. LANGE (Biochem. Z., 1931, **230**, 93—114).—The variation in the ratio of the horizontal to the vertical component of the polarised light from illuminated serum-albumin and -globulin solutions in presence of different concentrations of alkali has been investigated. Addition of alkali to the protein solution results in a temporary change of the ratio dependent on the amount added and the state of hydration of the particles. This effect is not apparent at low alkali concentrations where neutralisation of the acid valencies present only occurs. At high alkali concentrations a disintegration of the particles occurs, a phenomenon more apparent with globulin than with albumin. This disintegration is clearly shown by the depolarisation, but not so definitely by the absorption spectra. F. O. HOWITT.

Viscosity of alkaline protein solutions. G. ETTISCH and H. SACHSSE (Biochem. Z., 1931, **230**, 115—128).—The viscosities of ovalbumin and globulin in presence of acid and alkali have been examined. The effect of alkalis on the proteins is essentially a time reaction. Low concentrations of alkali (0·2—0·3%) do not increase the viscosity to any appreciable extent, but with a concentration of 0·5% the viscosity increases, reaching a maximum in 4 hrs. and then decreasing in the case of globulin. With albumin, a maximum is reached in about 8 hrs. and thereafter a steady value is maintained. The effect of addition of copper sulphate on the viscosity of an alkaline protein solution is small at low protein concentrations, but is very marked at high concentrations. The mechanism of these changes with reference to the splitting up of the protein particles is discussed.

F. O. HOWITT.

Calcium acetate gels. II. C. G. SMITH (Kolloid-Z., 1931, **54**, 181—190; cf. A., 1929, 879).—A further study of the formation of calcium acetate gels by adding a concentrated solution of the salt to alcohol indicates that the process is primarily one of dehydration. If dehydration takes place slowly, a gel having a definite structure is formed, but when the dehydration is too rapid, a structureless gelatinous precipitate is obtained. Rapid dehydration can be effected by the addition of acetone or pyridine, particularly the former; on the other hand, slow dehydration may be brought about by increasing the amount of water in the alcohol, with the production of more stable gels. Organic liquids which have no dehydrating effect have no influence on the gel formation. The gel is also formed by the addition of sodium or magnesium acetate, presumably through repression of dissociation, causing an association of the calcium acetate molecules. Electrolytes which react chemically with calcium acetate are inimical to the formation of the gel. The electrolytic dissociation of the calcium acetate is in any case never strong in the presence of the alcohol, and this factor is believed to be important in determining the conditions of gel formation. Photomicrographs of the gels show that these have in most cases a honeycomb type of structure, the calcium acetate being the disperse phase. Benzene, carbon disulphide, and acetone cause a phase reversal, droplets of the liquid being found in a network of calcium acetate. When the gel is kept, the particles of calcium acetate increase in size eventually to visible dimensions, the smaller particles disappearing; simultaneously an increase in opalescence is observed and syneresis occurs. When the calcium acetate forms the continuous medium the crystallites gradually accumulate at the knots of the network, forming clumps, so that the structure opens and the liquid is syneretically expressed. The force producing this change is probably molecular attraction due to the high residual valency of the calcium acetate and is also due to the affinity of the alcohol for the water of hydration. Both fine, hairlike crystals of the anhydrous salt and needles of the monohydrate can be observed in the gels. E. S. HEDGES.

Refractive index of gelatin solutions and the supposed hydration of the dispersed particles. G. ROSSI and A. MARESCOTTI (Gazzetta, 1931, **61**, 14—26).—The refractive index of solutions of gelatin is not exactly a linear function of the concentration. The deviations are ascribed to the hydration of the gelatin, and measurements at various temperatures indicate that the degree of hydration may vary with the temperature. Solutions of gelatin containing certain sodium salts, viz. iodide, bromide, citrate, and sulphate, behave differently, according as the salts increase or decrease the viscosity, but the actual changes in the refractive index are difficult to explain.

O. J. WALKER.

Diffusion in gelatin gels. W. STILES and G. S. ADAIR (J. Amer. Chem. Soc., 1931, **53**, 619—620).—The results of the authors (A., 1922, ii, 125) are said to be in essential agreement with those of Friedman and Kraemer (A., 1930, 693). J. G. A. GRIFFITHS.

Structure of gelatin gels. Gelatinisation temperature and strength as function of p_H. Y. GARREAU, P. GIRARD, and N. MARINESCO (Compt. rend. Soc. Biol., 1930, **103**, 551—554; Chem. Zentr., 1930, ii, 2238).—Consideration of the equilibrium between free and coupled dipoles in gelatin solution suggests that the p_H has a considerable influence on the degree of dissociation of the dipole and the physical properties dependent thereon. The gelatinisation temperature and strength are minimal at p_H 4·7 and change with the p_H similarly to change in dielectric constant. A. A. ELDRIDGE.

Swelling and hydration of gelatin. J. H. NORTHROP and M. KUNITZ (J. Physical Chem., 1931, **35**, 162—184).—A summary of previous work (J. Gen. Physiol., 1926—1930). The swelling, osmotic pressure, viscosity, and syneresis of gelatin sols or gels can be quantitatively explained by assuming that they are two-phase, three-component systems. The solid phase consists of micelles of an insoluble ingredient of gelatin, whilst the liquid phase is a solution of the "insoluble" fraction and of a "soluble" fraction in water. L. S. THEOBALD.

Silver migration in partly swollen gelatin layers. E. WAGNER and K. SCHAUM (Z. wiss. Phot., 1931, **28**, 325—328).—A test has been made to ascertain whether, when a drop of water on a silver in gelatin film dries, and a raised ring of gelatin with a central depression is formed, the silver is also displaced in a similar manner. A section of such a layer of gelatin was examined with the microscope when immersed in glycerol solution of the same refractive index as the gelatin. The gelatin surface was then invisible and the silver was seen to be heaped up in the same form as the gelatin surface. The effect is permanent, as a fourteen-year-old film showed a similar appearance. J. LEWKOWITSCH.

Hydrolysis during washing of the system gelatin plus silver nitrate. H. H. SCHMIDT and F. PRETSCHNER (Z. wiss. Phot., 1931, 28, 328—332).—If a mixture of silver nitrate and gelatin solution is gelled, shredded, washed, and then analysed, more silver is found than that equivalent to the nitrogen present (as nitrate). If washing is continued till the gel is free from nitrate, some silver still remains and the gel is light-sensitive and can be physically developed. The gel on melting and regelling turns turbid, and thereafter is transparent when melted and turbid when solid; the opacity is due to silver oxide. The silver cannot be entirely removed by washing or by sodium sulphite. When this gel is treated with potassium chloride, bromide, or iodide, washed, and analysed, free silver is still found, the amounts decreasing from chloride to iodide. These facts support the authors' theory of the occurrence of free silver in an emulsion (cf. B., 1930, 586, 587, 929; 1931, 223). J. LEWKOWITSCH.

Morphology of chemical reactions in gels. IV. F. M. SCHEMJAKIN (J. Russ. Phys. Chem. Soc., 1930, 62, 1885—1894; cf. this vol., 38).—The same variation in the appearance of the figure produced by placing a drop of one reagent on gelatin impregnated with another is produced by diminishing the concentration of the first or augmenting that of the second reagent. The structure of different periodic precipitation figures is described, and theories relating to the mechanism of these reactions are advanced. R. TRUSZKOWSKI.

Equilibrium between egg-albumin and calcium and potassium salts. M. GIUFFRÈ (Biochem. Z., 1930, 229, 296—310; cf. A., 1928, 1388).—When solutions of egg-albumin (purified by electro-ultrafiltration) are mixed with solutions of calcium salts (chloride, sulphate, thiocyanate) or of potassium chloride, adsorption of the salts by the albumin or loose combination between them takes place. The amount of salt adsorbed (or combined) increases as its concentration is increased and for ratios less than 500 millimols. of salt to 100 g. of albumin no saturation point is reached. With low or moderate concentrations of salt the extent to which the adsorption (or combination) takes place is greater with calcium than with potassium, but with the higher concentrations there is no difference in this respect between the two metals. When both calcium and potassium chlorides are present together each behaves towards the albumin as if the other were absent. With calcium sulphate the extent of adsorption (or combination) is 10% greater, with calcium thiocyanate 25% less, than with calcium chloride. W. MCCARTNEY.

Changes in the X-ray spectrum of inulin during swelling in water. J. R. KATZ and J. C. DERKSEN (Rec. trav. chim., 1931, 50, 248—251).—The changes taking place during the swelling of inulin have been studied by measuring the X-ray spectra of samples containing various amounts of water up to the fully saturated state. From this state down to about 8% of water there is no change in the spectrum, but below this amount changes in the intensities of interference rings are observed. At this degree of hydration, also, the water vapour-pressure curve of inulin begins to rise steeply. It is probable that the swelling of inulin is accompanied not only by the formation of aqueous shells round the micelles, but also by some other process the nature of which is not clear. O. J. WALKER.

Theory of thixotropy. E. A. HAUSER (J. Rheology, 1931, 2, 5—9).—A review of the literature leads to the conclusion that thixotropy depends on the presence of a disperse phase of anisotropic character, the particles being capable of forming solvated sheaths of a non-spherical shape. The gel condition is reached when these sheaths come into contact with their maximum possible surfaces. Agitation causes a mechanical disruption of the sheath structure, thereby transforming the gel into a sol. E. S. HEDGES.

Glue and gelatin. G. C. HERINGA and H. R. KRUYT (Chem. Weekblad, 1931, 28, 142—150).—A discussion of the relations between probable structures, and particularly of the results of X-ray examination. The reduction of Congo-red by formaldehyde proceeds more slowly when the indicator is adsorbed on the surface of the glue micelle. The dye is not only adsorbed on the surface of the micelle, but slowly diffuses into it. Abnormalities in swelling are described. The influence of colloids on one another is put forward as a basis for explanation of cell aggregation in living matter. S. I. LEVY.

Chylomicron emulsion. S. DE W. LUDLUM, A. E. TAFT, and R. L. NUGENT (J. Physical Chem., 1931, 35, 269—288).—The nature of the surface films surrounding chylomicrons has been investigated. The p_H of the isoelectric point of chylomicrons in human serum has been determined by a flocculation and by a cataphoretic method. In all cases the values lie between p_H 4·6 and 5·4, and between the accepted values for the isoelectric points of serum-albumin and serum-globulin. The more exact cataphoretic method indicates an isoelectric point between p_H 4·8 and 5·0. This affords strong evidence that the chylomicrons are surrounded by protein films, which may be composed of mixed serum-albumin and serum-globulin. Experiments with strong acid, alkali, 95% alcohol, and ammonium sulphate confirm the view that protein precipitants should cause aggregation of chylomicrons. The application of the Mudd interface technique indicates that the chylomicrons are lipoid droplets surrounded by protein films. L. S. THEOBALD.

Sol and coacervate of ichthyocoll. H. G. B. DE JONG and N. F. DE VRIES (Rec. trav. chim., 1931, 50, 238—247).—Ichthyocoll was prepared by making a hot aqueous extract of the drug ichthyocolla, centrifuging, filtering, adding sodium hydroxide, precipitating and washing with alcohol, and drying the product in air. The product had an ash content of 0·38% and dissolved readily in warm water. Experiments with the sol were conducted at 37°. A 0·73% sol behaved in accordance with Poiseuille's law. The curve connecting the viscosity with p_H closely resembles that of gelatin over the range p_H 1—4, but above p_H 4 marked differences occur. The curve is nearly flat between p_H 5 and 10, and there is a maximum at about p_H 8—9. When cooled, the sol is turbid between p_H 6·7 and 9·3, the maximum turbidity being at about p_H 9. The isoelectric point of ichthyocoll is also in the neighbourhood of p_H 8—9. The viscosity rises again above p_H 9 and passes through another maximum at p_H 12. The influence of electrolytes on the postively-charged ichthyocoll sol has been studied at different hydrogen-ion concentrations; potassium, calcium, and luteocobaltic chlorides have practically the same effect, but notable differences are shown by the effects of potassium chloride, sulphate, and ferricyanide, where the valency of the oppositely-charged ion is altered. Simple coacervation of the sol is brought about by the addition of alcohol, resorcinol, etc. to the isoelectric sol. Complex coacervation occurs when the positive ichthyocoll sol is added to the negative sols of gum arabic, thymus and yeast nucleates, egg and soya-bean lecithins, and when the negative ichthyocoll sol (above p_H 9) is added to the negative clupein sol. No coacervation results from mixing positive ichthyocoll with negative gelatin over the region p_H 5—9 and this is connected with the peculiar course of the viscosity curve over this region, the electrical attraction being insufficient to overcome the solvation tendency. E. S. HEDGES.

Swelling pressure of rubber. P. STAMBERGER (Nature, 1931, **127**, 274).—The swelling pressure, P, can be represented by the formula $P=KV^{-2}$, where V is the volume of solvent bound to unit weight of gel and K is a constant characteristic for all solvents and gels. L. S. THEOBALD.

Influence of size, shape, and conductivity on cataphoretic mobility, and its biological significance. A review. H. A. ABRAMSON (J. Physical Chem., 1931, **35**, 289—308).—Particles which have cataphoretic mobilities independent of size and shape are tabulated. The cataphoretic mobility of oil droplets and the data relating to the factor of proportionality in the general equation for cataphoretic and electroendosmotic mobilities are discussed. Size and shape do not primarily cause changes in the mobility of red blood cells. L. S. THEOBALD.

Effect of alkali salts on cataphoresis and precipitation of colloidal gold. Hofmeister series. A. LAGEMANN (Kolloidchem. Beih., 1931, **32**, 212—248).—The effect of alkali halides in reducing the charge of the particles of a gold sol has been measured by a cataphoretic method and has been compared with the coagulating effect. The positive alkali ions reduce the negative charge of the gold particles in the following order of increasing effectiveness: Li<Na<K<Rb. The halogen ions exert an antagonistic effect in the order Br<Cl<F. The univalent positive ions do not discharge the colloid particles completely; with increasing concentration of the electrolyte the charge is reduced at first rapidly and then slowly, tending asymptotically towards a limiting value, the maximum discharge increasing with the at. wt. of the ion. The variation of the charge on the colloid with concentration of the added electrolyte can be represented by an adsorption curve. The coagulation of colloidal gold by the same electrolytes follows the same ionic series as that observed in the discharging effect, but there is no proportionality between the coagulating and discharging effects. E. S. HEDGES.

Influence of surface-active substances and electrolytes representing both kinds of ions on the electrophoretic migration velocity of lyophobic sols. S. H. WHANG (Kolloidchem. Beih., 1931, **32**, 169—196).—Measurements of the electrical migration velocity of the particles of quartz suspensions and of sols of arsenious sulphide and ferric hydroxide have been made in the presence of surface-active compounds (alcohols, fatty acids, and amines) and also in the presence of a large number of inorganic electrolytes. The influence of the surface-active substances cannot be expressed by any simple and general rule. The addition of the lower alcohols causes a lowering of the cataphoretic migration velocity of a quartz suspension, whilst the velocity is increased by amyl and hexyl alcohols. The fatty acids lower the velocity of cataphoresis, but all bases, whether active or inactive in capillary properties, increase the velocity very considerably. The results obtained in the study of the influence of inorganic electrolytes are consistent in showing that the oppositely-charged ion reduces the migration velocity of the particle in proportion to the mobility of the ion. At the same time, the ion of similar charge to the particle has an antagonistic effect, increasing the velocity of the particle in proportion to the mobility of the ion. These results are discussed in relation to those of other investigators. E. S. HEDGES.

Electrophoresis and the diffuse ionic layer. M. MOONEY (J. Physical Chem., 1931, **35**, 331—344).—The theory of the diffuse ionic layer and its influence on the electrophoresis of a sphere is outlined. A formula for the limiting slope of the mobility–curvature curve is developed. The electrophoretic mobilities of oil drops in electrolytes, determined by the microscopic method, are in approximate agreement with the theory as applied to dilute aqueous solutions. Formulæ for surface charge and surface conductivity are given, and various anomalous effects in cataphoresis are discussed. The Debye–Hückel formula for cataphoresis is limited to conditions in which the colloidal particle is much smaller than its diffuse ionic layer. L. S. THEOBALD.

Equation for a perfect gas according to thermodynamics and the properties of electrons and protons. R. D. KLEEMAN (Z. anorg. Chem., 1931, **196**, 284—288).—Theoretical. E. S. HEDGES.

Diffusion as a pulsation process. W. JAZYNA (JACYNO) (Z. Physik, 1931, **67**, 278—288).—Theoretical. The various points of view regarding the process of diffusion are considered, and the pulsation theory is treated on the basis of formal thermodynamics. A. J. MEE.

Nuclear spin and the third law of thermodynamics. Entropy of iodine. W. F. GIAUQUE

(J. Amer. Chem. Soc., 1931, **53**, 507—514; cf. this vol., 294).—According to heat capacity, vapour pressure, and spectroscopic data for iodine, the heat of sublimation is 15,640 g.-cal. per mol. at 0° Abs. and 14,877 at 298° Abs.; the vapour pressure of the solid is given by $\log_{10} p(\text{atm.}) = -3512{\cdot}3/T - 2{\cdot}013 \log_{10} T + 13{\cdot}374$, whilst the entropy, S_{298}, of the gas is 62·29 and that of the solid 27·9 g.-cal. per 1° per mol. These values afford correct entropy changes in reactions, but are less than the absolute entropies by the (unknown) entropy due to nuclear spin, the effect of which persists to below 10° Abs. Molecular rotation of the type existing in solid hydrogen does not occur in solid iodine, but both para- and ortho-iodine retain their respective spin multiplicities in the solid state. J. G. A. Griffiths.

Le Chatelier–Braun principle. I. Thermodynamic proof. H. S. Frank (Lingnan Sci. J., 1930, **9**, 81—90).—A discussion of the principle and its application to salt solutions.

Chemical Abstracts.

Van 't Hoff's stability rule. B. Bružs (Rec. trav. chim., 1931, **50**, 230—237).—A simple thermodynamic derivation is given of van 't Hoff's stability rule that of two modifications of a system the one with the higher specific heat becomes stable at higher temperatures. The rule is shown to be supported by the experimental data at present available, although in the case of gas–solid systems and of the two forms of hydrogen low temperatures must be considered to obtain the correct result.

O. J. Walker.

Quantitative relation between the slopes *dP/dT* of the lines representing univariant equilibria at an invariant point. (Mlle.) A. E. Korvezee, (Mlle.) N. H. J. M. Voogd, and F. E. C. Scheffer (Rec. trav. chim., 1931, **50**, 252—255).—A relation between the slopes of the pressure–temperature curves and the compositions of the various phases at an invariant point is derived for binary and ternary systems. O. J. Walker.

Graphical treatment of the thermodynamics of the rectifying column. W. H. Keesom (Proc. K. Akad. Wetensch. Amsterdam, 1930, **33**, 901—908).—Using certain simplifying suppositions, the energy changes in a rectifying column used for separating the constituents of a binary mixture are deduced thermodynamically and the results set out in graphical form. J. W. Smith.

Superheating and intensive drying of liquids. A. Smits (Z. physikal. Chem., 1931, **153**, 253—254).—Polemical against Cohen and Cohen-de Meester (this vol., 294). H. F. Gillbe.

Influence of intensive drying on the establishment of internal equilibrium. I. A. Smits, E. L. Swart, P. Bruin, and W. M. Mazee (Z. physikal. Chem., 1931, **153**, 255—261).—The observed elevation of the b. p. of liquids after intensive drying is ascribed to superheating, caused possibly by the removal of dust by the prolonged contact with the drying agent. It is suggested that the presence of dust may act catalytically on the establishment of the internal equilibrium of the liquid, but no evidence could be obtained of the abnormally low vapour pressure of a dust-free liquid, resulting from surface evaporation, which would be anticipated on this view; removal of all traces of dust has, however, been shown to conduce to superheating. Sources of error in vapour-pressure measurements with dry liquids are noted, of which the principal is due to the presence of gas in the liquid. No effect of intensive drying for 8 months has been observed with liquids completely free from gases. H. F. Gillbe.

Equilibrium of the simplest *cis–trans*-isomerides (dichloroethylenes) in the vapour [phase]. L. Ebert and R. Büll (Z. physikal. Chem., 1931, **152**, 451—452).—Preliminary communication. The vapour of dichloroethylene at 300° contains about 63% of the *cis*-component, the same equilibrium being reached from either side. The b. p. of the pure liquids are: *cis*- 60·14±0·04°, *trans*- 47·48±0·04°.

F. L. Usher.

Cryoscopic study of paraldehyde in solutions of calcium and strontium chloride. F. Bourion and E. Rouyer (Compt. rend., 1931, **192**, 557—559).—The values of the cryoscopic constant are said to indicate that the triple molecule $(C_2H_4O)_3$ is stable in the salt solutions (cf. this vol., 35).

C. A. Silberrad.

Electrolytic dissociation. Fundamental hypotheses and assumptions of the electrostatic theory of electrolytic dissociation and an attempt to explain it without assuming dielectric action. K. Fredenhagen (Z. physikal. Chem., 1931, **152**, 321—379; cf. A., 1929, 648; 1930, 421, 537).—The author's views are amplified and summarised. It is not permissible, in view of the strict thermodynamic connexion between the effect of the dielectric constant on dissociation and its effect on solvent power, to consider either of these properties separately. The relative solvent powers of water, ammonia, hydrogen cyanide, and hydrogen fluoride for a number of salts are often in a sense opposite to that required by the electrostatic theory. The limited applicability of the Nernst–Thomson rule depends on the fact that the same factor, *i.e.*, internal pressure, is influential in determining both the value of the dielectric constant of a solvent and the extent of dissociation of a solute in it, but complete parallelism is found only among chemically similar solvents. The underlying cause of ionisation is the preferential (chemical) attraction of the solute for one or the other constituent of the polar solvent. The theory accounts for the large difference between the electrical conductivity of fused salts and that of pure ionising solvents, and serves to explain qualitatively a number of phenomena not accounted for by the electrostatic theory.

F. L. Usher.

Dissociation of strong electrolytes. III. Complete dissociation and optical properties. M. B. Jacobs and C. V. King (J. Physical Chem., 1931, **35**, 480—487; cf. A., 1930, 995).—A discussion of the views of previous workers on optical data. The view of the additivity of optical properties is no longer tenable, and percentage dissociation cannot be calculated with certainty from colour or absorption data. Evidence for the existence of a small number of undissociated molecules or ion groups even in the highly dissociated electrolytes continues to grow.

L. S. Theobald.

Raman effect and electrolytic dissociation. L. A. Woodward (Physikal. Z., 1931, **32**, 212—214).—Each molecular species of a scattering system gives its own characteristic Raman effect, with an intensity proportional to the corresponding concentration. For solutions of electrolytes, therefore, this can be used to find the degree of ionisation. For solutions of ordinary salts the Raman effect of the ions only is obtained; hence salts appear to be completely dissociated in solution. For nitric acid, results similar to those obtained by Rao were found. For sulphuric acid, anomalous intensity changes were found. A series of solutions was investigated so that the exposure times were inversely proportional to the concentrations. If there were no anomalies there should be the same intensity in each case. There are, however, variations in the curves showing the formation of the HSO_4' ion and the SO_4'' ion at different dilutions. Iodic and trichloroacetic acids of different concentrations have also been investigated. Both gave an intensive Raman effect, but no anomalies connected with ionisation were apparent. For a saturated solution of hydrogen chloride at 25°, no Raman line could be found. From the vapour pressure, however, it is known that undissociated HCl molecules must exist in the solution, but the concentration of these is evidently so small that no Raman effect can be produced.

A. J. Mee.

Selenium cells as colorimeters. III. A. Mickwitz (Z. anorg. Chem., 1931, **196**, 113—119).—Extrapolation of measurements with the selenium cell of the light absorption of colloidal nickel and cobalt sulphide solutions together with theoretical considerations relating to the composition of the disperse phase when formed by the action of sodium or hydrogen sulphide on a solution of a salt of the metal indicate that the solubility (expressed in terms of metal) is for Ni(SH)(OH) $0{\cdot}8\times10^{-5}$, for Co(SH)(OH) $0{\cdot}3\times10^{-5}$, and for $Co(SH)_2$ 1×10^{-5} parts per 100.

H. F. Gillbe.

Solubility of acids in salt solutions. IV. Solubility and activity coefficient of benzoic acid in aqueous benzoate solutions. E. Larsson (Z. physikal. Chem., 1931, **153**, 299—308).—The solubility of benzoic acid at 18° in solutions of chlorides, bromides, iodides, nitrates, perchlorates, di- and trichloroacetates, benzenesulphonates, and β-naphtholsulphonates containing sodium benzoate to repress the ionisation of the acid has been measured, and the activity coefficient of the benzoic acid molecule in each solution has been calculated. The influence of the alkali and alkaline-earth chlorides and nitrates decreases with increase of the at. wt. of the cation, and the analogous condition obtains for the potassium halides. The difference between the activity coefficient in a chloride and in a nitrate solution is independent of the nature of the cation, and it appears that the total effect is the resultant of two component effects, of which one is characteristic of the anion and the other of the cation. By assuming that the components are equal in the case of potassium chloride, the specific influences of the various ions have been calculated. The results are in general in accordance with the Debye–Hückel theory, but in certain cases, and notably those involving large organic anions which cannot be regarded as spherical and carrying a central point charge, the activity coefficient is less than unity, although benzoic acid lowers the dielectric constant of water.

H. F. Gillbe.

Dissociation of mercuric halides. H. Braune and S. Knoke (Z. physikal. Chem., 1931, **152**, 409—431; cf. A., 1928, 829).—The dissociation of mercuric chloride, bromide, and iodide has been determined at different temperatures up to 1200°, and the calculated heats of dissociation agree well with those furnished by calorimetric data. The calculated moments of inertia of the molecules are in the ratio 1 : 0·48 : 0·22 for the iodide, bromide, and chloride, respectively.

F. L. Usher.

Optical dissociation of mercury halides. V. Kondratéev (Z. physikal. Chem., 1931, B, **11**, 470—474; cf. Sponer, this vol., 432).—On the assumption that the optical dissociation of the mercuric halides is represented by the equation $HgX_2+h\nu=HgX+X^*$, the heats of formation of the di- and tri-atomic molecules are calculated from spectrographic and thermochemical data. The values thus obtained, considered correct within a few kg.-cal., are: (Hg,Cl) 27, (Hg,Br) 20, (Hg,I) 12; (HgCl,Cl) 79, (HgBr,Br) 65, (HgI,I) 53 kg.-cal.

F. L. Usher.

Equilibrium between chlorine, bromine, and bromine monochloride. W. Jost (Z. physikal. Chem., 1931, **153**, 143—152).—The chemical equilibrium in mixtures of gaseous bromine and chlorine has been examined by a spectro-photometric method and the existence of bromine monochloride has been confirmed. The heat of formation of this compound has been calculated to be 0·75±0·5 kg.-cal.

E. S. Hedges.

Equilibrium between vapour and liquid phase in the system acetic acid–ethyl acetate. L. L. Schmidt (J. Russ. Phys. Chem. Soc., 1930, **62**, 1847—1858).—The total and partial vapour-pressure curves of the above system show that the proportion of associated acetic acid molecules in the gaseous phase rises with concentration of acetic acid in the mixture; in general, Gibbs' dissociation law is applicable to such systems.

R. Truszkowski.

Melting diagram of the system zirconium dioxide–beryllium oxide. O. Ruff, F. Ebert, and H. von Wartenberg (Z. anorg. Chem., 1931, **196**, 335—336).—A reinvestigation of this system has failed to confirm the existence of the high-melting compound, $3BeO,2ZrO_2$, formerly reported (A., 1930, 847).

E. S. Hedges.

Binary system potassium nitrate–calcium nitrate. A. P. Rostkovski (J. Russ. Phys. Chem. Soc., 1930, **62**, 2055—2059).—The fusion diagram indicates the formation of a compound, $4KNO_3,Ca(NO_3)_2$, with a transition point at 174° and 71·3% KNO_3. The eutectic point is at 145° and 65·8% KNO_3. The system is characterised by the formation of viscid melts, which readily exhibit supercooling with the formation of vitreous masses. The above double compound is not formed in aqueous solutions.

R. Truszkowski.

Polymorphism of rubidium nitrate, and the system $RbNO_3$–RbCl. A. P. Rostkovski (J. Russ. Phys. Chem. Soc., 1930, **62**, 2067—2070).—A fourth polymorph of rubidium nitrate, transition point 290—292°, is described. The fusion diagram of the system $RbNO_3$–RbCl indicates the formation of two double compounds with transition points at 338° and 10·4 mol.-% $RbNO_3$ and 394° and 24 mol.-% $RbNO_3$.
R. Truszkowski.

Crystallisation of copper from fused cuprous chloride. V. Sihvonen (Z. Elektrochem., 1931, **37**, 80—82).—If a mixture of fused cuprous chloride and metallic copper be heated unevenly the metal separates in the cooler part of the system as dendritic crystals. The presence of thermoelectric currents reduces the yield of copper, as a result of the formation of cupric chloride by the chlorine ions which are discharged at the hotter electrode. The crystallisation effect is due to a displacement of the equilibrium $2Cu^{\cdot} \rightleftharpoons Cu+Cu^{\cdot\cdot}$, the direction of the displacement with temperature being the same as in aqueous solutions. H. F. Gillbe.

Cupric–cuprous equilibrium in cupric sulphate and perchlorate solutions, and the anodic behaviour of copper. E. Heinerth (Z. Elektrochem., 1931, **37**, 61—76).—The equilibria between cupric and cuprous ions in acid solutions of the sulphate and perchlorate have been investigated by shaking a solution of the cupric salt with powdered copper in an atmosphere of nitrogen and analysis of the resulting solution. Equilibrium is attained within a few hours. The ratio $[Cu^{\cdot\cdot}]^{\frac{1}{2}}/[Cu^{\cdot}]$ is independent of variations of concentration, acidity, and total ionic concentration within wide limits, and in the sulphate solutions falls from 1429 at 20° to 500 at 40° and 205 at 60°; in the perchlorate solutions the results are less readily reproducible. The heat tone of the reaction $Cu^{\cdot\cdot}+Cu \longrightarrow 2Cu^{\cdot}$ at 20—60° is 18·8 kg.-cal. The normal potential of the process $Cu \longrightarrow Cu^{\cdot}$ at 25° is 0·525 volt. It has been confirmed experimentally that on dilution of a solution which is in equilibrium with respect to cuprous and cupric ions supersaturation with respect to the former does not occur. The anodic dissolution of copper in acid solutions of the sulphate has been investigated by the determination of current density–voltage curves. The polarisation diminishes with rise of temperature and increases with increase of acidity, and the formation of an anode sludge follows a course parallel with that of the polarisation. H. F. Gillbe.

Water of hydration of crystalline compounds. III. Tensimetric analysis of the systems $CoSO_4$–H_2O, $Na_3[Fe(C_2O_4)_3]$–H_2O, and $K_3[Fe(C_2O_4)_3]$–H_2O. A. P. Rostkovski (J. Russ. Phys. Chem. Soc., 1930, **62**, 2061—2065).—The vapour-pressure isotherms of the above systems were determined at 25°. Cobalt sulphate forms hydrates with 1, 6, and 7 mols. of water, sodium ferrioxalate combines with 2 and 5, and potassium ferrioxalate with 3 mols. of water. In the first two systems there is no formation of solid solutions, but the last gives an uninterrupted series of solutions of trihydrate in anhydrous salt.
R. Truszkowski.

Oxide hydrates. XXXVI. System ferrous oxide–water and its conversion into the system ferric oxide–water. G. F. Hüttig and H. Möldner (Z. anorg. Chem., 1931, **196**, 177—187).—Observations on the dehydration of hydrated ferrous hydroxide indicate that the reaction $3FeO,H_2O \longrightarrow Fe_3O_4+2H_2O+H_2$ takes place to a small extent. Ferrous hydroxide exhibits a characteristic Debye diagram, and must be regarded as a definite compound. The primary decomposition is irreversible and occurs in two stages, viz., at 220—234° and at 261—277°; the remaining water (0·4 mol.) is evolved continuously on raising the temperature. The product of the oxidation of ferrous hydroxide, Fe_3O_4,nH_2O, has the same Debye diagram as magnetite, and loses water readily and continuously with rise of temperature. On ageing the water becomes still more loosely combined and the substance loses its ability to become oxidised completely in the air to the ferric state. The conversion of ferrous hydroxide into the ferric state is discussed. H. F. Gillbe.

Equilibrium constants for the decomposition of ammonium hydrogen carbonate. W. K. Hutchinson (J.C.S., 1931, 410—412).—By determining the partial pressure of ammonia, carbon dioxide, and water vapour in equilibrium with a saturated aqueous solution of ammonium hydrogen carbonate, the equilibrium constant, which is also the constant for the dissociation of the solid, has been calculated. The constant K is given by the equation $\log_{10} K=33{\cdot}88-40{,}600/2{\cdot}303RT$ and is satisfied over a wide range of concentrations of carbon dioxide and ammonia. The value 40,600 g.-cal. for the heat of formation of solid ammonium hydrogen carbonate is in good agreement with accepted values.
E. S. Hedges.

Equilibria in salt lake waters. The ternary system: sodium hydrogen carbonate–sodium sulphate–water. S. Z. Makarov and N. M. Waksberg (J. Russ. Phys. Chem. Soc., 1930, **62**, 1863—1870).—The phase diagram of the above system shows neither compound nor solid solution formation. Determinations must be made in an atmosphere of carbon dioxide, in order to avoid formation of sodium carbonate. R. Truszkowski.

Heats of formation of gaseous halides of mercury, cadmium, and zinc. H. Sponer (Z. physikal. Chem., 1931, **B**, **11**, 425—432).—Approximate values for the heats of formation of the diatomic molecules, and of the triatomic molecules from the former and a halogen atom, are calculated on the basis of Wieland's analysis (A., 1929, 1127) of the band spectra of the gaseous halides of mercury, cadmium, and zinc. The values in kg.-cal. are: (Hg,Cl) 32, (Hg,Br) 25, (Cd,Br) 60, (Cd,I) 32, (Zn,I) 46; (HgCl,Cl) 72, (HgBr,Br) 62, (CdI,I) 48. F. L. Usher.

Heats of formation of nitrides. I. Manganese and chromium nitrides. B. Neumann, C. Kröger, and H. Haebler (Z. anorg. Chem., 1931, **196**, 65—78).—A method and apparatus for the direct determination of the heat of formation of nitrides have been developed. The metal is heated electrically in a calorimeter bomb containing nitrogen under pressure to a temperature at which the reaction velocity is sufficiently high to ensure a reasonably high conversion into nitride. Measurements with manganese indicate that the quantity of nitrogen taken up by the metal does not alter with variation of pressure between 10 and 25 atm., and corresponds with the compound Mn_5N_2; the heat of formation is 57,180±400 g.-cal. Combustion of manganese containing nitride in oxygen yields a value of about 62 kg.-cal. The heat of formation of chromium nitride, CrN, is 29,500±500 g.-cal., whilst the value calculated from the dissociation pressure curve is 23·7—24·5 kg.-cal. at 20°. H. F. Gillbe.

Heats of combustion of mothane and carbon monoxide. F. D. Rossini (Bur. Stand. J. Res., 1931, 6, 37—49).—The heat of combustion of methane to form carbon dioxide and liquid water has been found to be 889,700±300 international joules per mol. at 30° under a constant pressure of 1 atm. The heat of combustion of carbon monoxide to form carbon dioxide is 282,925±120 international joules per mol. at 30° and 1 atm. R. Cuthill.

Vapour pressure and heat of dilution. VIII. Heat of dilution of sucrose in aqueous solution and of carbamide and calcium chloride in alcoholic solution. R. B. Vallender and E. P. Perman (Trans. Faraday Soc., 1931, 27, 124—135).—Using the method previously described (cf. A., 1929, 1389), the heats of dilution have been determined over wide ranges of concentration and temperature. For sucrose all the heats of dilution are negative and never greater than 3 g.-cal. per g. of water. At high concentrations the heat of dilution–concentration curves intersect at very nearly the same point. In ethyl alcohol solution carbamide gives very small positive and calcium chloride negative heats of dilution. Using the Kirchhoff equation to calculate the heats of dilution from the vapour pressure good agreement is obtained in the case of carbamide and of calcium chloride in alcohol, but not for the sugar solutions. The osmotic pressures of sucrose solutions calculated from the heats of dilution by means of Porter's equation (A., 1918, ii, 64) agree well with the experimental values. O. J. Walker.

Transport numbers of hydrogen chloride in ethyl alcohol. J. W. Woolcock, (Sir) H. Hartley, and O. L. Hughes (Phil. Mag., 1931, [vii], **11**, 222—225).—The most probable value for the transport number of the hydrogen ion at infinite dilution at 25° in hydrogen chloride solutions is given as 0·71±0·01; this is derived from measurements of the *E.M.F.* of cells of the type Ag,AgCl|HCl in EtOH (C_1) : HCl in EtOH(C_2)|AgCl,Ag, with and without liquid junctions. F. G. Tryhorn.

Determination of transport numbers of metals in the electrolysis of their alloys. I. R. Springer and R. Frena (Monatsh., 1931, 57, 112—164; cf. Kremann and others, A., 1930, 1253).—Amalgams of sodium, potassium, and tin, allowed to solidify in capillary tubes, have been electrolysed at various current densities and the resulting changes in composition along the length of the tube determined. From the results of these experiments and from data furnished by similar experiments by Kremann and his co-workers it is found that the nineteen alloys studied fall into three groups, viz., (1) potassium, lead, and tin amalgams, tin–lead, tin–antimony, bismuth–tin, bismuth–cadmium, and potassium–sodium, in which one component migrates to the cathode and the other to the anode; (2) amalgams of sodium and of bismuth, tin–zinc, tin–aluminium, silver–aluminium, silver–bismuth, and tin–cadmium, in which the components either behave as in (1) or both migrate to the anode, according to experimental conditions; and (3) silver–tin, silver–antimony, and lead–sodium, in which both metals migrate to the anode under all the conditions observed. It is considered that the normal behaviour is that shown by the first group, and that divergences are largely attributable to errors in analysis or to irregularities of composition not due to passage of the current. F. L. Usher.

Electrolytic transference of water in 0·1*N* solutions of hydrobromic and hydriodic acids and in *N*-potassium iodide solution. J. Baborovský and A. Wagner (Coll. Czech. Chem. Comm., 1931, 3, 53—60).—Measurements of the electrolytic transference of water (ω) have been made by Baborovský's method (A., 1927, 1140; cf. A., 1928, 954). In hydrobromic acid solutions the presence of a membrane increases the quantity of electrolyte transferred, and the values of ω are not the same at the anode and cathode. Hydriodic acid solutions, even at 0·1*N* concentration, yield uncertain results owing to oxidation and the formation of complexes, whilst difficulties arise with potassium iodide solutions as a result of the dissolution of silver iodide from the (silver) electrodes. After correction for this disturbance the anode values of ω are smaller than the cathode values. The transport number of the cation derived from the cathode measurements shows the better agreement with the accepted values. In *N* solution the iodide ion is associated with 2 mols. of water. H. F. Gillbe.

Conductivity of electrolytes. III. Design of cells. G. Jones and G. M. Bollinger (J. Amer. Chem. Soc., 1931, 53, 411—451; cf. A., 1929, 1161).—The ratio of the resistances of two cells filled with portions of the same solution varies with the conductivity in a less complicated manner than that observed by Parker (A., 1923, ii, 530, 722). The variations, when high frequencies and resistances are used to eliminate polarisation errors, have been traced to the existence, between the parts of the cell of opposite polarity, of a capacitative shunt which, in the usual design of cell, is of sufficient magnitude to make the observed resistance of the electrolyte less than the true resistance. The error varies as the square of the capacitance and directly as the resistance in the shunt, but is independent of the platinisation of the electrodes. With horizontal cells in which the distance between the vertical filling and electrical contact tubes of opposite polarity is about 15 cm., the effect is eliminated, and provided polarisation is absent, the results are trustworthy to 0·01%. The suitability of a cell is demonstrated by the constancy of the apparent resistance when the frequency is varied between 1090 and 4000 cycles per sec. The ratio of the resistances of a pair of cells filled with a common solution is independent of the electrolyte (cf. Randall and Scott, A., 1927, 421) and thus there is no longer any support for Parker's theory that adsorption is responsible for the effect previously observed (*loc. cit.*). J. G. A. Griffiths.

Conductivity measurements in methyl ethyl ketone and acetone. P. Walden and E. J. Birr (Z. physikal. Chem., 1931, **153**, 1—51).—Methyl ethyl ketone was purified until the product had a conductivity of 5×10^{-8} reciprocal ohm. Measurements of density and viscosity were made at different temperatures, and the variation of density with temperature can be represented by the formula $d^t=0{\cdot}82737(1-0{\cdot}0012635t)$. The conductivities of solutions of the following substances in methyl ethyl ketone have been determined at 25° up to dilutions of $10^{-5}M$: tetramethylammonium picrate, tetraethylammonium picrate, iodide, perchlorate, chloride, bromide, and nitrate, tetra-*n*-propylammonium picrate, iodide, and perchlorate, tetra-*n*-butylammonium picrate, tetra*iso*amylammonium picrate, iodide, and perchlorate, ethylammonium picrate, bromide, and iodide, *iso*butylammonium picrate and chloride, *iso*amylammonium picrate and chloride, *n*-cetylammonium picrate dimethylammonium picrate, diethylammonium picrate chloride, and iodide, di*iso*amylammonium picrate and chloride, triethylammonium picrate and chloride, tri*iso*amylammonium picrate, chloride, and iodide, lithium picrate, sodium picrate and iodide, potassium picrate and iodide, silver picrate, barium perchlorate, cadmium picrate and iodide, mercuric chloride and iodide. Conductivity values have also been determined for solutions of the picrates of lithium, tetra-*n*-propylammonium, tetra-*n*-butylammonium, and tetra*iso*amylammonium in acetone. The results establish the validity of Kohlrausch's square-root rule, the law of independent migration of ions, Stokes' law for ions, and Walden's rule for these non-aqueous solutions. Both strong and weak electrolytes exist. The ionic mobilities in methyl ethyl ketone and in acetone have been calculated from Walden's rule and calculation has been made of the degree of solvation of alkali and halogen ions in methyl ethyl ketone, methylamine, and ethylene dichloride. E. S. Hedges.

Conductivity data of aqueous mixtures of hydrogen peroxide and organic acids. W. H. Hatcher and M. G. Sturrock (Canad. J. Res., 1931, **4**, 35—38).—The conductivities of solutions of formic, acetic, propionic, and glycollic acids containing hydrogen peroxide have been determined. With formic acid the conductivity decreases to a constant value within 4 hrs., whereas with glycollic and acetic acids there is at first a rapid fall and then a slow rise to a constant value, which is attained within 30 hrs. The conductivity of the propionic acid solutions rises continuously to a maximum, and the change is completed within 3 hrs. It appears that the conductivity of the peracid formed in each case approximates to that of the complex ultimately formed.

H. F. Gillbe.

Interfacial electrical conductivity. K. Šandera (Coll. Czech. Chem. Comm., 1931, **3**, 96—102).—The influence of solids of large surface area, such as sand and activated carbon, on the conductivity of potassium chloride solutions has been studied. The size and form of the grains have a pronounced influence. Thus finely-divided calcium carbonate causes an increase of conductivity, and the effect increases with the volume of the powder added, whereas with sand, as a result of the smaller surface and greater screening effect, the conductivity decreases; with activated carbon the influence of the surface is still more marked. A theoretical equation relating the change of conductivity with the volume of solid present is in fair agreement with most of the observed values.

H. F. Gillbe.

Electro-osmosis and electrolytic transference in aqueous solutions. J. Velíšek and A. Vašíček (Coll. Czech. Chem. Comm., 1931, **3**, 111—115).—A discussion of the two principal methods for the study of electro-osmosis, viz., the chemical and the physical. The latter, although simpler and more rapid, is the less accurate, and does not serve to distinguish the fraction of the total transference due to the electrolyte and that due to the solvent. H. F. Gillbe.

Electro-endosmosis. IV. Electro-endosmosis of some organic liquids against a glass surface. F. Fairbrother and M. Balkin (J.C.S., 1931, 389—403).—The "bubble-tube" method has been used to measure the velocity of electro-endosmosis of formamide, furfuraldehyde, nitrobenzene, *o*-nitrotoluene, ethyl ether, chloroform, acetone, *n*-propyl alcohol, *n*-butyl alcohol, benzaldehyde, aniline, propionic acid, benzene, carbon tetrachloride, and water through a diaphragm of sintered Jena Geräte glass powder. Considerable attention was given to the purification and drying of the liquids, as it was observed that traces of impurities gave erroneous results even in solvents of low ionising power. The electrokinetic potential has been calculated in each case and the values are of the same order of magnitude. Benzene and carbon tetrachloride, having practically no dipole moment, give no electro-endosmosis even under a *P.D.* of 910 volts across a diaphragm only 5 mm. thick; ether is negatively charged towards the glass, and the rest of the organic liquids and water are positively charged. The product of the velocity of electro-endosmosis and the viscosity of the liquid increases with the dielectric constant, but the relation is not linear. The connexion between the velocity of electro-endosmosis and the dipole moment of the molecules is discussed, and the experimental results indicate a close relation between the electro-endosmosis and the product of the number of molecules in the interface and their dipole moment. E. S. Hedges.

Effect of breadth of junction on *E.M.F.* of simple concentration cell. G. Scatchard and and T. F. Buehrer (J. Amer. Chem. Soc., 1931, **53**, 574—578; cf. A., 1925, ii, 398).—The *E.M.F.* of a cell is independent of the thickness of a junction of the "mixture boundary" type (cf. Henderson, A., 1908, ii, 655). The *E.M.F.* of the cell $Hg,HgCl|HCl(C_1)|HCl(C_2)|HgCl,Hg$ increases by 0·005—0·058 millivolt when the flowing liquid junction is made very thin. This effect is attributed to thermal changes at the boundary due to mixing of the solutions.

J. G. A. Griffiths.

Change of *E.M.F.* of zinc with thermal working. A. Schukarev and L. Vereschthagin (Physikal. Z., 1931, **32**, 230).—A test piece of zinc was heated at 200° for a long period, and the changes in its *E.M.F.* were examined. There were marked variations with time, but the curve obtained does not correspond with any simple function. A. J. Mee.

Temperature measurements at working electrodes. IV. B. Bružs (Z. physikal. Chem., 1931, **153**, 309—319; cf. A., 1930, 546).—A method is described for measuring the heat effect at a working electrode. Determinations at a $Hg|Hg_2^{++}$ interface in 0·1—1·0*M*-perchlorate and -nitrate solutions yield for the entropy of the mercurous ion in *M* solutions 29±1 g.-cal. per degree; the entropy increases slowly with decrease of concentration. H. F. Gillbe.

Electrochemistry of magnesium. S. Bodforss (Z. physikal. Chem., 1931, **153**, 83—106).—The potential of magnesium has been measured in solutions of magnesium sulphate containing sulphuric acid, solutions of magnesium chloride containing hydrochloric acid, and in acetate, citrate, and tartrate buffer solutions. The results indicate that the magnesium potential is a function of the hydrogen-ion concentration of the solution. As the hydrogen-ion concentration is increased the potential becomes more negative, passes through a maximum, and then moves in the positive direction. The potential also depends on the nature of the anion, for at constant hydrogen-ion concentration the negative potential increases in the order acetate<tartrate<citrate. The addition of neutral substances which are known to promote the formation of complexes (*e.g.*, pyrocatechol) causes the potential to become more negative. A marked increase of the negative potential is brought about by the addition of ammonium salts, carbon dioxide, and carbon monoxide, even in small concentrations. The small quantities involved cannot exert any considerable influence on the reaction $Mg \longrightarrow Mg^{\cdot\cdot}+2\ominus$, and it is believed that this equation does not represent the process determining the electrode potential. The evidence adduced leads to a working hypothesis that the potential is determined by the reaction $Mg \longrightarrow Mg^{\cdot}+\ominus$ or $2Mg \longrightarrow Mg_2^{\cdot\cdot}+2\ominus$.

E. S. Hedges.

Potential of lead–gold alloys. F. Griengl and R. Baum (Monatsh., 1931, **57**, 165—176; cf. Laurie, J.C.S., 1894, **65**, 1031).—The curve obtained by plotting potential against composition is completely changed by tempering in air at 200—300° below the m. p., which causes a minimum to appear at 60% Au. This effect is attributed to a layer of oxide, since the potential of an alloy with 65% Au tempered in nitrogen is the same as that of the untempered metal. The results support Laurie's experiments and indicate that the potentials of the compounds AuPb and Au_2Pb are near to that of lead. F. L. Usher.

Reduction potential of quadrivalent to tervalent iridium in hydrochloric acid solution. S. C. Woo (J. Amer. Chem. Soc., 1931, **53**, 469—472).—The *E.M.F.* of the cell $Ir|IrCl_6'''(c)+IrCl_6''(c)+HCl(1N)|HCl(1N)|H_2(1\ atm.),Pt$ at 20° and 25° is −1·0313 and −1·0264 volts, respectively, when $c=0{\cdot}002$—$0{\cdot}008f$. The reduction potential of the reaction $IrCl_6'''(c)+1N\text{-}HCl=IrCl_6''(c)+1N\text{-}HCl+e$ is 1·021 at 25°, referred to the normal hydrogen electrode; the corresponding changes of free energy and heat content are −23,540 and −30,400 g.-cal., respectively.

J. G. A. Griffiths.

Reduction potential of thymoquinhydrone. E. Biilmann and J. Muus (Ber., 1931, **64**, [*B*], 310—314).—Measurements of the *E.M.F.* of $Pt^+|$benzquinhydrone, 0·1*N*-HCl, thymoquinhydrone$|Pt^-$ give 0·5923 and 0·5867 volt for the reduction potential of the thymoquinhydrone electrode at 18° and 25° respectively. Similarly the combination $Pt^+|$benzoquinhydrone, 0·01*N*-HCl, 0·09*N*-KCl, thymoquinhydrone$|Pt^-$ gives 0·5927 and 0·5866 volt respectively. H. Wren.

Oxidation–reduction potentials of alkali chlorites. II. G. R. Levi and D. Ghiron (Atti R. Accad. Lincei, 1930, [vi], **12**, 158—161).—At 20° the *E.M.F.* of the cell $Pt^-|0{\cdot}1N\text{-}KClO_2[\text{or } Ca(ClO_2)_2]:KMnO_4,0{\cdot}1N|Pt^+$ is 0·175 volt. In discharge, the chlorite is oxidised to chlorate and the permanganate reduced to manganese dioxide. For the cell $Pt^-|KClO_2,\ 0{\cdot}1N:\ NaClO,\ 0{\cdot}1N|Pt^+$ the initial *E.M.F.* at 20° is 0·084 volt, but rises in a few hours to 0·100 volt and then diminishes regularly with time. The reaction $NaClO_2+NaClO=NaCl+NaClO_3$ occurs. The cells $Pt^+|KClO_2,\ 0{\cdot}1N:\ H_2O_2,\ 0{\cdot}1M|Pt^-$, and $Pt^+|KClO_2,\ 0{\cdot}1N:\ FeSO_4,\ 0{\cdot}1M|Pt^-$ both have an *E.M.F.* of 0·25 volt. F. G. Tryhorn.

Electrokinetic potentials. VI. Electrical phenomena at interfaces. VII. Temperature coefficient of the ζ-potential. H. B. Bull and R. A. Gortner (J. Physical Chem., 1931, **35**, 308—330, 456—465; cf. A., 1930, 1124).—VI. The ζ-potential and surface conductance at a cellulose interface have been measured for aqueous solutions (up to $1{\cdot}6\times10^{-3}N$) of sodium, potassium, calcium, magnesium, and thallic chlorides, and potassium carbonate, sulphate, and phosphate by the streaming potential method previously described (*loc. cit.*). In general, the ζ-potential decreases with an increase in concentration of the electrolyte in the aqueous phase, but this decrease may be accompanied by an increase in the charge on the particle. The decrease in ζ-potential is more nearly related to a decrease in the thickness of the double layer. In agreement with the results of McClendon (A., 1928, 22), the thickness of the double layer is found to decrease with an increase in concentration of the electrolyte. From Smoluchowski's equation expressions have been derived for the charge per unit area at the interface and for the thickness of the double layer. In connexion with the effect of electrolytes on the stability of a colloid, the results suggest that salts do not reduce the charge on the particle to zero or to a critical value, but decrease the thickness of the double layer, allowing the particles to approach closely enough to adhere to each other.

VII. The temperature coefficients of the ζ-potential for the interfaces water–cellulose, cellulose–sodium chloride ($10^{-4}N$), and ethyl alcohol–cellulose have been determined between 20° and 51°. A marked positive coefficient is shown at the last-named interface, but the relationship is not strictly linear. The temperature coefficient is higher than those for the other two systems. A maximum at approximately 40°

occurs at these two interfaces. The temperature coefficient of aqueous systems can generally be neglected in streaming potentials measured under ordinary laboratory conditions. L. S. Theobald.

Theory of dissolution of metals. II. M. Straumanis (Z. physikal. Chem., 1931, **153**, 107—111).—A reply to the criticisms of Thiel (this vol., 46; cf. Straumanis, A., 1930, 1125). The "difference effect" cannot be treated as a pure resistance phenomenon. The displacement of potential in the positive direction through the electrolytic dissolution of metals is due partly to the vectorial properties of the metal space lattice. E. S. Hedges.

[Theory of dissolution of metals.] A. Thiel (Z. physikal. Chem., 1931, **153**, 112).—Polemical (cf. preceding abstract). E. S. Hedges.

Influence of foreign gases in gaseous decompositions. N. Nagasako (Z. physikal. Chem., 1931, B, **11**, 420—424).—The effect of the presence of a foreign gas on the course of a unimolecular gaseous decomposition can be expressed by introducing an empirical constant into the usual formula for the unimolecular reaction coefficient. This empirical constant is evaluated for several indifferent gases and applied to the decomposition of nitrous oxide and of methyl ether; good agreement is found between the observed and calculated velocity coefficients. F. L. Usher.

Debased ["entartete"] explosions and periods of induction. N. Semenov (Z. physikal. Chem., 1931, B, **11**, 464—469).—Theoretical. Explosive gas reactions, and the thermal decomposition of explosive solids or liquids, in which considerable initial retardation is observed, are considered as autocatalytic processes in which the catalyst is an intermediate rather than an end product. F. L. Usher.

Fifty years' experimental research on the influence of steam on the combustion of carbonic oxide. W. A. Bone (J.C.S., 1931, 338—361).—The third Liversidge lecture delivered on Dec. 11. R. Cuthill.

Flame speeds in the "inflammation" and "detonation" of moist carbon monoxide–oxygen mixtures. W. A. Bone and R. P. Fraser (Proc. Roy. Soc., 1931, A, **130**, 542—551; cf. Bone, Fraser, and Witt, A., 1927, 424).—The results of measurements by the electrical and photographic methods (*loc. cit.*) of the initial speeds of inflammation of moist carbon monoxide–oxygen mixtures, when ignited at the ordinary temperature and atmospheric pressure at the open end of a glass tube 2·5 cm. internal diameter and 126 cm. long, the other end being closed, show that the "lower limit" mixture for inflammation is one containing 15—20% of carbon monoxide, the explosion range extending up to about 92·5% of the monoxide. The mixture giving the maximum speed contains about 80% of carbon monoxide. A photographic method for measuring the speed of detonation of moist carbon monoxide–oxygen mixtures is described, two photographs of the horizontally-advancing detonation flame being taken at distances 60 m. apart. The final establishment of detonation (as distinct from the "pre-detonation" phase) is proved by the pronounced banded appearance of the advancing flame and the constancy of the flame speed. The experimental results show that the "detonation range" lies between about 40 and 80% carbon monoxide content, the observed rates of detonation in a tube 1·3 cm. internal diameter all lying between 1700 and 1800 m. per sec., approximately. The rate is sensibly higher in a tube 2·5 cm. in diameter. A well-marked maximum rate of detonation (as also of inflammation) occurs at the $3CO+O_2$ mixture, instead of at the theoretical $2CO+O_2$ mixture, indicating that whereas an excess of carbon monoxide (up to $3CO+O_2$) increases the flame speed, a corresponding excess of oxygen always diminishes it. This circumstance is unaltered by diluting the medium with argon, helium, or nitrogen. L. L. Bircumshaw.

Effect of anti-knock materials on the speed of flame in a closed tube. Y. Nagai.—See B., 1931, 188.

Extinction of benzine–air explosions by carbon tetrachloride. A. H. Belinfante.—See B., 1931, 188.

Thermal decomposition of nitrogen pentoxide at low pressures. J. H. Hodges and E. F. Linhorst (Proc. Nat. Acad. Sci., 1931, **17**, 28—33).—The velocity of thermal decomposition of nitrogen pentoxide has been measured at 35° and pressures between 0·12 and 0·001 mm. The reaction is unimolecular at nitrogen pentoxide partial pressures greater than 0·06 mm., and the velocity coefficient is 0·00801; at lower partial pressures the unimolecular coefficient decreases, and at about 0·004 mm. the reaction becomes bimolecular and has then a velocity coefficient of about 1·2. H. F. Gillbe.

Action of water vapour on phosphorus. J. Zawadzki and T. Borucki (Przemysł Chem., 1931, **15**, 76—82).—The velocity of reaction between phosphorus and water vapours in a porcelain tube is very small, even at 1000°. The presence of ferric oxide greatly accelerates reaction, practically the whole of the phosphoric oxide produced combining with the catalyst. When ferric phosphate is used as the catalyst, it retains a large proportion of the phosphoric oxide produced at the commencement of the reaction; only after saturation of the catalyst are phosphoric oxide and hydrogen found in equivalent proportions in the reaction mixture. Under these conditions the reaction proceeds very rapidly at 650°. The amounts of phosphine produced diminish as the reaction temperature is raised. Cupric oxide absorbs phosphorus from the vapours with the formation of phosphides; it only very feebly catalyses the reaction of formation of phosphoric oxide. R. Truszkowski.

Kinetics of polymerisation of ethylene at pressures above 1 atm. R. N. Pease (J. Amer. Chem. Soc., 613—619; cf. A., 1930, 709; Wheeler and Wood, *ibid.*, 1399).—The polymerisation of ethylene at 2·5, 5, and 10 atm. to C_nH_{2n} hydrocarbons in a copper bomb at temperatures between 350° and 500° is approximately bimolecular; the proportion of liquid polymeride increases during the reaction, but little hydrogen and methane are produced. The temperature coefficient is 2·3 per 25°. A mechanism is proposed which requires that the reaction at low pressures should be of the third order.

J. G. A. GRIFFITHS.

Decomposition of hypobromous acid. F. POLLAK and E. DOKTOR (Z. anorg. Chem., 1931, **196**, 89—112).—Dilute (up to 0·3M) solutions of hypobromous acid may be prepared by treatment of concentrated silver nitrate solution with bromine and distillation of the filtered solution in a vacuum. If mercuric oxide be used, the mercuric bromide remaining in solution causes reversal of the reaction on heating, whilst silver carbonate reacts but slowly and silver oxide causes decomposition of the acid. The distillate contains also nitric acid, bromine, and hydrobromic acid. The rate of decomposition of hypobromous acid diminishes with time. Of the two probable modes of decomposition, viz., $5HBrO \longrightarrow HBrO_3+2H_2O+2Br_2$ and $4HBrO \longrightarrow O_2+2H_2O+2Br_2$, the former predominates in the dark at the ordinary temperature; this reaction is bimolecular and appears to be independent of the hydrogen-ion concentration of the solution. Bubbling nitrogen through the solution is without influence. Although bromous acid is a probable intermediate product of the decomposition, it does not appear to be formed in measurable quantity. H. F. GILLBE.

Velocity of dissolution of oxygen in water. IV. S. MIYAMOTO and A. NAKATA (Bull. Chem. Soc. Japan, 1931, **6**, 9—22; cf. this vol., 175).—The velocity of dissolution of oxygen in water has been determined by measuring the velocity of oxidation of sodium sulphite solutions under conditions of zero concentration of oxygen in the surface solution/oxygen. The velocity of oxidation is independent of the concentration of sodium sulphite and is proportional to the boundary surface area. It is assumed that only those molecules of oxygen of which the component of velocity perpendicular to the boundary surface is greater than a threshold value u_0 can enter the liquid phase. The value of u_0 is found to be $1{\cdot}65\times10^5$ cm. per sec. and is independent of the temperature. The dissolution velocities of oxygen in water determined by various workers are compared. O. J. WALKER.

Kinetics of the transformation of the various forms and hydrates of calcium sulphate. W. FEITKNECHT (Helv. Chim. Acta, 1931, **14**, 85—90).—Measurements have been made of the velocity of dehydration of the various hydrated forms of calcium sulphate. The removal of water was allowed to proceed in a high vacuum over phosphorus pentoxide, and the resulting products were examined by means of the Debye–Scherrer diagrams. The dihydrate gives a characteristic S-shaped velocity–time curve, showing that the decomposition proceeds from single localised nuclei, which in the case of well-formed crystals require a certain time for their formation. The time increases rapidly with fall of temperature, so that at 20° the dihydrate can be kept for several hours in a vacuum without losing water. The crystalline hemihydrate shows no induction period, the dehydration velocity being greatest at the beginning. The resulting product, soluble anhydrite, has a lattice different from that of the hemihydrate. In this case the decomposition does not proceed from single nuclei, but takes place uniformly throughout the solid phase. In the transformation of the soluble anhydrite to native anhydrite there is a discontinuous change in the lattice structure. O. J. WALKER.

Reaction velocity in the system $Ag_2CO_3 \rightleftharpoons Ag_2O+CO_2$. W. D. SPENCER and B. TOPLEY (Trans. Faraday Soc., 1931, **27**, 94—102).—Reaction velocity measurements in the above system (cf. A., 1930, 39) have been extended to include the recombination of silver oxide with carbon dioxide and the decomposition of the "synthetic" carbonate so formed. The type of curve obtained for the recombination depends on the pressure of the gas and the state of dryness of the solid. At pressures several times greater than the equilibrium pressure the curves are in two distinct parts. The factors determining the amount of reaction in an assigned time interval are discussed, and the possibility of an optimum pressure is accounted for. In the region underlying the zone in which recombination has occurred the chemically unchanged silver oxide is made less reactive, but when this modified oxide is converted into carbonate the oxide which it yields on subsequent decomposition is as reactive as before. Water vapour appears to promote the reaction indirectly by facilitating penetration of carbon dioxide through the carbonate formed initially. The rapid reaction in the first part of the recombination is not much affected by a degree of dryness sufficient to inhibit almost completely the second part. O. J. WALKER.

Kinetics of dissolution. A. S. FEDOROV (J. Russ. Phys. Chem. Soc., 1930, **62**, 1859—1861).—Benzoic acid is fused on to a glass rod, which is rotated successively in four 100-c.c. portions of water, for 10, 15, 20, and 30 min., and the acidity of each portion is determined. The rate of dissolution is given by $K=\{\log_e C_s-\log_e (C_s-C)\}/t$, where C_s is the saturation concentration, and C is the concentration found after time t. R. TRUSZKOWSKI.

Rate of dissolution of metals in acids. Theory of local elements. W. GUERTLER and B. BLUMENTHAL (Z. physikal. Chem., 1931, **152**, 197—234).—The rate of dissolution of zinc in hydrochloric acid has been studied from the point of view of the theory of Ericson-Aurén and Palmaer. The chemical and mechanical conditions under which observations are reproducible were determined by preliminary experiments with iron, nickel, and copper. In the main series of experiments zinc was used, the rates of dissolution in 0·1N and 0·2N acid of two specimens, containing, respectively, 0·08 and 1·01% of lead, being measured. Contrary to the statement of Ericson-Aurén and Palmaer, the rate is not proportional to the concentration of acid nor to the electrical conductivity of the liquid, but is determined chiefly by the overvoltage of hydrogen, which decreases during the course of the dissolution in consequence of the increasing surface area of the cathodic impurities and the resulting diminution of the cathode current density. When the variation of the hydrogen overvoltage with time is taken into account, the observed rate of dissolution is in agreement with the theory of local elements and can be quantitatively expressed by the formula of Ericson-Aurén and Palmaer.

F. L. Usher.

Corrosion of copper. L. W. Haase.—See B., 1931, 204.

Corrosion of lead. M. Werner.—See B., 1931, 206.

Methods of corrosion testing. E. K. O. Schmidt.—See B., 1931, 204.

Effect of carbon tetrachloride, trichloroethylene, and tetrachloroethane on metals. J. Formánek.—See B., 1931, 206.

Corrosion of iron by carbon tetrachloride. J. Milbauer (Coll. Czech. Chem. Comm., 1931, 3, 73—75).—The presence of ethyl alcohol increases the rate of corrosion of iron by boiling carbon tetrachloride. Data are given of the quantity of iron dissolved in 1 hr. by various mixtures of the tetrachloride, water, and alcohol; the maximum effect is produced with a mixture containing carbon tetrachloride 70%, water 2·7%, and alcohol 27·3%. Other chlorinated hydrocarbons behave similarly, although the attack is less rapid.

H. F. Gillbe.

Kinetics of reduction of cuprous oxide. I. Reduction at low pressures. Oxidation of copper at low pressures. F. J. Wilkins (J.C.S., 1931, 330—335).—The rate of reduction of cuprous oxide by hydrogen at a pressure of 0·03—0·15 mm. and at 144—250° under such conditions that the area of the interface copper–cuprous oxide remains constant and the water is removed as it is formed may be represented by the equation $\log_e p_0/p=kt$, where p_0 is the initial gas pressure, p the pressure after time t, and k is a constant. The heat of activation calculated from the temperature coefficient is 18,000 g.-cal. It is considered that the reduction consists of the following consecutive reactions: (*a*) condensation of hydrogen at the oxide–hydrogen interface, (*b*) evaporation of hydrogen from this interface into the body of the oxide, (*c*) diffusion of hydrogen through the cuprous oxide, (*d*) reaction between hydrogen and oxide at the oxide–metal interface, (*e*) diffusion of water from the reaction centre through the oxide layer, (*f*) desorption of the water. If it is assumed that the rate of the reaction as a whole is determined by the rate of stage (*b*), the experimental velocity equation is accounted for, and the heat of activation must be supposed to represent the heat of evaporation of adsorbed hydrogen into cuprous oxide.

Measurements of the rate of oxidation of copper at oxygen pressures of about 0·01 mm. at 144—218° are in agreement with the theory previously advanced (following abstract).

R. Cuthill.

Kinetics of oxidation of copper: the establishment of sorption equilibria. F. J. Wilkins (Phil. Mag., 1931, [vii], 11, 422—432).—A general equation for the kinetics of the oxidation of copper is deduced on the assumption that the oxidation is the resultant of the following consecutive processes: condensation of oxygen at the oxide–oxygen interface, evaporation of the oxygen into the oxide, diffusion of oxygen through the oxide (cf. A., 1930, 1129). A simplified form of the equation, applicable when sorption equilibrium between the oxide and gas phase has been reached, *i.e.*, when the oxide has reached absorption and adsorption equilibrium, is in satisfactory agreement with the experimental data. The time necessary for the establishment of sorption equilibrium increases with increase in the degree of activation of the surface, which is considered to show that oxygen adsorbed on cuprous oxide is able to diffuse laterally.

R. Cuthill.

Detonation of solid explosives. P. Laffitte and M. Patry.—See B., 1931, 224.

Acid–base catalysis according to Brönsted. I. M. Kolthoff (Chem. Weekblad, 1931, 28, 110—121).—A survey.

H. F. Gillbe.

Inhibition of chemical reactions. IV. Site of anti-oxygenic action. Oxidation of sodium sulphite and benzaldehyde. K. C. Bailey and (Miss) V. H. ffrench (J.C.S., 1931, 420—428; cf. A., 1930, 429).—By passing a stream of air bubbles through an aqueous solution of *iso*propyl or *sec.*-butyl alcohol and analysing the bubble films, it has been shown that a layer of alcohol molecules 1—2 mols. deep is formed on the surface of the solution when the solute concentration reaches about 1·5—2 g. per litre. When these alcohols are used to inhibit the oxidation of sodium sulphite in aqueous solution, the graph of oxidation velocity against alcohol concentration does not, however, show any discontinuity at the above concentration. It is therefore concluded that the mechanism of the autoxidation of benzaldehyde is not the same as that of the oxidation of sodium sulphite, and it seems possible that in the former reaction accumulation of the inhibitor at the gas–liquid interface may be the deciding factor in inhibition.

R. Cuthill.

Properties of the chlorides of sulphur. V. Metastable states. T. M. Lowry and G. Jessop (J.C.S., 1931, 323—329; cf. A., 1930, 842).—The period of induction in the combination of sulphur monochloride with chlorine may be eliminated by adding iodine as catalyst and reduced by adding antimony pentachloride. The autocatalytic character of the reaction is ascribed to the presence in the reaction product of the chlorides SCl_4 and S_3Cl_4. Even at −80° sulphur dichloride and chlorine combine instantaneously to form the solid tetrachloride, and if an equilibrium mixture of chlorine, tetrachloride, and dichloride at −20° is frozen, then heated at −20° again, the original position of equilibrium is reached at once. The separation of tetrachloride on freezing a liquid mixture having the composition of the dichloride exhibits, however, a time-lag, and the same is true of the melting of solid tetrachloride in liquid dichloride. From observations on the density of such a liquid mixture it is deduced that the equilibrium concentration of dichloride is about 85% at 0° and about 75% at 100°.

R. Cuthill.

Catalytic influences in three-carbon tautomerism. II. Action of acid catalysts on ketones. G. A. R. Kon (J.C.S., 1931, 248—251; cf. A., 1929, 927).—In the isomeric change at 100° of *cyclo*hexylideneacetone into the βγ-form under the influence of aqueous-alcoholic sulphuric, hydrochloric, or oxalic acid, equilibrium is reached when 23% remains unchanged. The presence of impurities was the reason for the somewhat different value obtained using alkaline catalysts, but acid catalysts, especially oxalic acid, act much less rapidly than alkaline catalysts. The equilibrium point in the isomerisation of *iso*pulegone in presence of alcoholic sulphuric acid at 100° or sodium ethoxide at 25° corresponds with pure pulegone. R. Cuthill.

Active iron. VI. Characterisation by benzidine-peroxidase and catalase [reactions]. A. Simon and T. Reetz (Annalen, 1931, 485, 73—112).—The peroxidase activity of ferrous hydrogen carbonate (I), ferric chloride (II), sodium pentacyanomonoaquoferroate (III), and hæmoglobin, measured by the benzidine–hydrogen peroxide method (this vol., 57) in aqueous-alcoholic solutions of varying p_H, is greatest at p_H 3·92 (acetic acid, slightly different results being obtained with hydrochloric acid); under identical conditions I and II are equally active, III is less active, and hæmoglobin has an activity of a totally higher order. Sodium pentacyanomonoaquoferriate (IV) has a maximum activity similar to that of II at p_H 7·2. In aqueous solution the relation of activity to p_H is approximately the same except that III and IV now have their maxima at p_H 5, but the activity itself is much higher in the cases of I and II than of III and IV.

The identical behaviour of ferrous and ferric salts is due to the equilibrium $Fe^{\cdot\cdot} \rightleftharpoons Fe^{\cdot\cdot\cdot}$ resulting from the simultaneous oxidising and reducing properties of the solution, and the maxima at p_H 3·92 to the suppression of ionisation in more alkaline solutions and irreversible oxidation of ferrous to ferric ions in strongly acid media. Qualitative experiments show that at p_H 4 ferric salts can oxidise benzidine to benzidine-blue, but that the power is lost at p_H 2. Potential measurements confirm this, and indicate that the oxidation potential of benzidine di-imide, which is stable at p_H 2, is greater than that of ferric salts; in agreement with this, ferrous salts are immediately oxidised by the di-imide to ferric salts. The different behaviour of aqueous and alcoholic solutions is shown to be due to the oxidation of alcohol to acetaldehyde by hydrogen peroxide in the presence of ferrous iron (ferrous salts or ferric salts and benzidine); this reaction is catalysed to a much smaller extent by the complex salts or by hæmoglobin.

The peroxidase and catalase activity of mineral water (Canstatt) is slightly inferior to that of I, but of the same order, and is undoubtedly due to ferrous ions. The difference in behaviour of natural waters and synthetic ferrous hydrogen carbonate solutions observed by Baudisch is confirmed, and is due to incomplete dissolution of the iron which is present as an extremely fine suspension rapidly converted into ferrous carbonate on keeping: $Fe+Fe(HCO_3)_2= 2FeCO_3+H_2$. This reaction and the direct oxidation of the solution are catalysed by light, but a solution that maintains its activity indefinitely, even in the light, if oxygen is completely excluded is obtained by filtration of the solution prepared in the usual way under a high pressure of carbon dioxide.

The reduction of nitrates to ammonia by freshly-prepared ferrous hydroxide or carbonate in neutral solution in presence of oxygen (Baudisch, A., 1920, ii, 687) also occurs in absence of oxygen. Although reduced by small amounts of alkali, presumably on account of suppression of ionisation, the activity is regained in strongly alkaline solutions, possibly on account of dissolution of the iron as ferrite. In this case also preparations maintain their activity if preserved in complete absence of air.

The catalase activity of iron, measured by the velocity of decomposition of hydrogen peroxide in aqueous solution, is not influenced to the same extent by the hydrogen-ion concentration as is the peroxidase effect, although the ill-defined maxima are approximately the same. Ferrous salts (I and ferrous sulphate) show great activity, slightly dependent so far as magnitude is concerned on the anion, but this is rapidly lost on account of oxidation to the inactive ferric salt. The complex salts (III and IV) have an activity of a lower order, which, however, is almost unchanged with time. Hæmoglobin exerts its maximum activity at p_H 4·95, and only slightly less at p_H 7·2, and in general behaviour resembles the complex salts, except that its activity is of a considerably higher order. The activity of ox-blood is still greater, and reaches a maximum at p_H 7·2.

It is concluded that in the compounds I—IV the activity is a function of the ferrous ion, either present originally, or formed during the reaction. Hæmoglobin and blood possess in addition a specific activity. H. A. Piggott.

Catalysis of hydrogenation. A. S. Ginsberg and A. P. Ivanov (J. Russ. Phys. Chem. Soc., 1930, 62, 1991—1999).—A very active catalyst can be prepared by the addition of palladium or platinum chloride to 10 to 20 times its weight of powdered metal, the best results being given by aluminium, nickel, magnesium, beryllium, iron, tungsten, and tin, whilst arsenic, tellurium, zinc, silver, and mercury are unsuitable for the purpose. This catalyst is particularly suitable for the hydrogenation of aliphatic compounds, aromatic compounds being reduced only very slowly in its presence. R. Truszkowski.

Catalytic hydrogenation. III. Presence of hydrogen ions among thermions as ordinarily obtained. O. Schmidt (Z. physikal. Chem., 1931, 152, 269—283; cf. A., 1928, 582).—The suggestion that catalytic hydrogenation may be due to reaction in the gas phase with hydrogen ions emitted by the heated metallic catalyst is not in agreement with the theory of thermionic emission. The experiments of Hüttemann, who reported the presence of such ions, have been repeated with an improved form of mass spectrograph, using heated wires of platinum and of palladium–silver. No hydrogen ions (whether H_2^+ or H^+) could be detected. This result in no way precludes the possibility of reaction with protons in the metal phase. F. L. Usher.

Catalytic reduction and hydrogenation of phenols by hydrogen under pressure. H. Tropsch.—See B., 1931, 194.

Catalytic reduction of carbon monoxide at ordinary pressure. VII. Influence of alkalis on an iron–copper catalyst. S. Kodama and K.

Fujimura (J. Soc. Chem. Ind. Japan, 1931, 34, 14—16B).—With a fine iron–copper catalyst (1 : 1) prepared from the nitrates 140 litres of water-gas gave at 270°, with a space velocity of 230—240, 3·0 c.c. of oil together with a small amount of solid resembling vaseline. The addition of sodium carbonate (0·005—0·05 mol.) to the catalyst increased its initial activity and favoured the production of higher hydrocarbons. This increase in activity was, however, not permanent, and the unactivated catalyst retained its activity for a longer time. The loss of activity of the alkaline catalyst seems to be due to the deposition of the higher hydrocarbons on its surface. The best result, 3·1 c.c. of oil from 143 litres of gas, was obtained with a catalyst of the composition Fe : Cu : Na_2CO_3= 1 : 1 : 0·005. H. Ingleson.

Catalytic decomposition of cetyl alcohol. C. Sandonnini and S. Bezzi (Atti R. Accad. Lincei, 1930, [vi], **12**, 154—158).—Analyses have been made of the products obtained by passing cetyl alcohol vapour over the oxides of aluminium, zinc, chromium, and iron at temperatures of 340—350°. The behaviour of cetyl alcohol is analogous to that of alcohols lower in the series. A yield of approximately 60% of hexadecylene is obtained in the reaction employing alumina. F. G. Tryhorn.

"Triatomic hydrogen." E. Hiedemann (Z. physikal. Chem., 1931, **153**, 210—240).—By the action of an electric discharge in hydrogen contained in a glass vessel at about 0·06 mm. pressure a small yield is obtained of a gas which is condensed by liquid air; on admitting a further supply of hydrogen and repeating the discharge, no action takes place unless the vessel is heated and degassed beforehand. The condensate is shown by physical measurements to be neither hydrogen nor water vapour, and its reaction with sodium indicates that it consists of a mixture of compounds containing 4 and 6 atoms of hydrogen in the molecule. All the reactions of "hyzone" are exhibited by the mixture, together with others which show it to be composed principally of silicon hydrides, with disilane predominating. The gas yields a positive reaction with Nessler's reagent, even in total absence of nitrogen, and a brown coloration with lead acetate solution, and reduces tungstic oxide to the dioxide; these reactions are given also by silicon hydride mixtures prepared in the usual manner. The extensive literature relating to "hyzone" is reviewed, and in all cases the substance described appears to be silicon hydride or hydrogen sulphide; there is no evidence whatever for the existence of triatomic hydrogen. H. F. Gillbe.

Hyzone [triatomic hydrogen]. R. Schwarz and P. Royen (Z. anorg. Chem., 1931, **196**, 11—25).—Comparative dilatometric measurements with argon and hydrogen subjected to the silent electric discharge at 25°, −76°, and −185° and at pressures of 3—4 mm. show that at low temperatures hydrogen undergoes a considerable contraction over a period of 70—80 min.; at the ordinary temperature the effect is masked by thermal phenomena. The magnitude of the contraction is compatible with the formation of a unimolecular adsorption layer such that saturation of the surface corresponds with about 60% of the maximum density of packing, calculated from a maximum adsorption coefficient of 10^6 atoms per $cm.^2$ A contraction of the order reported by Wendt and Landauer (A., 1922, ii, 369), viz., 27%, could not be realised, and is ascribed to a "clean-up" effect. There is thus no evidence for the formation of triatomic hydrogen during the silent electric discharge. H. F. Gillbe.

Formation of ammonia from its elements in the electric discharge. M. Alsfeld and E. Wilhelmy (Ann. Physik, 1931, [v], 8, 89—123).—The influence of temperature on the ammonia synthesis in the ozoniser discharge becomes marked at 400°, and is correlated with adsorption phenomena. The Townshend, corona, glow, and arc discharges are compared. On development of the negative corona from the Townshend discharge, a pronounced diminution in yield is brought about by traces of electrically negative gases. In the glow discharge the cathode fall is important. The positive column is less sensitive to pressure changes than the negative corona. The cathode material does not appreciably influence the yield except for platinum, where the catalytic effect increases the yield by 30%. In the anomalous cathode fall the yield per unit current is greater than in the normal cathode fall; an oxide cathode decreases this yield, but, calculated with respect to energy, the yield is almost the same, due to diminished potential across the tube. The dependence of yield on the ratio of nitrogen to hydrogen is the same for the corona and glow discharges. The maximum yield takes place when the cathode fall is a minimum, and when the nitrogen content is approximately 60%.
A. B. D. Cassie.

Influence of electric discharges in the Siemens tube on sulphur vapour. R. Schwarz and P. Royen (Z. anorg. Chem., 1931, **196**, 1—10).—The influence of the silent electric discharge on sulphur vapour admixed with argon at 465° has been investigated by dilatometric measurements. The increased expansion of the mixture as compared with that observed with argon alone is ascribed solely to thermal dissociation and not to a breakdown of the sulphur molecules under the action of the discharge, but the nature of the subsequent contraction indicates that triatomic molecules of sulphur may be formed. Further knowledge of the physical constants of sulphur is necessary before the results can be fully interpreted.
H. F. Gillbe.

Reduction of arsenic acid and arsenates to arsine at the mercury cathode. I. W. V. Lloyd (Trans. Faraday Soc., 1931, **27**, 89—94).—The potential changes which take place at mercury and other cathodes during the reduction of arsenic acid in sulphuric acid solutions containing up to 180 mg. of elementary arsenic (in 10 c.c.) have been measured. The arsenic acid solution was admitted to the cathode during periods varying from 20 to 60 min. When measured by a commutator method the overvoltage of the mercury cathode decreases by 0·5 volt during the addition of the arsenic acid to a value representing the overvoltage of arsenic, which suggests that some arsenic is deposited on the mercury. The amount deposited is, however, very small. With uninterrupted current the decrease in overvoltage is less and varies directly with increasing concentration of the arsenic acid. In view of this decrease, the reduction of the whole of the arsenic acid to arsine is difficult. By using a zinc amalgam cathode or by adding zinc sulphate the decrease in overvoltage is smaller and a greater yield of arsine is obtained. The efficiency of the cathodes for reducing arsenic acid is, however, not dependent on the overvoltage alone, since lead and tin, which have approximately the same overvoltages as mercury, are not so efficient at the same apparent current densities. The reduction is facilitated by increasing the current density, the concentration of the acid electrolyte, and the time of electrolysis. The efficiency of the process, calculated as the percentage of hydrogen produced at the cathode which is converted into arsine, varied from 1·71 to 14·1% under the best conditions. O. J. Walker.

Simple deposition of reactive metals on noble metals. A. S. Russell (Nature, 1931, **127**, 273—274).—Evidence of the deposition of uranium, titanium, tungsten, and molybdenum on mercury, copper, and tin is obtained when a liquid amalgam is shaken with an acid solution of a compound of the metal in question. After the addition of pure zinc, the minimum concentration of sulphuric acid at which hydrogen is evolved may reach 0·001 of that with the amalgam alone. When these metals are deposited electrolytically on a mercury cathode they behave towards the evolution of hydrogen in the same way as does the amalgam shaken with a solution.

L. S. Theobald.

Formation of ethylene and acetylene during electric discharges in methane. K. Peters and O. H. Wagner (Z. physikal. Chem., 1931, **153**, 161—186).—The formation of acetylene and ethylene from mixtures of hydrogen and methane under the influence of the electric discharge has been studied under a variety of conditions of pressure, gas velocity and composition, energy input, and form of the reaction vessel. The minimum energy consumption for the production of acetylene is 13 kw.-hrs. per $m.^3$, and the most satisfactory value for the production of ethylene is 53 kw.-hrs. per $m.^3$ Under these conditions, and with a gas mixture containing 2 mols. of methane per mol. of hydrogen, the concentration of acetylene in the product is 4·2%, and of ethylene 0·8%. It is apparently impossible to repress the formation of acetylene and increase the yield of ethylene, except at very low pressures, when the energy consumption becomes much greater than at 10—40 mm. The concentration of acetylene in the product increases with increase of the quantity of energy dissipated, the maximum attainable concentration being about 20%, whilst with ethylene the maximum does not exceed 3%. Study of the spectrum of the gas mixture during the discharge indicates that two reaction zones are present; in one only the ⋮CH bands are visible, whilst in the other the Swan spectrum, the Balmer series, and the carbon line spectrum also appear. The mechanism of the reactions is discussed. In the zone from which the Swan spectrum is emitted acetylene may be produced either by combination of two ⋮CH radicals or by the action of active hydrogen on the ·C⋮C· radical. Ethylene is formed by the polymerisation of groups resulting from the decomposition of the methane molecule. H. F. Gillbe.

Photo-reaction of hydrogen and iodine monochloride. S. E. Ashley and W. West (Nature, 1931, **127**, 308).—In agreement with the observations of Mellor and Iredale (this vol., 180), hydrogen and iodine monochloride react under the influence of a mercury arc light, forming hydrogen chloride and iodine. No appreciable amount of hydrogen iodide has been observed. The photo-reaction between iodine chloride and methane, with a rate large compared with that of the hydrogen reaction, has also been established. L. S. Theobald.

Photochemical decomposition of hydrogen peroxide in aqueous solution in the presence of sodium nitroprusside. I. M. Qureshi (J. Physical Chem., 1931, **35**, 656—658).—An aqueous solution of hydrogen peroxide containing a small quantity of sodium nitroprusside decomposes on exposure to light and the decomposition continues after illumination ceases. Hydrogen peroxide solution also decomposes in the dark if the sodium nitroprusside solution is previously exposed to light.

L. S. Theobald.

Influence of the absorption of light on the velocity of photochemical reactions. A. K. Bhattacharya and N. R. Dhar (Z. anorg. Chem., 1931, **196**, 26—32).—The velocity of the reaction between potassium oxalate and iodine under the influence of radiation of wave-length 8500 Å. is approximately proportional to the quantity of energy absorbed. The reaction between ferrous sulphate and iodine has been studied under varied conditions; when the velocity of the thermal reaction is reduced by addition of suphuric acid and the mixture is exposed to sunlight, the exponent of the velocity–absorption or velocity–intensity relationship is about 0·2, but it increases with decrease of the ratio of the velocities of the photocatalysed and thermal reactions. Thus with radiation of wave-length 7304 Å., which is no longer absorbed by the reacting system, and in absence of sulphuric acid, the exponent is 1·5. A similar effect is observed with the reaction between citric and chromic acids; under the influence of continuous radiation from an electric lamp the exponent is 0·5, but at 5650 Å. the relationship becomes linear. The main factors governing the relationship between the velocity of a photochemical reaction and the quantity of light absorbed are the wave-length of the absorbed radiation and the relative acceleration caused by the absorption. H. F. Gillbe.

Direct photography of ionisation in insulating materials. A. Gemant (Naturwiss., 1931, **19**, 109).—A photo-sensitive film in an electric field between plate electrodes is blackened when a critical voltage is exceeded. This is due to the ionisation of neighbouring dielectrics. The effect is observed when liquid or solid insulating materials as well as when gases are introduced between the electrodes. Whether the primary action is due to charge carriers of high velocity or to the secondary action of the accompanying photo-phenomena is not yet decided, but the evidence so far favours the latter. When semi-conducting photographic paper is used as part of the electrode the structure of the insulator can be investigated by application of the breakdown potential. The ionisation process itself can also be investigated to some extent and, unlike other methods, by applying direct current. Some dielectrics glow with alternating current, but not with direct current.

J. W. Smith.

Photochemical polariser. F. Weigert and F. Stiebel (Naturwiss., 1931, 19, 108).—When clear transparent gaslight plates are insolated with polarised red light and then developed in the ordinary way, negative induced dichroism is produced. If, however, instead of being developed, the plate is treated with chromic acid, then insolated with non-polarised red light, and developed, a positive induced photodichroism is obtained. The initial insolation with polarised light, followed by the chromic acid treatment, converts the film into a photochemical polariser, and of the almost equal amounts of each component absorbed only that in a vibrational direction at right angles to the initial excitation is active. This effect is to be anticipated on the micellar theory of the latent image, and hence supports this view. On account of the close relationship between this new photo-dichroism and Albert's reversal, which is a general photographic phenomenon, the new property may also occur with highly sensitive, large-grained photographic emulsions. J. W. Smith.

Accumulation effect in photographic plates and its influence on the exactitude of photographic photometry. N. Barabaschev and B. Semejkin (Z. wiss. Phot., 1931, 28, 333—340).—The action of a given exposure on a plate increases with the time between exposure and development. The increase in density is greatest in the first two days. If the plate is slightly fogged before exposure, the effect is still apparent, but to a different degree. Old plates do not show the effect so strongly. The possible inaccuracies of characteristic curves in view of these results are discussed. J. Lewkowitsch.

Photochemical studies. XII. Photochemical reaction between nitric oxide and mercury vapour. W. A. Noyes, jun. (J. Amer. Chem. Soc., 1931, 53, 514—526).—The resonance radiation of mercury effects a decrease of pressure to approximately half the initial value in the system nitric oxide–mercury vapour at 25°; the residual gas is probably nitrogen. Mercury oxide is not deposited on the illuminated zones of the walls. The unimolecular velocity coefficient is independent of initial pressures of nitric oxide between 0·1 and 0·0035 mm. The reaction is sensitised by mercury and probably proceeds by $Hg(2^2P_1 \text{ or } 2^3P_0)+NO \longrightarrow NO(\text{excited})+Hg(1^1S_0)$. The quenching of the fluorescence of mercury vapour by nitric oxide at 600—700° is 10% less than at 25° and is ascribed, in part, to the production of mercury atoms in the 2^3P_0 state.

J. G. A. Griffiths.

Photochemical dissociation of triatomic molecules. II. Potassium cyanide. D. S. Villars (J. Amer. Chem. Soc., 1931, 53, 405—411).—Potassium cyanide vapour at 830° exhibits no absorption, but at 875° two regions are observed with longer wave-length boundaries at about 2175 Å. (5·7 volts) and 2900 Å. (4·3 volts). The former region is interpreted as the dissociation into a normal and an excited dissociation product, whilst the latter region indicates dissociation of the ionic molecule into a normal potassium atom and CN radical. This accords with the energy of dissociation, 3·8 volts, deduced from thermal data and an approximate evaluation of the heat of sublimation (48·75 kg.-cal.). The relation between the "ionic" and "atomic" forms of a molecule is discussed. J. G. A. Griffiths.

Photochemical interaction of ethylene and ammonia. H. S. Taylor and H. J. Emeléus (J. Amer. Chem. Soc., 1931, 53, 562—574; cf. A., 1930, 871).—It is now shown that the photo-decomposition of ammonia is unaffected by the presence of ethylene, but the yield of free hydrogen and nitrogen is diminished. Under the conditions employed, the polymerisation of ethylene alone is small, but in the presence of ammonia, an oily product is obtained which retards the reaction and contains, as almost non-volatile substances, most of the nitrogen from the decomposed ammonia. The velocity of reaction is independent of the pressure of ammonia when absorption of light is complete. The temperature coefficient is about 1·04 per 10°. The yield of saturated hydrocarbons is comparatively small, and the results afford evidence of the relative efficiency of the possible modes of formation of saturated hydrocarbons from ethylene and atomic hydrogen.

J. G. A. Griffiths.

Influence of light, carbon monoxide, and benzoquinone on the reduction of methylene-blue. H. Tamiya, T. Hida, and K. Tanaka (Acta Phytochim., 1930, 5, 119—155).—Pyruvic acid, kojic acid, ethyl acetoacetate, phloroglucinol, resorcinol, etc. in absence of oxygen and at suitable p_H and only under the influence of light are capable of decolorising methylene-blue. All these substances exhibit keto–enol tautomerism. The decolorisation of methylene-blue by the dehydrase of acetic bacteria or liver extract is also accelerated by light. Since screening with methylene-blue filters has the same effect as darkness, the effect is due to activation of the methylene-blue molecule. Carbon monoxide inhibits the bacterial reduction of methylene-blue but not the reduction by liver extract or the non-enzymic reduction. The degree of inhibition is determined mainly by the proportion of methylene-blue to carbon monoxide, and is not affected by light. It appears to be due to some effect of the gas in hindering the adsorption of the dye at the cell surface, and not to any effect on the enzyme itself. In the case of liver extract it is noted that in complete absence of oxygen decolorisation of methylene-blue takes place at the same rate whether hydrogen or carbon monoxide is present, whereas if a trace of oxygen is present, the rate with hydrogen is much slower, whilst that with carbon monoxide is unchanged. The explanation lies in the presence of a trace of hæmoglobin; in presence of hydrogen the trace of oxygen forms oxyhæmoglobin, the formation of which is prevented by carbon monoxide, and this is reduced before the methylene-blue, which is itself more readily reduced

than free oxygen. Here attempts to study the effect of light led to inconclusive results, since both the carbon monoxide-hæmoglobin and methylene-blue are affected by light. It is concluded that actions other than its combination with the iron-porphyrins must be taken into account when considering the action of carbon monoxide on cell processes. Both the chemical and enzymic decolorisation of methylene-blue are distinctly inhibited by $0 \cdot 001 M$-benzoquinone. The question whether this indicates the identity of the dehydrases which in the presence of suitable donators reduce methylene-blue and benzoquinone is discussed and left open. A modified Thunberg vessel for treating substrates containing volatile constituents is figured.
F. E. DAY.

Decomposition of cholesterol by *X*-rays. A. H. ROFFO and L. M. CORREA (Strahlenther., 1930, **36**, 528—532; Chem. Zentr., 1930, ii, 3002—3003).—Decomposition of cholesterol by *X*-rays occurs in solution only when the solvent contains chlorine; the effect is due to liberation of chlorine. Carbon tetrachloride is more sensitive than chloroform.
A. A. ELDRIDGE.

Effect of *X*-irradiation on cholesterol and its fatty acid esters *in vitro* and *in vivo*. R. HUMMEL (Strahlenther., 1930, **36**, 533—538; Chem. Zentr., 1930, ii, 3003).—In chloroform solution both free cholesterol and its fatty acid esters are decomposed by *X*-radiation. Similar decomposition was not observed in fat or blood-serum solutions or with deposits of cholesterol in mouse liver.
A. A. ELDRIDGE.

Action of short electromagnetic waves on photographic plates. M. LEVITSKY (Physikal Z., 1930, **31**, 769—771).—A number of experiments are described in confirmation of the author's earlier work on the action of radio-waves of short wave-length on a photographic plate after it has been given a short exposure to sunlight. The radiation from a spark was concentrated by means of a quartz lens and after passage through a 1 or 2 mm. grating was reflected on to the plate. Photographic reproductions of the diffraction patterns thus obtained are given. It is suggested that the radiation concerned produces resonance of the silver bromide lattice in the photographic film with the result that an increased blackening appears in those regions in which the radiation is concentrated by the diffraction grating.
R. W. LUNT.

Polysulphides of the alkali metals. II. Lithium. T. G. PEARSON and P. L. ROBINSON (J.C.S., 1931, 413—420; cf. A., 1930, 1136).—The action of sulphur on aqueous and alcoholic solutions of lithium monosulphide yields solutions which contain polysulphides but give no definite crystalline products. From a solution of sulphur in a solution of lithium hydrogen sulphide in absolute alcohol, however, *lithium tetrasulphide dialcoholate*, $Li_2S_4,2EtOH$, separates, being formed by the reaction $2LiHS+3S=Li_2S_4+H_2S$. Molten lithium and sulphur react under naphthalene to give a mixture of the monosulphide with a little disulphide. Thermal analysis of the system lithium monosulphide–sulphur indicates that the only sulphides stable at atmospheric pressure are the monosulphide, stable at its m. p., 900—975°, and the disulphide, slightly decomposed at its m. p., 369·5°.
R. CUTHILL.

Co-ordinated compounds of the alkali metals. III. F. M. BREWER (J.C.S., 1931, 361—368; cf. A., 1926, 71).—The following *compounds* have been prepared by interaction of salicylaldehyde with alkali hydroxides or carbonates: $C_7H_5O_2Li,C_7H_6O_2$, $C_7H_5O_2K,2C_7H_6O_2$, $C_7H_5O_2Rb$, $C_7H_5O_2Rb,C_7H_6O_2$, $C_7H_5O_2Rb,2C_7H_6O_2$, $C_7H_5O_2Cs,C_7H_6O_2$, and $C_7H_5O_2Cs,2C_7H_6O_2$. By the reaction of rubidium carbonate and benzoylacetone *rubidium benzoylacetone*, $C_{10}H_9O_2Rb$, m. p. 131°, is obtained. All these compounds are yellow. Taking into account the compounds previously described, the following covalency numbers are established: lithium, 4; sodium, 4; potassium, 4 and 6; rubidium, 4 and 6; cæsium, 4 and 6. The stability of the co-ordinated compounds of the alkali metals must depend on the atomic number and atomic volume of the metal. As the atomic number increases the increasing ease of ionisation opposes the tendency to co-ordination, but in the elements of higher atomic number the maximum co-ordination number increases, whereas with increasing atomic volume the nucleus holds additional electrons less and less readily.
R. CUTHILL.

Action of iron and nickel on alkali metal salts. L. HACKSPILL and H. J. PINCK (Bull. Soc. chim., 1931, [iv], **49**, 54—70).—The reaction between iron and nickel and alkali metal salts has been studied in an apparatus evacuated to a pressure of 10^{-3} mm. Iron displaces the alkali metals with the exception of lithium from the sulphates and arsenates heated at the m. p.; from the thiocyanates, after a preliminary decomposition to the cyanide, at 650°; from the borates and phosphates at about 1400°; and from the aluminates at the m. p. of iron. Lithium is formed when the oxide or silicate is heated with iron at 1300°. The other salts of lithium either decompose or volatilise without reaction. Nickel is able to displace the alkali metals only from their hydroxides or sulphides.
F. J. WILKINS.

Complex sodium silver thiosulphates. E. CARRIÈRE and RAULET (Compt. rend., 1931, **192**, 423—425).—The interaction of silver chloride and sodium thiosulphate occurs according to the equation, $AgCl+Na_2S_2O_3=NaCl+NaAgS_2O_3$. The value of $K(=[S_2O_3'']/[AgS_2O_3'][Cl'])$ at 20° for concentrations of sodium chloride and silver nitrate (to form the silver chloride) of $0 \cdot 009N$ is 8·6, and varies from 23 to 4 when the temperature varies from 5° to 45°. The heat of formation of AgS_2O_3' from Ag^+ and S_2O_3'' is 7·7 kg.-cal. Conductivity determinations confirm these results.
C. A. SILBERRAD.

Hypophosphites of cæsium and rubidium. L. HACKSPILL and J. WEISS (Compt. rend., 1931, **192**, 425—426).—Cæsium and rubidium hypophosphites are prepared either from the sulphates and barium hypophosphite, or from the free alkali and hypophosphorous acid. When dried over sulphuric acid they have compositions $CsH_2PO_2,0 \cdot 5H_2O$ ($d^{18 \cdot 5}$ 2·81), and RbH_2PO_2 (d^{17} 2·32). Both are very hygroscopic. On heating decomposition begins at 140°, is rapid at

200°, but is completed only at 500°. Below 300° it is represented by $5MH_2PO_2=MH_2PO_4+2M_2HPO_3+2PH_3$; above that temperature by $MH_2PO_4=MPO_3+H_2O$ and $2M_2HPO_3+H_2O=M_4P_2O_7+2H_2$, but the volume of hydrogen is always slightly in excess of that of phosphine, and a small quantity of a yellowish-brown insoluble solid, possibly a suboxide of phosphorus, is formed. C. A. Silberrad.

Stabilisation of blue cupric hydroxide. H. A. Neville and C. T. Oswald (J. Physical Chem., 1931, **35**, 60—72).—Precipitation in the presence of gelatin stabilises the blue compound formed by the action of sodium hydroxide (1·25*N*) on *N*-copper nitrate. The gelatin (0·025% by weight of mixed solutions) is completely removed from solution by adsorption on the precipitate. The blue compound can be prepared at 0° and under water remains stable at this temperature, but slowly turns black at the ordinary temperature. It is also stable at the ordinary temperature after being dried slowly in an electric refrigerator. An increase in alkalinity of the solution up to a certain concentration accelerates the blackening of the precipitate and then delays the change. *X*-Ray examination shows the blue preparations, both moist and dry, to have a definite crystal structure which differs from that of black copper oxide; from this and other evidence the blue substance is considered to be cupric hydroxide rather than hydrous cupric oxide. The ultimate particle size of the hydroxide is smaller than that of cupric oxide. A colloidal solution of copper hydroxide, peptised by the combined action of alkali and gelatin, has been obtained.
L. S. Theobald.

Modifications of silver iodide. R. Bloch and H. Möller (Z. physikal. Chem., 1931, **152**, 245—268).—*X*-Ray analysis confirms the existence of two modifications of silver iodide stable below 146°. The cubic variety (zinc blende type) can be prepared by grinding any coarsely crystalline preparation, whilst the hexagonal variety (wurtzite type) is obtained by crystallising the fused substance and protecting the resulting crystals from fracture or heating. The latter modification is also obtained by crystallising the iodide from its solution in a concentrated solution of potassium iodide, hydriodic acid, or mercuric nitrate. Ordinary precipitated silver iodide is a mixture of the two varieties. By heating above 146° a new cubic modification having a distinct *X*-ray diagram is formed. The conditions of stability of the three modifications are shown in a *p–t* diagram. When the "hot" cubic modification is formed by heating either of the other two, it reverts on cooling to the variety used to prepare it. This behaviour is attributed to the persistence of nuclei beyond the range of stability of the parent substance. The rate of formation of nuclei and the rate of growth of each of the modifications have been studied.
F. L. Usher.

Zinc and barium ferrites. J. Guillissen and P. J. van Rysselberge (Trans. Amer. Electrochem. Soc., **59**, Preprint, 11 pp.).—At temperatures below 580° the reaction between zinc and ferric oxides is very slow, but at higher temperatures zinc ferrite is formed. During the first two or three hours' heating the reaction is in accordance with Tammann's logarithmic law, but later an apparent equilibrium is attained. The ratio zinc as ferrite : total zinc rises from 78·8 at 600° to 98·8 at 890°. Thermal analysis yields no evidence of the formation of zinc ferrites more basic than $ZnFe_2O_4$ at temperatures up to 1070°. Zinc ferrite dissolves very slowly, and the more slowly the higher is its temperature of formation, in *N*- and 2*N*-sulphuric acid. Air containing 7·5% of sulphur dioxide when passed over the ferrite heated at 450° decomposes it slowly with the formation of zinc sulphate, but the reaction is too slow to be of technical importance. The reaction between barium carbonate and ferric oxide commences at temperatures below 700°; the formation of barium ferrite at 720° at first follows Tammann's law, but tends towards an equilibrium; on stirring, the reaction proceeds, although with reduced velocity. The results are discussed, and it appears that diffusion is the main factor in reactions between solids. H. F. Gillbe.

Reactions occurring in the solid state. (Mme.) Mathieu, Mathieu, and Paić (Compt. rend., 1931, **192**, 416—418).—The change in mol. volume occurring in the following reactions which take place in the dry state on pounding the ingredients together in a mortar has been determined: (1) $Hg+I_2=HgI_2$; (2) ZnS(wurtzite)=ZnS(blende); (3) $3K_2SO_4+Na_2SO_4=3K_2SO_4,Na_2SO_4$; (4) $HgSO_4+2HgO=SO_3,3HgO$; (5) $HgSO_4+HgI_2=HgSO_4,HgI_2$; (6) $(PbI)_2CO_3=PbI_2+PbCO_3$; (7) $[3HgO,2SO_3,2H_2O]=2[3HgO,SO_3]+2H_2O$. The occurrence of the reactions in all but (1) and (6), where colour changes occur, is proved by means of *X*-ray photographs. No connexion can be traced between the occurrence of such reactions and change in mol. volume, there being increases in (1), (4), and (6), decreases in (2) and (3), and practically no change in (5). C. A. Silberrad.

Principles of the genetic development of material. III. Chemical and structural forms of aluminium hydroxide. I. V. Kohlschütter [with W. Beutler, L. Sprenger, and M. Berlin] (Helv. Chim. Acta, 1931, **14**, 3—49).—A detailed study has been made of the various transformations undergone by α-aluminium hydroxide during ageing. The hydroxide was prepared by the anodic dissolution of aluminium and precipitation by the hydroxyl ions formed at the cathode during the electrolysis of 0·25*N*-sodium chloride (and in some cases of 0·25*N*-potassium nitrate) solutions under standard conditions. Small amounts of a reproducible standard α-hydroxide can be freshly prepared for each experiment in this way, and the product is probably a purer form of the α-hydroxide described by Willstätter, Kraut, and Erbacher (A., 1926, 34). This hydroxide, which has the approximate composition $Al_2O_3,4H_2O$ and is formed as a flocculent transparent gel, is the most active form of aluminium hydroxide. It is readily soluble in dilute hydrochloric acid, sodium hydroxide, and even in ammonia solution. By rapid centrifuging and washing it forms a faintly opalescent sol, which is very sensitive towards anions, particularly the sulphate ion. The positive character of the α-hydroxide is shown also by cataphoresis experiments.

During the ageing of the α-hydroxide two transformations take place. At the ordinary temperature, and more rapidly at 70°, the α-form is transformed into the β-hydroxide, which, although still transparent, is no longer loose and flocculent, but dense and plastic. The decrease in reactivity of the β-form is shown most clearly by its diminished solubility in hydrochloric acid and in ammonia solution, and also by its diminished absorbing power. It has the approximate composition $Al_2O_3,1\cdot16H_2O$. The $\alpha \longrightarrow \beta$ transformation is accelerated by the addition of methyl or ethyl alcohol, formaldehyde, acetone, ethyl ether, toluene, or chloroform, and is retarded by carbon dioxide. Before the change $\alpha \longrightarrow \beta$ is complete a further transformation to the third γ-form commences. The transparent plastic β-form gradually becomes opaque during 8—10 days, after which no further changes are observed. After shaking the γ-gel settles quickly to a small volume and forms with dilute hydrochloric acid a milky sol containing clear ultramicroscopic particles in rapid motion, a characteristic property of the γ-sol. The γ-hydroxide has the approximate composition $Al_2O_3,2\cdot39H_2O$ before, and $Al_2O_3,3H_2O$ after, treatment with dilute hydrochloric acid, and probably consists of bayerite dispersed in colloidal β-hydroxide.

The ageing process of α-aluminium hydroxide consists, therefore, of the two changes: (1) $\alpha \longrightarrow \beta$ and (2) $\alpha \longrightarrow$ bayerite, the γ-hydroxide being a mixed product of both changes. If (1) is accelerated by dehydrating agents (2) is suppressed and no γ-formation occurs, whereas acceleration of (2) by hydroxyl ions results in a coarse γ-hydroxide rich in bayerite.

O. J. Walker.

Preparation of anhydrous aluminium chloride from natural aluminous raw materials. V. I. Spitzin and O. M. Gvosdeva (Z. anorg. Chem., 1931, **196**, 289—311).—The conditions for the formation of anhydrous aluminium chloride from pure alumina, bauxite, and kaolin by mixing the substance with carbon in various forms and passing either chlorine or hydrogen chloride over the mixture have been investigated. The raw material can be freed from iron by a preliminary treatment with hydrogen chloride at 400—900°. The form of the carbon used is important; the best results are obtained with wood charcoal and the poorest with petroleum carbon. Pressing the mixture into briquette form has no deleterious effect. When hydrogen chloride is the reagent an excess of carbon is necessary and a rapid stream of gas is desirable, but when chlorine is used the velocity of the gas stream is unimportant and an excess of carbon is not essential. For small amounts of material chlorine and hydrogen chloride are almost equally effective, but chlorine is a more energetic reagent than hydrogen chloride where greater amounts are involved. When silica is present it is chlorinated simultaneously and the aluminium appears to act as a catalyst for this reaction. The most favourable temperature for reaction is 800°. Mixtures of chlorine and hydrogen chloride produce less attack on the silica; the lower is the percentage of chlorine the smaller is the relative amount of silicon tetrachloride formed, but the slower is the velocity of the whole reaction. A small addition of hydrogen chloride to chlorine gives a gas which is more reactive than pure chlorine. Addition of silicon tetrachloride vapour to the chlorine has the effect of reducing the attack on the silica without affecting the attack on the alumina.

E. S. Hedges.

Kaolin. R. Schwarz and W. Klös (Z. anorg. Chem., 1931, **196**, 213—219).—The behaviour of kaolin when heated from 20° to 1000° has been investigated by dilatometric measurements. After absorbed water has been evolved the kaolin expands continuously to a maximum at 582°, and thereafter the specific volume diminishes as the water of constitution is driven off. Discontinuities in the curve at 846° and 938° correspond with the decomposition of metakaolin and with the formation of mullite, respectively. The volume–temperature curve of the ignited material is approximately linear at temperatures up to 940°, the expansion coefficient being $3\cdot10—3\cdot93\times10^{-6}$ for material ignited at 1000° and $4\cdot37—5\cdot16\times10^{-6}$ for material ignited at 1500°. At temperatures above 940° the ignited kaolin contracts somewhat, an indication that the metakaolin is not wholly decomposed. The dilatometric behaviour of rehydrated kaolin and the influence of thermal treatment have been investigated, and results are given also for a number of mixtures of kaolin with felspar, quartz, and alumina.

H. F. Gillbe.

Concentration and isolation of the element of atomic number 61. L. Rolla (Atti R. Accad. Lincei, 1930, [vi], **12**, 270—272; cf. A., 1928, 261).—Details are given of the technique at present being used in the fractional crystallisation of large quantities of commercial didymium nitrate in order to obtain illinium in a state sufficiently pure to be examined by means of *X*-rays.

O. J. Walker.

Silicic acids. II. W. Dilthey and W. Nagel (J. pr. Chem., 1931, [ii], **129**, 178—188; cf. A., 1929, 280).—The principal factors affecting the degree of hydration of the silica obtained by interaction between silicon tetrachloride and triphenylcarbinol in a variety of solvents at various temperatures are the nature of the solvent and the temperature; the relative amount of triphenylcarbinol and the time of reaction are without marked effect. The water content of the preparations varies between 16·4% and 28·7%, and there is no evidence of the existence of a definite hydrate corresponding with metasilicic acid, $SiO(OH)_2$. The dehydrating action of solvents is in the order ether < chloroform < carbon tetrachloride. The various preparations have the same order of solubility in water (determined by dialysis), viz., about 6%, and in this respect resemble the silicic acid precipitated from aqueous silicates.

H. A. Piggott.

Silicic acid and silicates. I. F. W. Meier and L. Schuster (Z. anorg. Chem., 1931, **196**, 220—224). —The fraction of a sample of quartz powder soluble in water was about 1·4%, and was not increased by addition of hydrochloric acid; on the contrary, increase of the acid concentration from 0·1% to 2·5% caused a reduction of the quantity dissolved. The action of 0·5—20% sodium carbonate solutions on quartz and the subsequent action of hydrochloric acid have been investigated. The activation of part of the silica, whereby it becomes converted into a soluble form, is effected by the water as well as by the alkali, and the soluble material may be extracted, at least in part, by washing with 10% hydrochloric acid. If, however, the activated material is digested with acid for a longer period the activating action of the alkali becomes apparent, and the quantity which enters into solution is proportional to the concentration of the alkali. H. F. Gillbe.

Decomposition of carborundum. N. Slomnesco (Compt. rend., 1931, **192**, 361).—Carborundum in a very finely divided state is slowly dissolved with evolution of silicon tetrafluoride and carbon dioxide by concentrated hydrofluoric acid to which a little concentrated nitric acid has been added.

C. A. Silberrad.

Complex pyrocatechol derivatives of quadrivalent elements. A. Rosenheim, B. Raibmann, and G. Schendel (Z. anorg. Chem., 1931, **196**, 160—176).—A number of complex *compounds* of pyrocatechol with quadrivalent silicon have been prepared. By addition of freshly-precipitated silica to a solution of pyrocatechol containing the appropriate alkali, crystalline $(NH_4)_2[Si(C_6H_4O_2)_3],9H_2O$, $K_2[Si(C_6H_4O_2)_3],8H_2O$, and $Ba[Si(C_6H_4O_2)_3],C_6H_6O_2,17H_2O$ are obtained, whilst by double decomposition the guanidinium salt $(+7H_2O)$ separates; yellow crystals of the acid salts $(C_5H_6N)H[Si(C_6H_4O_2)_3]$ and $(C_6H_6{\cdot}NMe_2)H[Si(C_6H_4O_2)_3]$, and the compound $(NH_4)_2[Si(C_6H_3O_2{\cdot}CHO)_3],8H_2O$ have also been prepared. The sodium and normal pyridinium salts have been obtained only as syrupy liquids. By analogous methods the compounds $K_2[Ti(C_6H_4O_2)_3],5H_2O$ and $Rb_2[Ti(C_6H_4O_2)_3,5H_2O$, which readily lose 4 mols. of water to form the monohydrates, have been prepared, and crystalline magnesium, zinc, manganese, cobalt, nickel, and barium salts $(8H_2O)$, and the pyridinium $(4H_2O)$, quinolinium $(1H_2O)$, and xylidinium $(1H_2O)$ salts have been obtained. The anilinium and toluidinium salts are anomalous, in that they crystallise with $1H_2O$ and 1 mol. of the base. By dissolution of the monohydrated potassium and rubidium salts in hot aniline compounds are obtained wherein the water is replaced by 4 mols. of aniline. An optically active cinchoninium salt has been prepared; for the anion $[M]_D$ is about +3500. The complexes containing zirconium, thorium, or uranium are of more complicated structure than the silicon and titanium compounds; the following have been prepared:

$2\{(NH_4)_2[Zr(C_6H_4O_2)_3]\},C_6H_4(OH)_2,5H_2O$;
$(NH_4)_2[Zr(C_6H_4O_2)_3],C_6H_4(OH)_2,1{\cdot}5H_2O$;
$K_2[Zr_2(C_6H_4O_2)_5],20H_2O$;
$(CH_6N_3)_2[Zr(C_6H_4O_2)_3],6H_2O$;
$(C_5H_6N)_2[Zr(C_6H_4O_2)_5],7H_2O$;
$(NH_4)_2[Th(C_6H_4O_2)_3],5H_2O$;
$(NH_4)_2[Th_3(C_6H_4O_2)_6(OH)_2],10H_2O$;
$K_2[Th_3(C_6H_4O_2)_7],20H_2O$;
$(CH_6N_3)_2[Th_2(C_6H_4O_2)_3(OH)_4],10H_2O$;
$(C_5H_6N)_2[Th_2(C_6H_4O_2)_3(OH)_4],10H_2O$; and
$2\{(NH_4)_2[U(C_6H_4O_2)_3]\}C_6H_6O_2,8H_2O$.

H. F. Gillbe.

Potassium fluotitanate. II. H. Ginsberg and G. Holder (Z. anorg. Chem., 1931, **196**, 188—192; cf. A., 1930, 1007).—Isothermal dehydration curves of moist hydrated potassium fluotitanate indicate that a monohydrate exists; it has been isolated by exposing the material to the air at 24° and 59% humidity. Under these conditions the monohydrate is stable, but at 32—35° the anhydrous salt is formed within 48 hrs. The anhydrous salt may be obtained also by crystallisation from solutions containing from 20% to 40% of hydrofluoric acid. It is apparently impossible to prepare the compound K_2TiF_6,HF in the pure state; mixtures of the normal and acid compounds are always obtained. The oxy-salt K_2TiOF_6 has been prepared by heating the anhydrous fluotitanate in dry air, fluorine being evolved.

H. F. Gillbe.

Preparation of titanium white. P. Askenasy and K. Heise (Z. anorg. Chem., 1931, **196**, 257—283).—The presence of titanium interferes with the determination of iron by the thiocyanate colorimetric method, but the procedure is made applicable to ferriferous titanium compounds by shaking the coloured liquid with ethyl ether freed from traces of alcohol, in which case no colour is given by the titanium. The effects of variation of the concentration of acid, temperature, and reaction time on the decomposition of ilmenite by sulphuric acid have been examined in detail; the amount of the precipitated mixture of basic titanium sulphate and metatitanic acid depends on the concentration of acid. When iron is present, the product is coloured yellow by ferric oxide, even when care is taken to reduce the iron to the ferrous state. The iron can be removed by treatment with acid at the expense of a considerable loss of titanium, but the methods recommended for purification are to pass sulphur monochloride vapour over the yellow product at 800° or to pass chlorine after a preliminary reduction of the ferric oxide with hydrogen. When the metatitanic acid is precipitated from concentrated sulphuric acid under pressure the iron content is only 0·3%, and this is reduced to 0·1% by the addition of sodium, ammonium, or magnesium sulphate to the reaction mixture. A product free from iron is obtained by precipitating the titanium as potassium titanium oxalate and hydrolysing the product. Orthotitanic acid is precipitated quantitatively in the cold at p_H 4·0. Under these conditions ferrous sulphate remains in solution and by redissolving the orthotitanic acid in sulphuric acid and precipitating again by hydrolysis at 95° an iron-free metatitanic acid which has the requisite properties for a pigment is produced. A more opaque white pigment is produced by the simultaneous precipitation of metatitanic acid and barium sulphate than by mechanically mixing the two pigments. E. S. Hedges.

Germanium. IV. R. Schwarz, P. W. Schenk, and H. Giese (Ber., 1931, **64**, [*B*], 362—368; cf. A., 1929, 1407).—Ethyl orthogermanate was hydrolysed by water at 0° and the product subjected to isothermal dehydration. Evidence of the existence of a hydrated germanium dioxide was not obtained. The Röntgen diagram showed that the material very rapidly became crystalline and had the same lattice as the anhydrous dioxide.

Determinations of the m. p. of germanium dioxide by the method of Shepherd and Rankin (A., 1909, ii, 725) gave the value 1115°±3°.

If a mixture of germanium tetrachloride and oxygen is circulated over granular quartz or felspar at 950°, *germanium oxychloride*, Ge_2OCl_6, a colourless liquid, b. p. 70°/13 mm., m. p. about −60°, d^{20} 2·057, is produced. It decomposes when boiled at the atmospheric pressure with evolution of white clouds of the dioxide. An oxychloride, $GeOCl_2$, could not be prepared.

Germanium tetrachloride is converted by sulphur trioxide (1 : 6) at 160° into *germanium sulphate*, $Ge(SO_4)_2$, a colourless, odourless powder, d^{22} 3·92, which is hydrolysed by water and yields sodium germanate and sulphate when treated with sodium hydroxide. It suffers incipient thermal decomposition at 200°. H. WREN.

Behaviour of nitroso-*R*-salt with certain mineral salts. A. BERNARDI and M. A. SCHWARZ (Annali Chim. Appl., 1931, **21**, 45—50).—The following compounds are obtained by treating inorganic salts with nitroso-*R*-salt (cf. van Klooster, A., 1921, ii, 415): $(C_{10}H_5O_8NS_2Na_2)_2Pb,PbNO_3$; $(C_{10}H_5O_8NS_2Na_2)Ag,AgNO_3,3$ and $8H_2O$; $(C_{10}H_5O_8NS_2Na_2)_2Ba,BaCl_2,6H_2O$; $(C_{10}H_5O_8NS_2Na_2)_2Ca,CaCl_2$. Aqueous solutions of barium chloride (1·5% or more) and calcium chloride (5% or more) but not those of strontium chloride are precipitated by the reagent, the calcium compound redissolving on heating. In aqueous solutions acidified with hydrochloric acid calcium is not precipitated, strontium is precipitated only from its concentrated solutions as a greyish-green crystalline mass, and barium gives an orange-yellow precipitate at a much lower concentration, this and the strontium precipitate being dissolved on heating. In aqueous solution rendered alkaline with ammonia all three metals are precipitated. All these precipitations are slow and are complete only after the lapse of at least 24 hrs. The presence of alcohol in the solutions favours the precipitation. The reaction furnishes a means of separating calcium from barium. T. H. POPE.

Reactions in the solid state at high temperatures. VII. Reactions of niobium and tantalum pentoxides with metal oxides and alkaline-earth carbonates. W. JANDER and H. FREY (Z. anorg. Chem., 1931, **196**, 321—334).—By means of heating curves reactions between barium, strontium, calcium, magnesium, zinc, and cupric oxides, and barium, strontium, and calcium carbonates with tantalum and niobium pentoxides in the solid state have been investigated. The curves for the alkaline-earth oxides showed evidence of chemical reaction, but no such evidence was obtained for magnesium, zinc, and cupric oxides. The reactions with the alkaline-earth carbonates begin about 400—500° and among the products the following new *compounds* have been found: $2BaO,Ta_2O_5$; $4BaO,Ta_2O_5$; $2SrO,Ta_2O_5$; $4SrO,Ta_2O_5$; $4CaO,Ta_2O_5$; BaO,Nb_2O_5; $4BaO,Nb_2O_5$; SrO,Nb_2O_5; $4SrO,Nb_2O_5$; $5CaO,Nb_2O_5$. These substances are readily decomposed by acids. E. S. HEDGES.

Production of oxygen from lime and chlorine. O. R. SWEENEY, J. W. HUSSEY, and W. RALSTON.—See B., 1931, 199.

Complexity of sulphur trioxide. A. SMITS [with P. SCHOENMAKER] (Z. physikal. Chem., 1931, **152**, 432—450; cf. A., 1925, ii, 267; 1926, 669, 785).—A review of previous work and an account of the principal results of the author's investigations. F. L. USHER.

Chromatic reactions of the molybdenumoctacyanides. G. A. BARBIERI (Atti R. Accad. Lincei, 1930, [vi], **12**, 148—153).—The parallelism between the ions $[Mo^{IV}(CN)_8]''''$ and $[Mo^{V}(CN)_8]'''$ on the one hand, and $[Fe^{II}(CN)_6]''''$ and $[Fe^{III}(CN)_6]'''$ on the other, is shown by the strongly coloured products which they form in reaction with such substances as ferric and ferrous salts, uranyl salts, molybdic acid, and salts of silver and copper. F. G. TRYHORN.

Crystal formation in sintered tungsten rods. M. HÜNIGER (Tech.-Wiss Abh. Osram-Konzern, 1930, **1**, 124—132; Chem. Zentr., 1930, ii, 2992).—Tungsten powder with or without addition of thorium dioxide affords by relatively brief heating crystals of varying size up to single crystals. Crystal growth is conditioned not by the colour, density, etc. of the tungsten powder but by its mode of preparation and mechanical treatment and by the thoria content. The conditions of reduction are more important than the mode of preparation of the tungstic acid. A. A. ELDRIDGE.

Existence of violet tungsten oxide, W_4O_{11}. E. TARJÁN (Naturwiss., 1931, **19**, 166—167).—Blue tungsten oxide, W_2O_5, does not exist in presence of hydrogen–water vapour mixtures at 700—1000°, but the oxide W_4O_{11} has been isolated; it exists under conditions which are within the limits of stability of W_2O_5, as stated by Chaudron (A., 1920, ii, 379), *e.g.*, with 15—30% of hydrogen in the gaseous phase at 900°, and is formed also in presence of carbon monoxide–carbon dioxide mixtures under conditions within the limits calculated by van Liempt for the existence of W_2O_5, *e.g.*, with 25% of carbon monoxide in the gaseous phase at 900°. On reduction W_4O_{11} yields first the dioxide and then tungsten, without the formation of intermediate products. It possesses a well-defined crystalline structure and appears as reddish-violet needles with a metallic lustre; the *X*-ray diagram indicates a characteristic lattice of triclinic symmetry. The same oxide is produced when a compressed mixture of tungstic oxide and the dioxide is heated in an inert atmosphere; in many of its properties, such as its chemical inertness and metallic conductivity, it resembles the tungsten-bronzes obtained by heating tungstates with tungsten dioxide. Conflicting reports on the tungsten oxides are in part due to confusion between blue reduction products and the violet oxide. H. F. GILLBE.

Complex bromine derivatives of quinquevalent tungsten. H. PAULSSEN-VON BECK (Z. anorg. Chem., 1931, **196**, 85—88).—By the action of hydrobromic acid on potassium oxalatotungstate and treatment of the product with rubidium or cæsium sulphate the *compounds* $Rb_2(WOBr_5)$ and $Cs_2(WOBr_5)$ have been prepared, the former as olive-brown octahedral

crystals and the latter as a greenish-yellow crystalline powder; the *ammonium* salt is similar but unstable. The *compounds* (C_5H_5NH)($WOBr_4$) and (Et_4N)($WOBr_4,H_2O$) have also been prepared. All these compounds are less soluble in hydrobromic acid than are the corresponding chlorine derivatives in hydrochloric acid, and the solutions are green. The bromine compounds hydrolyse more readily than the chlorine compounds, but may be kept without decomposition in an atmosphere of carbon dioxide.
H. F. Gillbe.

Determination of the degree of aggregation of isopolyacid ions with the aid of dialysis coefficients. H. Brintzinger and W. Brintzinger (Z. anorg. Chem., 1931, **196**, 55—60).—The dialysis coefficients of tungstate solutions at various values of p_H show that monotungstate alone exists above p_H 6·6±0·1, and that in more strongly acid solutions (p_H 6·6—4·5) a hexatungstate ion, W_6O_{21}'''''', is present. Analogous measurements with molybdate solutions show that the simple molybdate is converted into a trimolybdate at p_H 6·2±0·1, that a hexamolybdate is produced at p_H 4·7±0·15, and that a dodecamolybdate is formed at p_H 1·8±0·2. The measurements are independent of the cation provided that the same cation is present in the external solution. The results accord closely with those of Jander derived from diffusion measurements and the method has the advantages of simplicity and rapidity.
H. F. Gillbe.

Purification of perchloric acid by vacuum distillation. G. F. Smith and O. E. Goehler (Ind. Eng. Chem. [Anal.], 1931, **3**, 48—52).—Conditions governing the vacuum distillation of perchloric acid are described and dimensioned drawings are given of suitable types of still-head, including four designs of the cold-target type, which is particularly suitable since the mechanism of the distillation probably involves the projection of gaseous molecules through a surface layer of oxonium perchlorate. Any tendency to ebullition due to the evolution of dissolved gases may be checked by previously cooling the acid to −5° to −10°, which serves also to remove metallic perchlorates, or by heating to 200° and constant composition (72%). Data relating to the rate of distillation and the composition of the product at various temperatures and pressures are given; the rate is proportional to the degree of superheating employed, whilst the maximum difference of composition of acids distilled at 0·5 mm. and 7 mm. pressure is 0·30%. The composition corresponds with the dihydrate when the pressure is 5·7 mm. If not more than 4% of sulphuric acid is present in the crude acid the quantity in the distillate does not exceed 0·001% if the process is carried out at a low temperature and pressure; with up to 36% of phosphoric acid in the crude acid only a trace is found in the distillate.
H. F. Gillbe.

Dissociation of concentrated perchloric acid during vacuum distillation at moderately low pressures. Preparation of anhydrous perchloric acid. O. E. Goehler and G. F. Smith (Ind. Eng. Chem. [Anal.], 1931, **3**, 55—58).—An apparatus is described whereby 7—10% yields of anhydrous perchloric acid may be prepared by direct distillation of the 73·3—73·6% acid, without the aid of a dehydrating agent, at a pressure of 12—15 mm. The process is non-dangerous if the detailed directions given are followed closely, and the product appears to be more stable than that prepared by other methods; it does not discolour if kept at the temperature of liquid air for two months, and does not explode at the ordinary temperature until it has been stored for about 4 weeks. The mechanism of the process involves the reactions $4HClO_4,2H_2O \longrightarrow 2HClO_4,3H_2O+2OH_3ClO_4$ and $2OH_3ClO_4 \longrightarrow HClO_4,2H_2O+HClO_4$. The first equation represents the formation of a surface film of oriented oxonium perchlorate molecules, which accounts for the superheating and absence of ebullition during the distillation. On account of the low distillation temperature (110—120°) the decomposition into dihydrate and anhydrous acid, which is known to take place at 110°, is not disturbed by the vapour of the lower hydrates.
H. F. Gillbe.

Oxonium structure of hydrated perchloric acid. G. F. Smith and O. E. Goehler (Ind. Eng. Chem. [Anal.], 1931, **3**, 58—61).—On seeding a supercooled solution of perchloric acid having approximately the composition of the dihydrate (*i.e.*, 73·6%) the crystal at first formed undergoes a transformation at about −19° with absorption of heat. The product of this change is oxonium perchlorate monohydrate, OH_3ClO_4,H_2O. The α and β forms of perchloric acid trihydrate are regarded as the result of an analogous transition, viz., $HClO_4,3H_2O \longrightarrow OH_3ClO_4,2H_2O$. The m.-p. of oxonium perchlorate is 49·905°±0·005, and the m. p. curve shows no indication of a transition $OH_3ClO_4 \longrightarrow HClO_4,H_2O$. It appears therefore that the oxonium structure is common to all the hydrated perchloric acids.
H. F. Gillbe.

Working up iodine residues. F. T. van Voorst (Chem. Weekblad, 1931, **28**, 129—130).—The methods described in the literature are reviewed. If thiocyanates are absent, cuprous iodide may be precipitated by addition of copper sulphate and sodium hydrogen sulphite solutions; iodine is liberated from the precipitate by treatment with sulphuric acid and sodium dichromate, distilled from the resulting liquor, washed, and dried.
S. I. Levy.

Physical and chemical properties of rhenium. C. Agte, H. Alterthum, K. Becker, G. Heyne, and K. Moers (Z. anorg. Chem., 1931, **196**, 129—159).—New determinations of the principal physical properties of rhenium are given (see this vol., 288). Methods of isolation of the metal are compared; by reduction of potassium perrhenate with hydrogen at 1000° fairly pure rhenium is obtained in 95% yield as a light crystalline powder. The separation of the metal by passage of the vapour of the mixture of chlorides obtained by heating the metal at 500—1000° in a current of chlorine over a tungsten filament at 1800° and low pressure, and the growth of the crystals obtained, are described; tungsten, molybdenum, tantalum, or platinum filaments do not alloy with rhenium during the process. The yield of metal is only 10—20%. The vapour of the peroxide may be reduced in the same manner. At high temperatures rhenium is more resistant to the action of oxidising gases than is tungsten; it oxidises in air, although more slowly than tungsten, at temperatures above 1000°, but in presence of only 10% of oxygen it is not attacked below 1600°. Rhenium is not attacked by moist hydrogen at any temperature, but in moist nitrogen corrosion commences at 1900°; the metal is rendered passive towards water vapour, but not towards oxygen, by heating at 2000° in moist hydrogen. Various reactions of rhenium are described, especially in relation to their analytical applications (cf. A., 1929, 1408). Mercurous and thallous perrhenates are precipitated from a 0·1% solution of the potassium salt, and characteristic precipitates are formed with brucine and veratrine. For the microchemical detection of rhenium the colourless crystalline precipitate of cæsium perrhenate, which is rendered violet by potassium permanganate, and the blue needles formed in presence of methylene-blue are characteristic. The metal is best determined as ammonium perrhenate. The spectral lines at 3000, 3425, 3452, and 3462 Å. are the most persistent (cf. A., 1928, 1344). Rhenium dissolves readily in nitric acid, with formation of perrhenic acid, with difficulty in sulphuric acid, and inappreciably in hydrochloric and hydrofluoric acids. No carbide, nitride, or carbonyl could be prepared, but a boride appears to exist. Attempts to prepare an amalgam by various methods were unsuccessful.

H. F. Gillbe.

Iron nitrosyls and their behaviour on autoxidation. H. Reihlen, E. Elben, and J. Everet (Annalen, 1931, 485, 43—52).—The compound $Fe(NO)_2(S\cdot CS\cdot OEt)_2$ (cf. Manchot and Davidson, A., 1929, 526) is formed with theoretical absorption of nitric oxide and in quantitative yield when prepared in a mixture of chloroform and water, thus confirming the above constitution in which the iron is most probably bivalent. It is completely decomposed at 60° in a high vacuum, giving ethyl dithiocarbonate free from nitrosyl xanthate; during its formation there is no evidence of a labile additive product of ferrous xanthate and nitric oxide. In carefully dried benzene solution it absorbs one atom of oxygen with great rapidity, and appears to yield a mixture of $FeNO_2(NO)(S\cdot CS\cdot OEt)_2$ and $FeNO_2(S\cdot CS\cdot OEt)_2$. A totally different behaviour is shown by the compound $[Fe(SEt)(NO)_2]_2$, which in dry chloroform or benzene absorbs only about 0·03 atom of oxygen in 20 min.—1 hr., and then decomposes completely. The *compound* $Fe(S\cdot CO_2Et)(NO)_2$, obtained as dark brown crystals by interaction of potassium ethyl thiocarbonate (Bender's salt), ferrous sulphate, and nitric oxide in aqueous chloroform, shows a similar behaviour, but the period of induction is shorter. This behaviour towards oxygen is used as an argument against the univalency of iron in compounds of the latter type, which are regarded as complexes of tervalent iron in which the nitrosyl radicals are present as acidic residues.

H. A. Piggott.

Cobaltic sulphate as oxidising agent. S. Swann, jun., and T. S. Xanthakos (J. Amer. Chem. Soc., 1931, 53, 400—404).—Optimal yields of cobaltic sulphate are obtained electrolytically from solutions of cobaltous sulphate 10N with respect to sulphuric acid and maintained below 10°. Current densities of 0·01—0·2 amp. per cm.^{2} at a platinum anode are employed. The resulting suspension of cobaltic sulphate is a strong oxidising agent towards many organic compounds; formic, tartaric, citric, and malic acids are converted almost quantitatively into carbon dioxide.

J. G. A. Griffiths.

Quantitative chemical analysis by means of absorption of X-rays. N. H. Moxnes (Z. physikal. Chem., 1931, 152, 380—408; cf. A., 1929, 1254).—The procedure used in measuring the absorption of X-ray spectral lines is described in detail. A photographic photometric method was used. The method applied to zinc and nickel has yielded results 75% too high and 30% too low, respectively.

F. L. Usher.

Radioactivity method for the examination of pulverised substances. W. Šebesta (Z. Physik, 1930, 66, 598—618).—Measurements of the range of α-particles emitted by a mixture of a pulverised substance and a normal radioactive preparation may be readily applied to the analysis of powdered mixtures. The powder is spread in a layer such that an increase in its thickness leaves the range of emitted α-particles unchanged; the ionisation current due to emission in all directions above the layer then gives a measure of the quantity of one substance in the mixture. The method is described in detail.

A. B. D. Cassie.

Analysis of a mixture of volatile liquids. M. Lemarchands (Bull. Soc. chim., 1931, [iv], 49, 80—84).—A method of determining the relative proportions of the constituents of a liquid mixture depends on the measurement of the latent heat of vaporisation of the mixture.

F. J. Wilkins.

Hydrogen-ion determinations with low-resistance glass electrodes. G. R. Robertson (Ind. Eng. Chem. [Anal.], 1931, 3, 5—7).—By the use of glass electrodes of 2—3 megohms resistance in conjunction with a d'Arsonval type of galvanometer, p_H measurements may be carried out to within 0·02. Owing to the variability of the glass surface potentials it is necessary to obtain the p_H of the solution under investigation by interpolation, using two buffer solutions of higher and lower p_H respectively. By decreasing the resistance of the glass electrodes the resistance to polarisation appears to have been increased; recovery after polarisation by large currents is, however, slower than with the quinhydrone electrode.

H. F. Gillbe.

Application of hydrazine in electrometric titrations. G. Holst (Svensk Kem. Tidskr., 1931, 43, 2—17).—The potentials of gold, mercury, and platinum electrodes in dilute solutions of hydrazine have been measured against a normal calomel electrode. Solutions of p_H 2·2—8·0, containing 1% of 0·1M-hydrazine sulphate, were employed. In acid solutions the platinum electrode is more positive than the gold, whilst in neutral and alkaline solutions the reverse is the case. Both electrodes show increasing negative potentials with an increase of the p_H of the solution, but the results are somewhat irregular. Using a platinised platinum electrode in a closed nitrogen-filled cell the results showed the potential to be a linear decreasing function of the hydrogen-ion concentration between the limits $p_{\rm H}$ 1—13. Experiments with a Michaelis hydrogen electrode in buffer solutions of $p_{\rm H}$ 4·16 and 8·30 showed that the addition of a hydrazine solution of similar $p_{\rm H}$ had no effect on the potential. A mercury electrode in dilute hydrazine solutions is uniformly more positive than either gold or platinum, but a long period, up to 15 hrs., is necessary before equilibrium is reached. Both potassium dichromate and vanadic acid can be sharply titrated electrometrically with hydrazine sulphate solution, using gold or platinum electrodes, but attempts to determine copper and mercury either in ammoniacal solution or in one containing sodium hydroxide and tartrates were not satisfactory; experiments to determine molybdates and ferric salts also failed. Hydrochloric acid can be titrated with sodium hydroxide after addition of 1 c.c. of 0·1*M*-hydrazine sulphate; the change in potential is sharp if a platinised platinum electrode is used, but less satisfactory with one of gold. H. F. Harwood.

Measurement of $p_{\rm H}$ by means of a glass electrode and a triode valve. S. O. Rawling and G. B. Harrison (Phot. J., 1931, **71**, 108—112).—The significance of $p_{\rm H}$ is indicated and a simple method for its measurement is described (cf. A., 1930, 1151). H. F. Gillbe.

Differential potentiometric titration. IV. (*a*) Adaptation to hydrogen electrodes. (*b*) Test of standards for precise acidimetry. D. A. MacInnes and I. A. Cowperthwaite (J. Amer. Chem. Soc., 1931, **53**, 555—562).—(*a*) The application to hydrogen electrodes of the method previously described (A., 1929, 666) requires hydrogen free from the smallest traces of oxygen. (*b*) The end-point of the titration of 0·2*N*-sodium hydroxide with diluted constant-boiling hydrochloric acid, potassium hydrogen phthalate, and benzoic acid is determined to within 0·01%. J. G. A. Griffiths.

Tables for the calculation of $p_{\rm H}$ from the *E.M.F.* determined with the quinhydrone electrode. V. Morani (Annali Chim. Appl., 1931, **21**, 83—104).—Introduction into Nernst's concentration cell formula of the most recent values for *R* and *F* gives for the thermodynamic factor the value 0·0577457 at 18°. In calculations of $p_{\rm H}$ from the results of potentiometric determinations of *E.M.F.*, this factor is rounded off to 0·577 which, although it comes within the errors of the determination with the quinhydrone electrode, may vitiate the most exact calculations. This difficulty may be obviated by considering the values obtained as valid at 17·77° instead of at 18°. Tables are given showing (1) correction factors for converting the *E.M.F.* at any temperature between 10° and 26° into the corresponding value at 17·77° and (2) values of $p_{\rm H}$ (0 to 8·5) calculated from values of the *E.M.F.* varying from −0·1176 to 0·3728 at 17·77° in accordance with the expression $p_{\rm H}=2{\cdot}04+v^{17\cdot77}/0{\cdot}0577$. T. H. Pope.

Determination of hydrogen-ion concentration by means of indicators. E. Leikola and P. Noponen (Acta Soc. Med. Fenn. "Duodecim," 1929, **11**, 18 pp.; Chem. Zentr., 1930, ii, 2922).—Leikola and Kerppola's method of colour imitation (A., 1930, 446) is employed, solutions of cobalt nitrate (6%), potassium dichromate (0·1%), nickel sulphate (15%), and (ammoniacal) copper sulphate (0·5%) being used to prepare the standard solutions.

A. A. Eldridge.

Perchloric acid as a new standard in acidimetry. G. F. Smith and W. W. Koch (Ind. Eng. Chem. [Anal.], 1931, **3**, 52—55).—By distillation of pure 72% perchloric acid in a special type of Claisen flask until 50% has been removed and collecting the remainder of the distillate separately an acid of 73·6%±0·03 concentration and d_4^{25} 1·7128±0·0004 is obtained. The rate of distillation is not of importance and varies according to the temperature, which may be between 60° and 95°; the most satisfactory pressure is 5—6 mm., but the composition is almost constant between the limits 2 and 7 mm. If the acid used contains 70 or 71% of perchloric acid, the first 65 or 60%, respectively, should be rejected. A normal solution is obtained by dissolving 136·4201 g. of the redistilled acid in 1 litre. The advantages of perchloric acid over constant-boiling hydrochloric acid for the preparation of standard solutions are the absence of the need for exact pressure control, the freedom from troubles due to entrainment and bumping, and the rapidity of the process.

H. F. Gillbe.

Analysis of mixtures of hydrogen, methane, and ethane. O. J. Walker and S. N. Shukla (J.C.S., 1931, 368—370).—The ethane is determined from the contraction in volume which occurs when the gas mixture is cooled with liquid air to condense out the ethane, and the hydrogen from the contraction which occurs when the residue is treated with palladium; the amount of methane is obtained by difference. With 5—10 c.c. of mixture the average errors are: ethane ±0·8%, hydrogen ±1·1%, and methane ±2·6%. Increased precision is attained by exploding the residual methane. R. Cuthill.

Determination of small concentrations of chlorine. V. N. Kolitscheva and R. V. Teis (J. Russ. Phys. Chem. Soc., 1930, **62**, 1957—1973).—0·007 Mg.-% of chloride ion can be determined with an error not exceeding 1%, using Kleinman's nephelometer, whilst electrotitrimetrically trustworthy values may be obtained for solutions containing not less than 0·014 mg. Porter's colorimetric method (A., 1926, 927) is suitable for quantities of chlorine not less than 0·001 mg., whilst by means of Alfthan's method, depending on the coloration produced by the action of chlorine on hydrochloric acid solutions of dimethyl-*p*-phenylenediamine, 0·0007 mg. can be determined. Iodometric methods, depending on the absorption of chlorine from air by potassium iodide or arsenious acid solutions, give trustworthy results for solutions containing not less than 0·07—0·10 mg. of chloride ion. R. Truszkowski.

Mercurimetry. O. Tomíček and O. Pročke (Coll. Czech. Chem. Comm., 1931, **3**, 116—125).—The theory of the use of sodium nitroprusside as indicator for the titration of chloride and bromide with a mercuric salt is discussed. The solubility of mercuric nitroprusside is less than 5×10^{-5} g.-mol. per litre. The potentiometric titration of halide, thiocyanate, and nitroprusside with mercuric nitrate is described. Cyanide may be determined by adding the greater part of the nitrate solution to the slightly acid solution, and then stirring and completing the titration in the usual manner. Reverse titration is not satisfactory, as reduction of the mercuric salt takes place. The use of nitroprusside as indicator yields practically the same end-point as the potentiometric method if allowance be made for the volume of nitrate solution required to produce turbidity, which is about 0·2—0·4 c.c. of $0·1N$-solution in a total volume of 200 c.c. when 0·1 g. of the indicator is present. Mercurous nitrate cannot be used satisfactorily for the titration. H. F. GILLBE.

Detection of chlorate in the presence of perchlorate and nitrate. T. P. RAIKOVA-KOVATSCHEVA (Z. anal. Chem., 1930, **82**, 415—417).—Chlorate may be detected in perchlorates or nitrates by shaking the solid salt with 5 c.c. of saturated aqueous hydrogen sulphide; as little as 0·01 mg. of chlorate produces an opalescence, due to separation of sulphur, in 5 min. A. R. POWELL.

Oxonium perchlorate as a reference standard for the construction of a density–composition table for concentrated perchloric acid solutions. G. F. SMITH and O. E. GOEHLER (Ind. Eng. Chem. [Anal.], 1931, **3**, 61—63).—The lack of a satisfactory chemical method for the analysis of 65—75% perchloric acid solutions has led to the adoption of oxonium perchlorate, the purity of which may be checked by determination of the m. p. (49·905°), as a standard for the preparation of solutions of known composition. A density–composition table has been prepared for 63—75% perchloric acid solutions; for the 70—73% acid dd/dC, where C is the percentage concentration, is approximately linear and equal to 0·01343, whilst for more dilute solutions the value may be taken as 0·01351. The solution of composition corresponding with the dihydrate (73·6%) has $d^{25}_{4\,\text{calc.}}$ 1·71282±0·00005, and the 72·4% constant-boiling acid (203°/760 mm.) has d^{25}_{4} 1·6964 approximately. H. F. GILLBE.

Direct and reverse titration of sulphuric acid with barium hydroxide. I. M. KOLTHOFF and E. B. SANDELL (Ind. Eng. Chem. [Anal.], 1931, **3**, 115—117).—The best results in the titration of sulphuric acid with barium hydroxide are obtained by working at the ordinary temperature and adding more base after the first colour change of the indicator, boiling and adding more hydroxide until the colour persists for 15—30 sec., and then cooling and completing the titration. In the reverse method hydroxide is partly adsorbed and partly occluded by the precipitate, and after boiling with acid to remove the adsorbed portion the error due to occlusion is still about 1%. The most satisfactory procedure is to add the barium hydroxide solution to an excess of potassium sulphate solution at the ordinary temperature, titrate, boil, and complete the titration in the cooled solution; the error is 0·0—0·2%. Addition of the potassium sulphate solution to the hydroxide causes large errors (1%). Precipitation of the acid by barium chloride is unsatisfactory. It is advisable to use potassium hydrogen phthalate for the standardisation of barium hydroxide solutions.

H. F. GILLBE.

Determination of sulphur by means of the turbidimeter. S. W. PARR and W. D. STALEY (Ind. Eng. Chem. [Anal.], 1931, **3**, 66—67).—The turbidimeter described contains a centrally placed hollow plunger fitted with an optical glass plate at the lower end and an eyepiece at the upper end; the plunger can be raised or lowered by means of a rack and pinion. Beneath the optical glass bottom of the turbidimeter tube is placed a 2 c.-p. lamp supplied with constant current adjusted by a rheostat and voltmeter. In making a determination the plunger is moved until the filament just disappears, and a calibration curve is constructed showing the relationship between the height of the plunger and the sulphate content of the solution. The instrument is very compact and gives satisfactorily concordant and rapid results even in unskilled hands.

H. F. GILLBE.

Volumetric determination of persulphate. A. KURTENACKER and H. KUBINA (Z. anal. Chem., 1931, **83**, 14—36).—Various methods which have been proposed by previous authors have been critically examined and modifications introduced in some cases to increase their accuracy. Reduction of persulphate with ferrous sulphate proceeds instantaneously at the ordinary temperature when the solution contains 10 c.c. of phosphoric acid (d 1·7) per 100 c.c. Reduction with methyl alcohol followed by titration with alkali gives high results, probably due to the formation of formic acid. The decomposition of persulphates on boiling their aqueous solutions is accelerated by the addition of 10 c.c. of $0·1N$-silver nitrate per 100 c.c.; the resulting sulphuric acid may be titrated with alkali. Methods involving reduction of the persulphate with oxalic acid, alkali arsenite, or alkali iodide all yield erratic results due to catalytic action in the presence of air.

A. R. POWELL.

Polarographic studies with the dropping mercury cathode. XVII. Reduction of nitric oxide and the determination of nitrites. J. HEYROVSKÝ and V. NEJEDLÝ (Coll. Czech. Chem. Comm., 1931, **3**, 126—133).—Neutral or alkaline solutions of nitrite are not reduced at the dropping mercury cathode, but with acidified solutions there is a wave in the polarograph curve at —0·77 volt (N-calomel electrode). The saturation current increases to a maximum on addition of acid up to a five-fold excess, and in more strongly acid solutions is proportional only to the nitrite concentration. The wave is due to the reduction of nitric oxide produced by decomposition of the liberated nitrous acid, as is shown by the appearance of a similar wave in an acidified solution of nitrogen peroxide. The actual reduction process is a secondary reaction caused by electrically deposited hydrogen atoms, and the product is ammonia. Since the polarographic method serves to detect 1 part of nitrite in 10^6, and the height of the wave is proportional to the nitrite concentration, the method may be employed to determine nitrite, *e.g.*, in explosives. H. F. Gillbe.

Volumetric determination of phosphoric acid. R. Biazzo (Annali Chim. Appl., 1931, **21**, 75—81).—The phosphoric acid is precipitated by means of excess of standard ammonium molybdate, the excess of this being determined in the filtrate by titration with standard lead acetate. When this titration is nearing completion, a little of the clear filtered solution is tested with a drop of the lead acetate, this procedure being repeated until no further precipitation is produced in this way. The titres of the two standard solutions are determined by tests on known amounts of phosphoric acid. The titration occupies 10—15 min. and parallel determinations give concordant results. T. H. Pope.

Determination of arsenic in bismuth and barium salts. L. W. Green and R. E. Schoetzow.—See B., 1931, 199.

Determination of carbon monoxide. E. Dittrich.—See B., 1931, 230.

Influence of hydrogen on determination of carbon monoxide with the Dräger apparatus. J. G. de Voogd and A. van der Linden (Chem. Weekblad, 1931, **28**, 133—134).—Relatively large quantities of hydrogen introduce only slight errors. S. I. Levy.

Determination of helium and neon. V. A. Sokolov (Neft. Choz., 1930, **19**, 292—297).—A method for the analysis of mixtures of helium and neon, depending on the difference in density, and an appropriate balance are described. Chemical Abstracts.

Determination of potassium by the sodium cobaltinitrite method. P. J. Van Rysselberge (Ind. Eng. Chem. [Anal.], 1931, **3**, 3—4).—The weight of a sodium potassium cobaltinitrite precipitate increases with the time of settling to a limit which varies with the concentration and volume of the solution and with the manner of addition of the reagent. For accurate results, *i.e.*, within 1·3%, several solutions, of known and unknown composition, must be treated with the cobaltinitrite reagent under identical conditions, and the precipitate, after being kept for 24 hrs. and being filtered and washed, must be dried at 120° for a constant time. The potassium content of the "unknown" precipitates may be deduced from the composition of the "known" precipitates. The ratio of sodium to potassium in the solution to be analysed should be not less than 25, and should be approximately the same for all the solutions. H. F. Gillbe.

Rapid colorimetric determination of potassium. E. R. Caley (J. Amer. Chem. Soc., 1931, **53**, 539—545; cf. A., 1930, 562).—0·001—0·01 G. of potassium (as chloride) in 1 c.c. of water is precipitated as picrate by means of 7·5 c.c. of saturated picric acid in 95% alcohol. After 40 min. at 20°, the precipitate is collected in a medium-porosity sintered glass funnel and freed from picric acid by washing with ether. The precipitate is dissolved in 50 c.c. of water and compared colorimetrically with standards prepared in a similar manner. Rubidium and cæsium behave similarly. Alkaline-earth, aluminium, and ferric chlorides do not interfere; in presence of unknown quantities of sodium the sample should not weigh more than 20 mg. J. G. A. Griffiths.

Oxalate method of determining the titre of potassium thiocyanate, using borax. N. A. Tananaev and N. A. Lazarkiewitsch.—See B., 1931, 245.

Determination of sodium carbonate in sodium hydrogen carbonate. A. K. Babko.—See B., 1931, 244.

Volumetric determination of small quantities of silver. J. Golse (Bull. Soc. Pharm. Bordeaux, 1930, **68**, 53—64; Chem. Zentr., 1930, ii, 2677).—A solution of 2·5 g. of potassium iodide and 3·5 g. of mercuric iodide per litre is used as precipitant. The precipitate, $2AgI,HgI_2$, always contains silver iodide; hence for less than 15 mg. the quantity of silver a must be increased by $0{\cdot}002a^2$, or for larger quantities by $0{\cdot}00125(10a+a^2)$. A micro-procedure is described (cf. A., 1930, 1264). A. A. Eldridge.

Rapid determination of calcium in lead alloys of low calcium content. L. I. Shaw, C. F. Whittemore, and T. H. Westby.—See B., 1931, 254.

Determination of beryllium in aluminium. H. V. Churchill, R. W. Bridges, and M. F. Lee.—See B., 1931, 253.

Separation of beryllia and alumina. A. Travers and Schnoutka (Compt. rend., 1931, **192**, 285—287).—Berthier's sulphite method has been re-investigated. A solution of beryllium hydrogen sulphite evaporated to dryness on the water-bath or heated under pressure (2 kg.) gives no precipitate. Aluminium hydrogen sulphite similarly treated is quantitatively precipitated as an ill-defined basic sulphite, which when prepared under pressure is partly oxidised to the soluble sulphate. On prolonged ebullition the solution of beryllium sulphite deposits the hydroxide, which, however, redissolves on cooling if ebullition has not been too prolonged; in presence of an alkali hydrogen sulphite a precipitate is formed only from a dilute solution, and this redissolves on cooling; from a concentrated solution one is formed only on prolonged ebullition, and redissolves on dilution and cooling. The product is a complex soluble basic beryllium sodium sulphite, stable in the cold, but partly decomposed on boiling. The behaviour of aluminium hydrogen sulphite is unchanged by addition of alkali hydrogen sulphite. Beryllium and aluminium may therefore be separated as follows: the freshly-precipitated gel of the mixed hydroxides is dissolved in excess of alkali, the solution is saturated with sulphur dioxide, boiled for about 10 min., allowed to cool, and kept for several hours. The aluminium is precipitated quantitatively, but carries down a little beryllium, which is completely separated on repeating the process. Precipitation of aluminium in a medium of p_H 4 prevents formation of beryllium aluminate. C. A. Silberrad.

Effect of ammonium chloride on the results obtained by Schmitz' method of determining magnesium. J. Majdel (Z. anal. Chem., 1930, **82**, 425—429).—The results for magnesium obtained by this method (A., 1906, ii, 705) are about 3% low when no ammonium chloride is present in the solution before addition of phosphate. The best results (0·22% low) are obtained with 2—3 g. of ammonium chloride; with large amounts lower figures are obtained until with 4—6 g. of chloride there is a constant error of −1·1% of the magnesia. Hence it is advisable to remove all ammonium salts from a magnesium solution before precipitation and then to add the optimum quantity of ammonium chloride (2—2·5 g.).

A. R. POWELL.

Luminescence analysis. III. Alkaline-earth group and numerical characterisation of luminescence. E. BEUTEL and A. KUTZELNIGG (Monatsh., 1931, 57, 15—19; cf. B., 1931, 403).—The nitrides of magnesium, calcium, and barium, and oxides, hydroxides, carbonates, and sulphates of calcium, strontium, and barium give luminescence effects which cannot always be distinguished visually. The use of a step photometer with three filters enables the effect given by each substance to be defined by four numbers. The electronegative constituent of the compound exercises a greater influence than does the metal.

F. L. USHER.

Distinction between magnesite and dolomite by means of *X*-rays. F. HALLA (Monatsh., 1931, 57, 1—8).—Photographs taken with a small Debye-Scherrer camera afford a means of discriminating rapidly between dolomite and a mixture of its components.

F. L. USHER.

Determination of calcium and magnesium in dolomitic limestones by means of sucrose. A. C. SHEAD and B. J. HEINRICH.—See B., 1931, 245.

Determination of small quantities of zinc in presence of lead. M. E. STAS (Pharm. Weekblad, 1931, 68, 93—97).—The influence of lead on the determination of small quantities of zinc by precipitation with 8-hydroxyquinoline and titration of the precipitate with bromate–bromide has been investigated. Lead at concentrations below 2 g. per litre does not interfere, but at higher concentrations the lead compound separates. The method is more accurate and is applicable to a wider concentration range than nephelometric methods.

H. F. GILLBE.

Rapid determination of various elements after precipitation by the classical methods. II. J. DICK (Z. anal. Chem., 1930, 82, 401—415; cf. A., 1930, 901).—The precipitates obtained by treating hot neutral solutions of zinc, manganese, cadmium, or cobalt salts with a large excess of ammonium dihydrogen phosphate may be weighed as $M^{II}NH_4PO_4,H_2O$ after washing with cold 0·1% ammonium phosphate solution, 65% alcohol, and 95% ether in succession and drying in a vacuum desiccator for 30 min. Washing with alcohol and ether followed by vacuum drying is also applicable to the preparation of bismuth, selenium, tellurium, and cuprous thiocyanate precipitates for weighing.

A. R. POWELL.

Gravimetric and direct volumetric determination of cadmium. R. C. WILEY (Ind. Eng. Chem. [Anal.], 1931, 3, 14—15).—Cadmium may be determined by precipitation at the b. p. from a neutral or slightly acid solution with ammonium molybdate solution rendered slightly acid to litmus by addition of acetic acid. The crystalline precipitate, which is readily collected if kept for 2 hrs. or more at the b. p., should be dried at 120°. If during the precipitation the stirrer strikes the sides of the vessel crystals of cadmium molybdate adhere tenaciously, and are difficult to remove. For the volumetric determination of cadmium the solution is rendered just acid by addition of ammonia and acetic acid and titrated with an ammonium molybdate solution containing 714 g. of molybdenum trioxide per litre. The end-point is recognised by employing as an external indicator a chloroform solution of pyrogallol, which assumes a deep brown colour in presence of molybdate ion. Ammonium salts increase the solubility of cadmium molybdate and influence the results of the volumetric method appreciably. The end-point is sharper with ammonium molybdate than with the sodium salt.

H. F. GILLBE.

Separation of lead, barium, and calcium sulphates by ammonium acetate. W. W. SCOTT and S. M. ALLDREDGE (Ind. Eng. Chem. [Anal.], 1931, 3, 32—33).—Whereas lead may be completely separated from barium by extraction of the sulphates with hot 50% ammonium acetate solution the separation from calcium is incomplete; up to 8·5% of the calcium present may enter the solution, but the quantity appears to be governed by physical factors such as the time required for filtration and the degree of cooling during filtration. With increase of the Ba : Pb ratio the difficulty of extracting all the lead increases, until with a ratio of 100 : 1 only 95% of the lead dissolves; the cause may be the formation of an insoluble lead–barium complex salt, or, more probably, occlusion. The presence of barium reduces the tendency of calcium sulphate to dissolve in ammonium acetate solution.

H. F. GILLBE.

Separation of lead from barium, strontium, and calcium with ammonium acetate. J. MAJDEL (Z. anal. Chem., 1931, 83, 36—45).—When a solution containing lead and barium is evaporated with sulphuric acid until copious fumes are evolved and, after cooling, water is added the precipitate invariably contains more or less of a double sulphate of lead and barium which is insoluble in ammonium acetate solution. With a lead : barium ratio of 1 : 0·1 the proportion of insoluble lead is 5·5%, with a 1 : 1 ratio 46·5%, and with a 1 : 2 ratio 80·5%. Strontium also forms a double sulphate with lead, but this compound is completely soluble in ammonium acetate solution, and hence high results are obtained in the gravimetric determination of lead in the presence of strontium. With small quantities of calcium there is no interference, but with larger quantities high results for lead are obtained gravimetrically. The only satisfactory procedure for separating lead from the alkaline earths is that involving precipitation of the lead with hydrogen sulphide in hydrochloric acid solution.

A. R. POWELL.

Determination of lead dioxide and red lead. G. BRUHNS.—See B., 1931, 246.

The Spacu reaction. Volumetric determination of copper. J. Golse (Bull. Soc. chim., 1931, [iv], 49, 84—100).—The Spacu reaction gives rise to the formation of copper dipyridine thiocyanate, $[Cu(C_5H_5N)_2](SCN)_2$, when pyridine and an alkali metal thiocyanate are added to a solution of a cupric salt. In the presence of excess of the thiocyanate this reaction is complete. A method for the volumetric determination of copper depends on the determination of the excess of thiocyanate. The conditions under which satisfactory results are obtained when permanganate is used are described. It is, however, more satisfactory to use the Volhard or the hypobromite method for the determination of the thiocyanate. Detailed directions are given.

F. J. Wilkins.

Iodide method for [determination of] copper. B. Park (Ind. Eng. Chem. [Anal.], 1931, 3, 77—82).—In presence of much arsenic the usual iodide method for the determination of copper yields high results, but the extent to which the reaction $H_3AsO_4+2HI \longrightarrow H_3AsO_3+I_2+H_2O$ proceeds depends on the iodine and iodide concentrations and on the temperature, and increases with increase of acidity of the solution. Both experimentally and theoretically by consideration of the electrode potentials of solutions of arsenious and arsenic acid and of iodine and iodide it is found that if the p_H of the solution during titration be maintained at a value higher than 3·5 no iodine is liberated by the arsenic. Study of the reaction between the cupric and iodide ions in various buffer solutions of different p_H values shows the influence of different acids to be specific and that in certain cases low results are obtained even when a precipitate is not formed. Of a number of organic acids investigated phthalic is the most satisfactory, as the whole of the copper may be titrated if the p_H does not exceed 5·7. The following method is recommended for the determination in presence of iron and arsenic. To 30 c.c. of the solution are added sufficient ammonia to precipitate all the iron, and then, in succession, ammonium hydrogen fluoride (2 g.), potassium hydrogen phthalate (1 g.), and potassium iodide (3 g.). The solution is titrated immediately with thiosulphate, and the starch–iodide colour should not return within 30 min. All the arsenic present should be in the quinquevalent state. In presence of large amounts of iron or aluminium more ammonium hydrogen fluoride must be added.

H. F. Gillbe.

Analysis of the aluminium group. S. Ato (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1930, 14, 287—311).—The elements of the aluminium group are separated from those of the iron group by boiling the nitric acid solution for 5 min. with an excess of 5 c.c. of 6*N*-sodium hydroxide solution, 1—5 g. of sodium peroxide, and 5 c.c. of 3*N*-sodium carbonate solution. The iron group precipitate is removed and the filtrate treated with acetic acid to render it *N* with respect to that acid and boiled for 5 min. to precipitate titania. The filtrate is boiled with 10—20 c.c. of 3*N*-lead acetate solution, the precipitate dissolved in nitric acid, the solution evaporated with sulphuric acid to remove lead, the chromium reduced with sulphur dioxide and separated from the vanadium by precipitation with sodium hydroxide, and the alkaline filtrate treated with ammonia, ammonium chloride, and hydrogen sulphide to confirm the presence of vanadium. The filtrate from the lead precipitate is treated with ammonia, the precipitate collected, and the filtrate tested for zinc; the ammonia precipitate is dissolved in nitric acid, any lead removed with hydrogen sulphide, and the solution evaporated to dryness. The residue is dissolved in 15 c.c. of 1 : 1 nitric acid and the uranium extracted with ether, three treatments being required to ensure complete separation. The aqueous layer is evaporated to dryness, the nitrates are converted into chlorides by treatment with hydrochloric acid, and the aluminium is separated from beryllium by treatment of the solution with ether and hydrogen chloride, which precipitates $AlCl_3,6H_2O$; small amounts of aluminium are more readily separated by the sodium hydrogen carbonate method. Beryllium is tested for by means of alizarin-red S in a neutral chloride solution.

A. R. Powell.

Detection of manganese in minerals and rocks. H. Leitmeier (Tsch. Min. Petr. Mitt., 1931, 41, 87—94).—Manganese hydroxide, even in traces, in the presence of an acetic acid solution of benzidine gives a blue coloration. To the solution of the mineral on filter-paper a drop of potassium hydroxide is added and then the benzidine solution.

L. J. Spencer.

Oxidation of ferrous iron by iodine in presence of phosphate, and the non-existence of a ferriphosphate complex. W. D. Bonner and H. Romeyn, jun. (Ind. Eng. Chem. [Anal.], 1931, 3, 85—87).—The oxidation of ferrous iron by iodine in presence of phosphate proceeds to completion, although very slowly: at 0·1*N* concentrations in sulphuric acid solution 15 hrs. are required for completion at 40°. The velocity increases with decrease of p_H, and in neutral solution the presence of phosphate is unnecessary, as the ferric iron is precipitated as hydroxide, but the results become erratic. Completion of the reaction is rendered possible as a result of the decrease of the $Fe^{\cdots}/Fe^{\cdot\cdot}$ ratio caused by the presence of phosphate, but potentiometric titration of a ferrous–ferric salt solution with phosphoric acid shows no indication of the formation of a complex. The behaviour of such solutions is therefore attributed to the formation of a weak electrolyte which probably has a composition ranging from $FePO_4$ in solutions containing little phosphate to $Fe(H_2PO_4)_3$ in presence of an excess of phosphate.

H. F. Gillbe.

Colorimetric determination of cobalt alone and in the presence of nickel. E. S. Tomula (Z. anal. Chem., 1931, 83, 6—14).—The neutral cobalt solution (40 c.c.) is treated with 5 g. of ammonium thiocyanate and 50 c.c. of acetone and diluted to 100 c.c. The resulting blue colour is compared with that produced under the same conditions in a standard cobalt solution containing not less than half and not more than twice as much cobalt. The depth of the solution in the standard tube should not exceed 20 mm. and the white plate below the colorimeter tubes should be covered with a piece of glazed yellow gelatin paper if nickel is present.

A. R. Powell.

Detection and determination of nickel with dimethylglyoxime in the presence of much cobalt. F. Feigl and H. J. Kapulitzas (Z. anal. Chem., 1930, **82**, 417—425).—The solution is treated with a concentrated solution of potassium cyanide until the precipitate first formed just redissolves, an excess of hydrogen peroxide is added to convert the cobalto- into cobalti-cyanide, and the solution is evaporated to one quarter its volume to destroy the excess of peroxide. On addition of dimethylglyoxime to the hot solution, followed by formaldehyde until its odour is apparent in the solution, the nickel is precipitated as the characteristic red glyoxime compound together with excess of the precipitant; the compound is purified by dissolution in hydrochloric acid and precipitation in the usual way. The method is based on the reaction $K_2Ni(CN)_4+2H\cdot CHO=Ni(CN)_2+2CN\cdot CH_2\cdot OK$. A. R. Powell.

Arc spectrographic determination of chromium in rubies. J. Papish and W. J. O'Leary (Ind. Eng. Chem. [Anal.], 1931, **3**, 11—13).—The persistence of the arc lines of chromium between 5785·8 and 3120·4 Å. has been investigated by photographing the carbon arc spectrum with from 1·0 to 0·0001 mg. of chromium trioxide placed on the electrodes. Nineteen lines suitable for the spectrographic determination of chromium are given. The smallest recognisable quantity of chromium corresponds with 0·001 mg. of chromium trioxide, but in synthetic rubies made by fusing alumina with the trioxide 0·00006 mg. may be detected. The chromium content of natural rubies, which is too small for determination by chemical means, may be determined spectrographically, and results (0·01—0·1% Cr) are given for a number of specimens. H. F. Gillbe.

Detection of chromium in minerals and rocks. H. Leitmeier and F. Feigl (Tsch. Min. Petr. Mitt., 1931, **41**, 95—102).—A red alcoholic solution of diphenylcarbazide turns violet in the presence of even a trace of a chromate. The mineral to be tested is first fused with sodium carbonate or sodium peroxide. L. J. Spencer.

Detection of germanium. W. Geilmann and K. Brünger (Z. anorg. Chem., 1931, **196**, 312—320).—Germanium can be separated from accompanying elements by the distillation of a hydrochloric acid solution of the substance with the aid of a slow stream of carbon dioxide. The optimal concentration is 3—4*N*-hydrochloric acid; no germanium appears in the distillate when the concentration of acid is less than 0·75*N* or greater than 7·5*N*. Germanium can be detected in the distillate by spectral analysis so long as the concentration is greater than 0·001%, but a procedure is recommended for use with smaller quantities. The germanium is precipitated as sulphide by means of hydrogen sulphide and the precipitate is dissolved in a drop of 1—1·5*N*-potassium hydroxide solution, the spectrum of which is then examined. At this concentration of potassium hydroxide the precipitate is readily soluble and the spectral lines are not affected; in more concentrated solutions the lines are weakened. The method enables germanium to be detected at a concentration of 2×10^{-5}%. Arsenic, selenium, and antimony must be removed by distillation with hydrochloric acid in a stream of chlorine. Results obtained in mineral analysis are given. E. S. Hedges.

Determination of antimony in lead–antimony alloys of low antimony content. L. I. Shaw, C. P. Whittemore, and T. H. Westby.—See B., 1931, 254.

Micromanipulations. E. A. Hauser (Rev. gén. Colloid., 1930, **8**, 358—361).—A brief account of manipulation in ultramicroscopical observations. E. S. Hedges.

Accessory apparatus to the petrographical microscope. K. H. Scheumann (Tsch. Min. Petr. Mitt., 1931, **41**, 58—63).—A refractometer combined with the microscope enables the refractive index of a liquid to be determined at the moment that it is matched with an immersed mineral grain. L. J. Spencer.

Photomicrography with the 365 $\mu\mu$ mercury line. A. P. H. Trivelli and L. V. Foster (J. Opt. Soc. Amer., 1931, **21**, 124—131).—An account of experimental technique is given. Photomicrography with the 365 $\mu\mu$ mercury line can give 19% more resolving power than the best microscopic systems can produce with the Wratten C filter. It has the advantages that the focussing is simplified, that a glass lens system can be used instead of quartz, and a mercury arc instead of a cadmium arc. C. W. Gibby.

Polarisation apparatus for the determination of optical and magnetic rotation dispersion in the ultra-violet. A. Hagenbach (Helv. phys. Acta, 1930, **2**, 168—179; Chem. Zentr., 1930, ii, 2805).—An apparatus for the measurement of magnetic rotation, which is attached to a Cotton and Descamps spectropolarimeter, is described. A. A. Eldridge.

Modification of the Le Chatelier–Bronievski apparatus. A. Regner (Coll. Czech. Chem. Comm., 1931, **3**, 103—110).—The apparatus has been improved by correcting the optical system and increasing the resistances of the two galvanometers to 105 and 443 ohms, and the sensitivities, at a scale distance of 75 cm., to $7\cdot3\times10^{-6}$ and $2\cdot9\times10^{-5}$ volt, respectively. The clock mechanism has been replaced by an electrical device, and temperature measurements are made with the aid of a single differential pyrometer. H. F. Gillbe.

Modified balance for approximate and quick weighing. E. Karrer (Ind. Eng. Chem. [Anal.], 1931, **3**, 112—114).—By the use of an ordinary beam balance modified by addition of a spring and extended pointer the difference between the weights of two objects may be estimated closely within 2 sec. H. F. Gillbe.

Density determinations with solids, and especially with inorganic salts. P. Wulff and A. Heigl (Z. physikal. Chem., 1931, **153**, 187—209).—A critical study has been made of the pyknometric and flotation methods for the determination of the densities of solids and the literature relating to measurements with various halides is reviewed. Measurements with cæsium chloride show that on account of the impossibility of removing air occluded or adsorbed by the solid, results by the pyknometric method always involve a negative error of the order of 0·1%; this view is confirmed by comparison of the densities of certain halides obtained by the pyknometric and by the X-ray and immersion methods. Accurate results, *i.e.*, with a mean error of 0·02%, may be obtained by selecting under the microscope crystals free from inclusions, washing them with an inert solvent, and floating in a mixture of suitable liquids, such as toluene and tetrabromoethane. Convenient apparatus for the determination, and for the subsequent measurement of the density of the liquid, is described. For solids having $d>3$, the displacement method, using a torsion balance, yields results with a maximum error of about 0·1%. H. F. Gillbe.

Device for estimating density of gems and small amounts of solids. E. W. Blank (Ind. Eng. Chem. [Anal.], 1931, 3, 9—11).—The specimen is placed in a narrow (6—8 mm.) tube previously filled with liquid to a marked level in a capillary side tube, and more liquid is then added from a weight burette in order to bring the level to a second mark. Knowing the additional weight of liquid required in absence of the solid, the displacement weight is readily calculated. Ether, despite its volatility, is a very suitable liquid for most substances. The density of 0·01 g. of material may be determined to within 0·01—0·07. H. F. Gillbe.

Glass electrode and vacuum tube potentiometers. D. H. Cameron (J. Amer. Leather Chem. Assoc., 1931, 26, 7—23).—Of three simple forms of glass electrodes, which are described, the MacInnes type (A., 1929, 673) is preferred because of its compactness and simplicity. Each electrode must be calibrated by means of buffer solutions of known p_H value. The suitability of the electrode is affected by the composition of the glass. The potential is measured by employing a vacuum tube potentiometer. In the apparatus described two radio tubes, UX 199 type, replace the variable resistances. The glass electrode has been used by the author for titrating some acid fractions of vegetable tan liquors in presence of pyrogallol and kindred substances. The glass electrode is not poisoned nor affected by oxidising or reducing materials. It functions as rapidly as the quinhydrone electrode. Its upper limit is p_H 9. D. Woodroffe.

[Reproducibility of] quinhydrone electrode. I. [In air.] J. L. R. Morgan, O. M. Lammert, and M. A. Campbell. **II. [In nitrogen.]** O. M. Lammert, J. L. R. Morgan, and M. A. Campbell (J. Amer. Chem. Soc., 1931, 53, 454—469, 597—604; cf. Biilmann and Jensen, A., 1927, 421).—I. The electrode has been investigated in 0·1N-hydrochloric acid. Since cracks and other imperfections in the glass of the electrodes may cause deviations as great as 0·1 volt, the electrodes are annealed and then cleaned by immersion in cold chromic acid–sulphuric acid mixture which is heated at 125° and then allowed to cool to the ordinary temperature. The electrodes are washed with conductivity water, rinsed with ethyl alcohol, and then dried in a current of purified air. Short-circuiting the electrodes in pairs during the cleaning hastens the attainment of the equilibrium potential in quinhydrone solution. The reproducibility is related to the size of the metal exposed to the quinhydrone solution; very small short wires give erratic results and larger short wires yield less consistent results than foil or longer wires. The *P.D.* between two foils of dimensions greater than 1 cm.^{2} is less than 10^{-5} volt, and is little affected by the composition or age of the metal. With smaller electrodes, old roughened platinum gives more reproducible results than new platinum alone or alloyed with other metals; gold is still less efficient. The solutions should be stirred.

II. If oxygen is excluded from the electrode liquid by stirring with nitrogen, equilibrium potentials are attained very rapidly and the results are much more reproducible. Under these conditions, electrodes dried in nitrogen exhibit no improvement as compared with those dried in air, and short circuiting in pairs during pre-treatment is without effect. J. G. A. Griffiths.

Glass electrode measurements by a galvanometer with condenser attachment. M. Dole (J. Amer. Chem. Soc., 1931, 53, 620—622).—The galvanometer system of Jones and Kaplan (A., 1928, 954) is applicable to measurements with the glass electrode (cf. MacInnes and Dole, A., 1930, 423). No drift of potential due to polarisation of the electrodes by the current charging the condenser is observed. J. G. A. Griffiths.

Nephelometric titrations. I. The equal-opalesence end-point. C. R. Johnson (J. Physical Chem., 1931, 35, 540—542).—The unbalanced action of certain ions, mainly multivalent, on the colloidal suspensions employed may cause differences in the light-reflecting power of the sols large enough to introduce serious constant errors in nephelometric titrations. L. S. Theobald.

Colour measurement and spectrophotometry. J. A. A. Ketelaar (Chem. Weekblad, 1931, 28, 132—133; cf. Schoen, *ibid.*, 105).—There is a fundamental difference between the colour observed and the light giving rise to the colour impression; different combinations of radiations of different frequencies may give rise to the same colour effect. A method of colour measurement by comparison with a blend of three radiations of chosen frequencies is foreshadowed. S. I. Levy.

Colour measurement. M. J. Schoen (Chem. Weekblad, 1931, 28, 133).—A reply (cf. preceding abstract). Even in "synthetic" methods, as in Guild's trichromatic colorimeter, the subjective factor is important. S. I. Levy.

Spot apparatus for colorimetric p_H determination. F. Tödt (Chem. Weekblad, 1931, 28, 164—165).—A reply to the criticism of Kolthoff (this vol., 325). S. I. Levy.

Flask in two parts for vacuum evaporation, reflux distillation, and extraction. A. Lubinski (Chem. Fabr., 1931, 78).—The bulb of the flask is connected to the distillation head by a flanged joint made with rubber in such a way that no contact between the contents and the jointing material is possible. It is practicable by this means, for example, to extract a substance in a Soxhlet apparatus, then without removing the liquid from the flask to distil in a vacuum. If an annular container for phosphorus pentoxide etc. is provided in the upper half of the flask the apparatus can be used as a "drying pistol" or desiccator capable of being heated. An air bath is provided for heating purposes warmed by acetone or alcohol vapour as required. C. IRWIN.

Distillation analysis [of small quantities of liquids]. H. WOLFF and J. RABINOWICZ (Chem. Fabr., 1931, 37—38).—The fractional distillation of 2—4 c.c. of liquid is accomplished by the use of a small bulb immersed in a water-bath and joined glass-to-glass to a narrow glass tube bent at two right angles. This is closed at the end, immersed in a graduated cooling vessel, and has a hole in the side to equalise pressure. Temperatures are read by a thermometer in the water-bath and a correction which is applied is determined by comparing the true initial b. p., obtained by heating the sample in a test tube, and the apparent initial b. p. in the apparatus. Curves are given which show that this micro-apparatus gives better fractionation than the usual Engler method. C. IRWIN.

Simple distilling apparatus. R. S. GIBBS (Chemist-Analyst, 1931, 20, No. 1, 22—23).—The liquid is placed in a 300-c.c. beaker in which is suspended a 30-c.c. beaker; a 3·5-inch funnel which rests in a collar on the larger beaker has the stem cut off and the apex fused together, and is filled with ice. CHEMICAL ABSTRACTS.

[Preparation of] conductivity water. G. W. TOMPKIN (Chemist-Analyst, 1931, 20, No. 1, 16—17).—Distilled water was fed into a distilling flask provided with a glass float valve, the steam being partly condensed in a flask submerged in a water-bath and provided with an automatic siphon. CHEMICAL ABSTRACTS.

Laboratory thermostat for continuous operation. P. W. SCHENK (Ber., 1931, 64, [B], 368—370).—An electrically heated and controlled apparatus whereby a temperature constant to within ±0·02° can be secured over long periods is figured and described. The special feature lies in the use of two relays. H. WREN.

Furnace for metallographic examination of specimens at high temperatures. B. A. ROGERS (Met. and Alloys, 1931, 2, 9—12).—The furnace comprises a small zirconia tube wound with molybdenum wire and embedded in magnesia inside a water-jacket which is covered with a silica window. A slow current of pure hydrogen is passed through the case during use to prevent oxidation of the heating wire and of the specimen. The whole apparatus is mounted on a levelling device in a large mechanical stage of an ordinary metallurgical microscope; in this way observations of polished metal specimens may be made at a magnification of 150 diam. at temperatures up to 1000° and at 50—75 diam. at 1500°. Photographs of the surfaces of electrolytic iron and cobalt show that characteristic changes occur at the transformation points; the changes are in the nature of eruptions and sweep across the field of view abruptly at a definite temperature depending on the purity of the metal. Silicon and molybdenum raise the temperature of the A3 point in electrolytic iron, whilst manganese and chromium depress it. A. R. POWELL.

Shaking apparatus. P. DICKENS (Chem. Fabr., 1931, 61—62).—All kinds of glass apparatus can be shaken on a round plate provided with a variety of clamps, supported on suitable guides, and shaken by an eccentric projection on a motor-driven pulley. It is possible to apply heat by means of an electric hot plate and to work with exclusion of air by a slight adaptation. A larger-scale apparatus described varies only in detail. The use of shaking apparatus is of great benefit in the precipitation of barium sulphate, calcium oxalate, and magnesium ammonium phosphate. The author also uses it in the determination of silicon and phosphorus in iron. C. IRWIN.

Analysis of gas mixtures by combustion and absorption. M. SHEPHERD (Bur. Stand. J. Res., 1931, 6, 121—167).—The defects in design of the various parts of gas analysis apparatus of the Orsat type are discussed, and the construction and manipulation of a greatly improved form are described. R. CUTHILL.

Apparatus for the exact analysis of gas mixtures in amounts down to 3—4 c.c. A. SCHMIDT.—See B., 1931, 186.

Polarimetry of solutions having low optical rotations. Use of the mercury-vapour lamp. H. N. NAUMANN (Biochem. Z., 1930, 229, 269—270).—The accuracy of the methods described by the author (cf. A., 1930, 1153) is doubled or trebled if a mercury-vapour lamp in conjunction with a nickel sulphate filter is used for illumination instead of an arc lamp. A potassium dichromate filter should not be used for micro-work. W. MCCARTNEY.

One-piece electrodialysis apparatus. L. REINER (J. Physical Chem., 1931, 35, 423—424).—The apparatus incorporates Jena glass filter plates as a support for collodion membranes. L. S. THEOBALD.

Use of zinc wire spiral as a Jones reductor. G. F. SMITH and J. RICH (J. Chem. Educ., 1930, 7, 2948—2952).—A spiral of amalgamated zinc wire is used for the reduction of iron; reduction is complete in 30 min. in presence of 6—10 vol.-% of sulphuric acid. CHEMICAL ABSTRACTS.

Holder for mercuric chloride paper in Gutzeit test. G. H. DAVIS (Analyst, 1931, 56, 30).—The paper is held over the hole (8 mm.) of a rubber bung by means of a tin screw cap arrangement cut from a "Cardboard Screw Cap Post Box" and provided with a hole to coincide with that in the bung. A. R. POWELL.

Apparatus for the detection of traces of fluoride by the etching method. R. E. ESSERY (Analyst, 1931, 56, 28—29).—A lead casting 2 in. high with a bottom diameter of 2 in. and a top diameter of 1½ in. is ground flat and polished on the upper surface after cutting out a cavity ½ in. diameter and 1 in. deep. The material to be tested is placed in the cavity with a few drops of sulphuric acid, a Bunsen flame is passed over the top to warm the metal, and a waxed cover-glass is placed over the cavity so that the wax melts round the side and hermetically closes the cavity without disturbing the design previously bared on the waxed surface. After incubating overnight at 37° the slide is melted off, the wax removed with ether, and the slide examined for etching by means of a powerful lens in reflected light.

A. R. Powell.

Apparatus for continuous leaching with suction. J. F. Fudge (Ind. Eng. Chem. [Anal.], 1931, **3**, 114). H. F. Gillbe.

Apparatus for the extraction of solutions lighter than the solvent. E. Mameli (Annali Chim. Appl., 1931, **21**, 38—41).—Two modified forms of the Soxhlet apparatus suitable for this purpose are described, the extraction being effected by either the liquid solvent or its vapour. The amounts of benzoic acid extracted from its dilute aqueous solution by three different solvents are greater than those extracted in other similar apparatus. T. H. Pope.

Distillation method for producing antimony–bismuth vacuum thermo-elements. H. C. Burger and P. H. van Cittert (Z. Physik, 1930, **66**, 210—217).—A vacuum distillation method for the production of small vacuum thermo-elements of antimony and bismuth is described; the sensitivity is 2·5 times that of the Moll–Burger element. The advantages and limitations of the device are discussed.

R. W. Lunt.

Preservation of silvered mirrors. H. C. Burger and P. H. van Cittert (Z. Physik, 1930, **66**, 218).—The reflective power of a silvered glass mirror may be preserved and discoloration by the atmosphere avoided by depositing an exceedingly thin film of silica over the silver surface. The technique developed by the authors for the production of thermocouples by distillation in a vacuum (cf. preceding abstract) has been developed to this end. R. W. Lunt.

Micro-absorption tube with mercury seals. R. T. K. Cornwell (Ind. Eng. Chem. [Anal.], 1931, **3**, 4—5).—A straight tube resembling the original Pregl micro-absorption tube is fitted at each end with a hollow ground glass stopper enclosing mercury seals which can be opened by rotating the tube through 180°. The tube may readily be cleaned and can be weighed when filled with any desired gas. H. F. Gillbe.

Mill for small samples. W. H. Cook, E. P. Griffing, and C. L. Alsberg (Ind. Eng. Chem. [Anal.], 1931, **3**, 102—103).—The mill described is suitable for grinding small quantities of biological materials. It consists essentially of a four-bladed rotating knife which cuts against an adjustable stationary blade; when the mill is operated at 5600 r.p.m. and with a clearance between the blades of 0·0005 in. a single charge of material, *e.g.*, several wheat leaves or five to eight wheat kernels, is reduced to pass an 80-mesh sieve within 3—4 min.

H. F. Gillbe.

Electrically heated m.-p. apparatus. C. E. Sando (Ind. Eng. Chem. [Anal.], 1931, **3**, 65).—Within the vertical portion of a pyrex glass Thiels–Dennis m.-p. tube is sealed a small side tube which extends 1—2 in. below the point of attachment of the side arm; the latter is heated by an asbestos-covered chromel heating element. A mixture of sulphuric acid and potassium hydrogen sulphate is employed as the heating liquid, and a calcium chloride tube is fitted to prevent the ingress of water.

H. F. Gillbe.

Absorption tube for combustion analysis. W. D. Turner (Ind. Eng. Chem. [Anal.], 1931, **3**, 63).—The stopper, into which the outlet and inlet tubes are sealed, is ground internally, and by rotation the tubes may be closed and the entry of air during disconnexion prevented. The tube is of simple and robust construction and is easy to clean.

H. F. Gillbe.

Geochemistry.

Absorption of radiation in the lower atmosphere. Determination of ozone. C. Fabry and H. Buisson (Compt. rend., 1931, **192**, 457—461).—On plotting the coefficient of absorption of ozone for light of wave-lengths 5780—2482 Å. against the optical density of 1 km. of air at the earth's surface for the same light (cf. A., 1930, 731) it appears that atmospheric absorption is explicable as due to a layer of ozone 0·0022 cm. (at *N.T.P.*) thick per km., together with some other cause of absorption, which is independent of wave-length for values of λ greater than 2600 Å., but increases rapidly for shorter wave-lengths. It is probably due to oxygen (cf. Granath, A., 1929, 1350).

C. A. Silberrad.

Chemical and chemico-physical data concerning the sulphur water of S. Giorgio in Angarano (Bassano del Grappa). G. Bragagnolo (Annali Chim. Appl., 1931, **21**, 12—26).—The composition and physico-chemical constants of the water and the composition of the dissolved gases are given.

T. H. Pope.

Relation between fixed residue and electrical conductivity of mineral waters. E. Bovalini and E. Vallesi (Annali Chim. Appl., 1931, **21**, 51—75).—For a number of dilute mixed salt solutions resembling in composition natural mineral waters, determinations have been made of the fixed residue (g. per litre) and of the specific electrical conductivity at 18°. The ratio between these two magnitudes indicates in some cases the type of the water and is not greatly changed by considerable change of the concentration alone. T. H. Pope.

Biochemical formation of soda in soda lakes. W. Gubin and W. Tzechomskaja (Zentr. Bakt. Par., 1930, II, **81**, 396—401).—Mud from Siberian soda lakes always contained iron sulphide produced as a result of the biochemical reduction of sulphates to hydrogen sulphide. The presence of sulphate-reducing organisms was demonstrated in nearly all cases. The bearing of these facts on the biological formation of soda lakes is discussed.

A. G. Pollard.

Absorption and refraction of brown Ceylon spinel. K. Schlossmacher (Z. Krist., 1931, **76**, 370—376).—Absorption and dispersion curves for four samples of brown Ceylon spinel, determined by means of a photo-electric cell (cf. A., 1930, 1267), show that the colour is predominantly due to tervalent iron; there are slight indications of bivalent iron and of chromiun (cf. following abstract).

C. A. Silberrad.

Colouring material of red, blue, and violet Ceylon spinel. K. Schlossmacher (Z. Krist., 1931, **76**, 377—385).—The colours of pure blue and brown Ceylon spinels are due, respectively, to bi- and tervalent iron: blue spinel 2·17—2·23% Fe (0·2% Fe^{III}), cobalt, manganese, and chromium definitely proved absent; brown spinel (cf. preceding abstract) 4·71% Fe, manganese and titanium absent, a trace of chromium in one sample; in another 1·04% Fe^{III} and 0·13% Fe^{II}. Brown crystals that luminesced in ultra-violet light contained 0·0014% Cr. Intermediate colours, *e.g.*, reddish-brown and violet, are due to mixtures.

C. A. Silberrad.

Genetic and crystallographic considerations of some recent barytes formations. (Frl.) Buschendorf (Z. Krist., 1931, **76**, 460—462).—Recently formed occurrences of barytes in fan-shaped aggregates and in tubular stalactitic and stalagmitic forms in drusy cavities in the Silberbach mine at Stolberg (E. Harz) are described. The deposition is considered to be due to diminution in solubility of the barium sulphate on escape of carbon dioxide from the water in which it was dissolved.

C. A. Silberrad.

Amethyst and smoky quartz colorations. J. Hoffmann (Z. anorg. Chem., 1931, **196**, 225—246).—The colours of amethyst and smoky quartz can be imitated by irradiating silicate- and quartz-glasses with radium rays. Amethyst quartz is free from manganese and the colour is due to iron, which is generally accompanied by titanium or zirconium. Constitutional changes in the quartz crystal cell are held to be the cause of the colour changes.

E. S. Hedges.

Caliche in Arizona. J. F. Breazeale and H. V. Smith (Arizona Agric. Exp. Sta. Bull., 1930, No. 131, 419—441).—The nature and formation of the lime hardpan ("caliche") are discussed.

A. G. Pollard.

New radioactive mineral in Japan. S. Iimori, T. Yoshimura, and S. Hata (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1930, **15**, 83—88).—A new radioactive mineral similar to allanite has been found occurring irregularly in pegmatite in the Bijozan Range. Analysis gives the formula $4R''O_2,3R'''O_3,6(SiO_2,P_2O_5),2H_2O$, where R''=Ca, Fe, and R'''=Ce, La, Y, Al, Fe, and Th. The name nagatelite is suggested. The mineral belongs to the epidote group; *H* 5·5, *d* 3·91. C. W. Gibby.

Relation between crystallisation and differentiation in basaltic magmas. E. Lehmann (Tsch. Min. Petr. Mitt., 1931, **41**, 8—57).—Chemical analyses of rocks from Nyasaland form the basis of a discussion on the derivation of various rock types (basanite, tephrite, trachyte, phonolite, etc.) from a basaltic magma. L. J. Spencer.

Wearing of minerals by transportation in water. F. W. Freise (Tsch. Min. Petr. Mitt., 1931, **41**, 1—7).—Experiments on the wearing hardness of minerals found in the gold, diamond, and monazite sands of Brazil are described. Cut cubes of the minerals were placed with water in a rotating drum and the loss of weight was determined.

L. J. Spencer.

Geochemical and genetic classification of granite-pegmatites. A. Fersman (Tsch. Min. Petr. Mitt., 1931, **41**, 64—83).—A repetition of earlier papers. The magmatic, pegmatoidal, and hydrothermal phases of pegmatites are further emphasised, and twenty types are distinguished according to the predominating minerals. Schematic tables suggest the temperature ranges of the different phases and the ranges of separation of the various minerals.

L. J. Spencer.

Transportation of constituents of [mineral] deposits by humic acids. F. W. Freise (Metall u. Erz, 1930, **27**, 442—445; Chem. Zentr., 1930, ii, 2951).—A study of the reappearance of alluvial gold in exploited layers after a period of years. In the absence of oxygen, humic acid in small concentration (0·25—0·3%) slowly dissolves gold; the solubility is unaffected by the presence of silver or palladium. Experiments with natural waters are described.

A. A. Eldridge.

Isomorphism in the hornblende group. W. Kunitz (Neues Jahrb. Min., 1930, **A**, **60**, Beil.-b., 171—250; Chem. Zentr., 1930, ii, 3008—3009).—The formulæ anthophyllite $H_2Mg_7Si_8O_{24}$, actinolite $H_2Ca_2Mg_5Si_8O_{24}$, glaucophanite $H_2Na_2Al_2Mg_3Si_8O_{24}$, green hornblende $H_2Ca_2Mg_5Si_8O_{24}$, syntagmatitic hornblende $H_2Ca_2Mg_4Al_2Si_6O_{22}$, and arfvedsonitic hornblende $H_2Na_2Mg_4Si_2Si_6O_{22}$ can be referred to complex silicic acids. A method for the determination of the density of small quantities of material depends on the measured dilution of a heavy liquid.

A. A. Eldridge.

Composition and genesis of natural ferrous sulphate. R. Scharizer (Z. Krist., 1930, **75**, 67—87; Chem. Zentr., 1930, ii, 3125—3126).—Römerite is formed from rhomboclase and ferrous sulphate in moist air in presence of sufficient sulphuric acid to form hydroferrisulphuric acid. Natural and artificial voltaite are apparently mixtures of a potassium ferrous salt of hydroferri-tetra- and -hepta-sulphuric acids.

A. A. Eldridge.

Soils of Madagascar. H. Erhart (Ernähr. Pflanze, 1931, **27**, 77—82).

Mineralisation of humus nitrogen in low moor soils. R. Reincke (Zentr. Bakt. Par., 1930, II, **81**, 210—221).—The production of nitrate and ammonia in low moor pastures at different seasons is recorded and the effect of growing plant roots on bacterial activity examined. A. G. Pollard.

Soil investigations at Echmiadzin. K. Mirimanian (Bull. univ. état. R.S.S. Arménie, 1930, No. 5, 45—81).—Four soils are described and analyses are recorded. Chemical Abstracts.

Soil in the Arazdajan steppe of Armenia. B. Galstian (Bull. univ. état. R.S.S. Arménie, 1930, No. 5, 5—39).—An account of soil varieties and evolution. Chemical Abstracts.

Hydrogen sulphide and the formation of petroleum deposits. A. F. von Stahl (Petroleum, 1931, 8, 145—146).—Petroleum deposits are invariably found in the immediate neighbourhood of sulphur springs. It is assumed that hydrogen sulphide is a product of disintegration of proteins in decaying salt-water sludge and remains absorbed in the sludge. It is considered highly probable that the pressure of overlying strata liquefies the hydrogen sulphide, which penetrates and reacts on the rock and intermingles with water. E. Doctor.

Geological aspects of the formation of coal. C. S. Fox.—See B., 1931, 184.

Geological history of coal. H. G. A. Hickling (Proc. S. Wales Inst. Eng., 1931, 46, 911—950).—A lecture. C. W. Gibby.

Organic Chemistry.

Chromic acid oxidation of organic compounds, especially nitro- and amino-compounds. F. Friedmann (Z. ges. Schiess- u. Sprengstoffw., 1929, 24, 208—210).—The use of 2*N*-potassium dichromate and 95—96% sulphuric acid is recommended for the oxidation of organic compounds. The amount of dichromate used should be 20% in excess of the theoretical value; when the substance is unknown a preliminary trial is advised. For the treatment of difficultly oxidisable compounds the amount of sulphuric acid may be increased. E. S. Hedges.

Electrochemical oxidation of paraffin. II. I. A. Atanasiu (Ber., 1931, 64, [*B*], 252—260).—The electrochemical oxidation of paraffin, m. p. 53°, 51°, 47°, 44°, and 38°, and of an oil, after thorough refinement with 98% sulphuric acid, has been examined in a lead cell which serves as anode and in which the material is kept stirred with sulphuric acid containing various catalysts. The lead cathode is immersed in sulphuric acid (*d* 1·2) contained in a porcelain cell. The paraffins are relatively easily oxidised in presence of a suitable catalyst such as potassium dichromate or, in particular, cerium sulphate. The action is essentially chemical, the catalyst being alternately reduced and electrochemically re-oxidised. The products of the oxidation are carbon dioxide, unsaponifiable matter, and, mainly, fatty acids. A paraffin from which the oxidised portions are periodically removed is much more easily oxidised than a fresh paraffin. Soft paraffins are easily oxidised, but give more unsaponifiable matter and difficultly separable resins than hard paraffins; most unsaponifiable matter is obtained from the oils. Since oxidation proceeds slowly, the highest yields are obtained with the smaller current densities. The absence of hydroxy-acids and the small loss in volatile products are advantages of the electrochemical process. The mixture of fatty acids varies with the nature of the paraffin, the acid value of the products lying between 150 and 200 and m. p. between 37° and 50°. The individual components of the mixtures are, in general, the same, but their relative proportions vary. H. Wren.

Production of liquid hydrocarbons from butylenes. A. Mailhe and Renaudie (Compt. rend., 1931, 192, 429—431; cf. this vol., 60).—Δ^α-Butene passed over silica gel at 650—670° gives methane, propylene, benzene, toluene, and *m*-xylene, and some tar. No naphthalene or anthracene was found. β-Methylpropene gave similar products under the same conditions. With Δ^β-butene at 700° the products were similar, but the proportion of aromatic hydrocarbons was increased, and naphthalene and anthracene were found in the tar. It is concluded from this and previous work that a higher temperature favours cyclisation of ethylenic hydrocarbons. A. A. Levi.

Catalytic condensation of amylenes. A. Mailhe and Renaudie (Compt. rend., 1931, 192, 561—563).—Catalytic polymerisation of γ-methyl-Δ^α-butene with a silica gel catalyst at 670°/1 atm. affords a gaseous product consisting of ethylenic hydrocarbons (mainly ethylene and propylene) 47%, methane 30%, and hydrogen 7%, and a liquid product containing γ-methyl-Δ^α-butene, benzene, toluene, and *m*-xylene. Similar polymerisation of Δ^β-pentene furnishes gaseous ethylenic hydrocarbons (mainly propylene and butylene) 52%, methane 34%, and hydrogen 5—6%, and the same liquid products as in the previous case. In both cases solid residues of low m. p. were obtained. J. W. Baker.

Conjugated compounds. XI. Addition of hydrogen bromide to βγ- and αδ-dimethylbutadiene. E. H. Farmer and F. C. B. Marshall (J.C.S., 1931, 129—137).—The mode of addition of hydrogen bromide to αδ- and βγ-dimethylbutadiene was investigated, and the conclusions of Bergman (A., 1922, i, 1106) and of Claisen (A., 1923, i, 1050) were shown to be incorrect. On hydrobromination of βγ-dimethylbutadiene at temperatures between −72° and −20° the sole product was the αδ-hydrobromide, m. p. −32°, b. p. 53—54°/20 mm., yielding on ozonolysis acetone and bromoacetone. The irregularity of b. p., interpreted by Claisen as due to the presence of αβ-hydrobromide, was shown to be caused by the presence of excess of hydrocarbon. αδ-Dimethylbutadiene on hydrobromination yielded a mixture of αβ- and αδ-hydrobromides, b. p. 37—47°/10 mm., which could not be separated. On ozonolysis acetaldehyde and propaldehyde were isolated, and on oxidation with potassium permanganate followed by potassium dichromate and sulphuric acid acetic and propionic acids were obtained, together with bromo-acids, which were identified by conversion into the nitriles and then into the malonic acids, methyl- and ethyl-malonic acid being obtained. The αβ : αδ ratio, determined by isolating the acetic and propionic acid formed, is about 9 : 1, on an isolation of the acids in 91% yield. G. DISCOMBE.

Action of magnesium on iodoform in ethereal solution. C. L. TSENG and E. J. H. CHU (Nat. Centr. Univ. Sci. Rep., **A**, 1930, **1**, 15—22).—In anhydrous ether acetylene and the compound $MgI_2,2H_2O,2Et_2O$ are formed. Only the trimagnesium compound is formed, and reacts immediately with iodoform. Chloroform and iodoform do not react similarly. CHEMICAL ABSTRACTS.

Preparation of nitromethane by Kolbe's synthesis. A. B. WANG and C. L. TSENG (Nat. Centr. Univ. Sci. Rep., **A**, 1930, **1**, 27—28).—Addition of a mol. proportion of boric acid to the sodium nitrite–chloroacetate mixture gives a 58% yield of nitromethane; loss of trichloroacetic acid by formation of sodium glycollate is thus avoided.

CHEMICAL ABSTRACTS.

Preparation of anhydrous alcohols. H. LUND and J. BJERRUM (Ber., 1931, **64**, [*B*], 210—213).—The method is based on the reactions $Mg+2EtOH \longrightarrow H_2+Mg(OEt)_2$ and $Mg(OEt)_2+2H_2O \longrightarrow Mg(OH)_2+2EtOH$. Its inception requires the use of absolute alcohol, but 96% alcohol can be used subsequently provided that an excess of ethoxide is always present. Magnesium turnings (5 g.) covered with absolute alcohol (50—75 c.c.) are heated under a reflux condenser with iodine (0·5 g.) until the halogen has disappeared. If a vigorous evolution of hydrogen has not then commenced, a further portion of iodine (0·5 g.) is added. The heating is continued until nearly all the magnesium has been converted into the ethoxide. Not more than 900 c.c. of absolute alcohol are added and ebullition is continued for half an hour, after which the product is distilled. Fractionation appears to be superfluous, but for the purest specimens only the first two thirds of the mixture should be distilled. Removal of possible volatile bases is effected by distillation over 2 : 4 : 6-tribromobenzoic acid; the procedure does not alter the electric conductivity of ethyl alcohol, but is essential for the production of electrolyte-free methyl alcohol. The following data are recorded: ethyl alcohol, d_4^{25} 0·78503; propyl alcohol, d_4^{0} 0·81925, d_4^{10} 0·81144, d_4^{15} 0·80738, d_4^{20} 0·80335, d_4^{25} 0·79934; methyl alcohol, d_4^{25} 0·78651. H. WREN.

Preparation of pentamethylethanol, and the ketol condensation of pinacolin. V. M. TOLSTOPJATOV (J. Russ. Phys. Chem. Soc., 1930, **62**, 1813—1828).—Interaction of magnesium methyl iodide with pinacolin gives a mixture of pentamethylethanol and ββγξξ-pentamethylheptan-γ-ol-ε-one, b. p. 106°/15 mm., d_0^{21} 0·8999, the latter being a condensation product of pinacolin. Condensation of pinacolin by magnesium *n*-butyl bromide gives this ketol. Dehydration by anhydrous oxalic acid gives the corresponding *ketone*, b. p. 95·5—96°/18·5 mm., d_0^{21} 0·8433 (*semicarbazone*, m. p. 117—118°; *oximes*, m. p. 116—117° and m. p. 73—92° respectively). E. B. UVAROV.

Catalytic decomposition of cetyl alcohol. C. SANDONNINI and S. BEZZI.—See this vol., 440.

αα-Dichloro- and αα-diethoxy-tertiary alcohols and the corresponding aldehyde alcohols. A. AVY (Bull. Soc. chim., 1931, [iv], **49**, 12—18).—Dichloro-tertiary alcohols, $OH{\cdot}CRR'{\cdot}CHCl_2$, are obtained by the action of Grignard reagents on ethyl dichloroacetate, but the yields are good only in the case of the lower members. The corresponding diethoxy-alcohols are similarly obtained from ethyl diethoxyacetate in good yield and on hydrolysis with hydrochloric acid afford an insoluble semiacetal from which in one case only the corresponding aldehyde alcohol was obtained. Attempts to obtain α-hydroxy*iso*butaldehyde from αα-dichloro-β-methylpropan-β-ol were unsuccessful, but in the case of αα-dichloro-β-ethylbutan-β-ol, *α-hydroxy-β-ethylbutaldehyde*, b. p. 55—57°/15 mm. [*semicarbazone*, m. p. 204—205°, from which is regenerated an aldehyde, b. p. 28°/13 mm. (*semicarbazone*, m. p. 210°; *oxime*, m. p. 62°)], is obtained by refluxing with an aqueous suspension of calcium carbonate.

The following are described: αα-dichloro-β-methylpropan-β-ol, m. p. 8°, b. p. 38°/5 mm., 52°/10 mm., d_4^{19} 1·2363, n_D^{19} 1·4598, *αα-dichloro-β-ethylbutan-β-ol*, b. p. 76°/14 mm., d_4^{21} 1·175 n_D^{21} 1·999 [together with dichloromethyl ethyl ketone, b. p. 139° (semicarbazone, m. p. 142°)]. αα-Dichloro-β-propylpentan-β-ol and αα-dichloro-β-butylhexan-β-ol could be obtained only in 15% yield. Magnesium phenyl bromide yields *diphenyldichloromethylcarbinol*, m. p. 95—96°, b. p. 200°/5 mm., together with traces of a *substance* containing C 80·47%, H 5·49%, but magnesium benzyl bromide yields dibenzyl and a viscous residue, decomp. about 220°. *αα-Diethoxy-β-methylpropan-β-ol* has b. p. 75°/19 mm., d_4^{24} 0·9277, n_D^{21} 1·41109; *αα-diethoxy-β-ethylbutan-β-ol*, b. p. 95°/18 mm., d_4^{21} 0·923, n_D^{21} 1·42555; *αα-diethoxy-β-propylpentan-β-ol*, b. p. 98°/5 mm., d_4^{22} 0·9073, n_D^{24} 1·4285; *αα-diethoxy-β-butylhexan-β-ol*, b. p. 101°/3 mm., d_4^{20} 0·9001, n_D^{20} 1·4315; *diphenyldiethoxymethylcarbinol*, m. p. 125°, b. p. 170°/4 mm. Hydrolysis of αα-diethoxy-β-methylpropan-β-ol with hydrochloric acid for 24 hrs. at the ordinary temperature affords an insoluble *compound*, $C_{10}H_{20}O_4$, b. p. 105°/12 mm. ββ-Diethoxy-β-ethylbutan-β-ol similarly affords a *compound*, $C_6H_{12}O_2$, b. p. 114—115°/6 mm.; with warm dilute hydrochloric acid a 65% yield of the semicarbazone of β-hydroxy-β-ethylbutaldehyde is obtained. αα-Diethoxy-β-propylpentan-β-ol with cold hydrochloric acid yields the *compound*, $C_{18}H_{36}O_4$, m. p. 87°, and αα-diethoxy-β-butylhexan-β-ol the compound, $C_{22}H_{42}O_4$, m. p. 90—91, from which *β-hydroxy-β-butylhexaldehyde*, b. p. 94—97°/6 mm., d^{22} 0·9207, n_D^{22} 1·4379, is obtained by distillation with dilute hydrochloric acid.

R. BRIGHTMAN.

Oxidations with quadrivalent lead salts. II. Oxidative fission of glycols. R. CRIEGEE (Ber., 1931, **64**, [*B*], 260—266; cf. A., 1930, 1278).—Glycols, or more generally substances containing at least two hydroxyl groups attached to two neighbouring carbon atoms are oxidised by lead tetra-acetate in accordance with the scheme $OH{\cdot}CR'R''{\cdot}CR'''R''''{\cdot}OH$

$+Pb(OAc)_4 \longrightarrow R'\cdot CO\cdot R''+R'''\cdot CO\cdot R''''+2AcOH+Pb(OAc)_2$. The following instances are cited: ethylene glycol to formaldehyde, pinacol to acetone, ethyl tartrate to ethyl glyoxylate, hydrobenzoin to benzaldehyde, *p*-αβ-dihydroxypropylanisole to anisaldehyde, *cis*- and *trans-cyclo*hexane-1 : 2-diol to adipdialdehyde. The reaction appears to be of general applicability and is specific. Among saturated alcohols and their derivatives only those are attacked which have at least two hydroxy-groups in vicinal positions. Monohydric alcohols and glycols with partly or completely masked groups are indifferent. Thus pentaerythritol is not attacked, although possessing four free hydroxyl groups. The change proceeds so readily that its quantitative nature is established by titration of glycols with a 0·1*N*-lead tetra-acetate solution in acetic acid. Δ^4-*cyclo*Pentene-1 : 2-diol and dihydroxyhydrindene reduce an excess of the reagent owing to further oxidation of the aldehyde produced. In general, reaction occurs most rapidly with glycols containing those substituents which cause greatest rate of addition at the double linking. The mechanism of the reaction does not consist in a preliminary dehydrogenation $>C(OH)\cdot C(OH)< \longrightarrow {}^-O\cdot\ddot{C}\cdot\ddot{C}\cdot O^-$, since it is not effected by dichloroquinizarinquinone, which, according to Dimroth (unpublished work), can replace lead tetra-acetate as a dehydrogenating agent. The following scheme is therefore adopted: $OH\cdot\ddot{C}\cdot\ddot{C}\cdot OH \longrightarrow 2OH\cdot\ddot{C}\cdot OAc \longrightarrow 2\ddot{C}{:}O$. The applicability of the method in the study of the sugars is illustrated by the production of formaldehyde from *iso*propylideneglucose, thus confirming the furanose structure, and in that of the glycerides by the observation that the β-acetylglycerol of Bergmann and Carter contains 40% of the α-isomeride. H. WREN.

Reaction of glycerol and calcium glycerophosphate. L. EKKERT (Pharm. Zentr., 1931, 72, 85—86).—Superposition of dilute aqueous glycerol on sulphuric acid containing a little codeine gives a blue or violet ring, and after mixing, a blue or violet solution. Calcium glycerophosphate gives, similarly, a blue ring with a white precipitate and a bright blue, turbid solution. H. E. F. NOTTON.

Aliphatic ethers. H. HENSTOCK (J.C.S., 1931, 371—372).—The lower aliphatic ethers, unlike many aromatic and tertiary aliphatic ethers, are not attacked by sodium, potassium, or an alloy of the two, even under pressure at 200°. n-*Propyl* iso*butyl ether*, b. p. 106°/720 mm., d^{15} 0·7549, $n_{5461}^{24\cdot9}$ 1·3852, and iso*propyl* n-*butyl ether*, b. p. 108°/738 mm., d^{15} 0·7594, $n_{5461}^{24\cdot9}$ 1·3889, are described. J. D. A. JOHNSON.

Reaction of complex esters containing a trichloromethoxyl group. IV. Action of aluminium chloride on alkyl trichloromethyl carbonates. N. N. MELNIKOV (J. Russ. Phys. Chem. Soc., 1930, 62, 2019—2022).—The action of aluminium chloride on methyl, ethyl, and propyl trichloromethyl carbonates gives carbon dioxide, carbonyl chloride, and the corresponding alkyl chloride. E. B. UVAROV.

ψ-Halogens. XII. Formulation. Trichloromethyl perchlorate. L. BIRCKENBACH and J. GOUBEAU (Ber., 1931, 64, [*B*], 218—227; cf. A., 1930, 1564).—ψ-Halogens are defined as groups which fulfil the condition, Σ outer electrons +Σ valency electrons $=8n[+2m]-1$, where *n* is the number of atoms surrounded by octets and *m* the number of hydrogen atoms. An exact analogy of such groups of atoms with the halogens is not to be expected. Thus the isolation of the permanganate residue by the action of halogens on silver permanganate fails, since the group as such is too reactive and its proper decomposition ($MnO_4=MnO_2+O_2$) precedes the reaction of the total group. It has not been found possible to secure a solvent stable to the ClO_4 group for a study of the interaction of halogens and silver perchlorate. Pure carbon tetrachloride does not appear to react with completely anhydrous silver perchlorate, but in presence of a trace of hydrogen chloride a change proceeds slowly, probably in accordance with the scheme $AgClO_4+HCl \longrightarrow AgCl+HClO_4$ and $HClO_4+CCl_4 \rightleftharpoons CCl_3\cdot ClO_4+HCl$. The main product is *trichloromethyl perchlorate* with about 10% each of chlorine and carbonyl chloride. The last-named compound probably results from the secondary reaction $HClO_4+CCl_3\cdot ClO_4 \longrightarrow Cl_2O_7+COCl_2+HCl$, since the isolation of chlorine heptoxide has been effected in individual cases. Trichloromethyl perchlorate is a colourless mobile liquid, f. p. about −55°, which has not been obtained completely homogeneous. It may be preserved unchanged at a low temperature in the dark, but gradually decomposes at the ordinary temperature in the light; the change becomes vigorous at 40—50° and explosive at higher temperatures with production of chlorine and its oxides. It interacts very briskly with alcohol, benzene, and fats. Its solutions in ethylene bromide and phosphoryl chloride are unstable. It is immediately hydrolysed by water to perchloric acid and (?) trichloromethyl alcohol. H. WREN.

Esters of sulphurous acid. I. N. VOSS and E. BLANKE. **II. Preparation of acetals and glucosides.** W. VOSS (Annalen, 1931, 485, 258—283, 283—298).—I. Symmetrical alkyl sulphites are obtained in good yield by gradual addition of thionyl chloride (1 mol.) to the dry alcohol (2·2 mols.) at the ordinary temperature in a rapid stream of carbon dioxide, and then heating until hydrogen chloride ceases to be evolved. Alkyl chlorosulphinates are formed intermediately, and may readily be isolated in good yield by addition of the alcohol (1 mol.) to thionyl chloride (1 mol.) cooled in ice and salt. The lower chlorosulphinates are immediately hydrolysed by water, and decompose, slowly on keeping, and rapidly when heated, into the alkyl halide and sulphur dioxide; the poor yields of alkyl sulphite obtained by Arbusoff (A., 1909, ii, 573) are ascribed to this ready thermal decomposition. Methyl ethyl sulphite is obtained by interaction of methyl alcohol with ethyl chlorosulphinate in presence of a suitable base, *e.g.*, pyridine. If the base is omitted a mixture of methyl, ethyl, and methyl ethyl sulphites results. The reversibility of the reactions $Et_2SO_3+2MeOH \rightleftharpoons MeEtSO_3+MeOH+EtOH \rightleftharpoons Me_2SO_3+2EtOH$ in presence of hydrogen chloride is established experimentally. Poor yields of alkyl sulphite are obtained by interaction of thionyl chloride and an alcoholic solution of sodium alkoxide, on account of decomposition, $SO(OR)_2 + NaOR = R_2O + NaO{\cdot}SO{\cdot}OR$. Better results are obtained with the alcohol-free alkoxide in an indifferent medium; thus phenyl sulphite, previously isolated in an impure condition by Richter (A., 1917, i, 24), is obtained in 40% yield by interaction of dry sodium phenoxide and thionyl chloride in dry ether. The following are described: *methyl*, b. p. 35°/60 mm., d_4^{18} 1·4186; *ethyl*, b. p. 32°/16 mm., d_4^{17} 1·2826, and iso*propyl*, b. p. 34°/24·5 mm., d_4^{18} 1·2005, *chlorosulphinates*; *methyl ethyl*, b. p. 53°/20 mm., 141·5°/769 mm., d_4^{18} 1·1364, $n_{H\alpha}^{10·8}$ 1·41417; *n*- and *iso*-propyl; n-*butyl*, b. p. 114—115°/15 mm., d_4^{22} 0·9944, $n_{H\alpha}^{10·6}$ 1·43051; iso*amyl*, b. p. 127—128°/15 mm., $d_4^{16·2}$ 0·97293, $n_{H\alpha}^{12·3}$ 1·43547; cyclo*hexyl*, b. p. 182°/19 mm., $d_4^{17·8}$ 1·0974, $n_{H\alpha}^{13·7}$ 1·48396, and phenyl, b. p. 143°/0·7 mm., 152°/1·8 mm., $d_4^{20·2}$ 1·2404, $n_{H\alpha}^{13·4}$ 1·56899, sulphites. Methyl methanesulphonate is best prepared from the silver salt and methyl iodide at 100°; silver sulphite gives only a small yield. *Sodium methyl sulphite* is obtained from methyl sulphite and the calculated quantity of 5% sodium methoxide, a little methanesulphonate being also formed. It is immediately hydrolysed by acid or alkali in aqueous solution.

Propyl and the lower alkyl sulphites may be distilled unchanged at atmospheric pressure, but continued heating of the former gives traces of propyl alcohol. They are not hydrolysed by pure water. Methyl methanesulphonate is hydrolysed by water according to a unimolecular reaction, $k=2·98\times10^{-4}$, which therefore is not catalysed by hydrogen ions; in alkaline solution hydrolysis is accelerated. In the case of methyl sulphite also alkaline hydrolysis is more rapid than acid hydrolysis; both reactions, although actually the result of two consecutive reactions, have unimolecular velocity coefficients on account of the immediate hydrolysis of the sodium methyl or methyl hydrogen sulphite formed intermediately.

Alkyl sulphites may be used as alkylating agents in other than aqueous alkaline media. Phenyl ethers are obtained in yields of 55—90% by heating the sodium phenoxide (1 mol.) with the alkyl sulphite (1·1 mols. in the case of monohydric and 3 mols. in the case of dihydric phenols; in the latter case the dialkyl ether is readily produced) in toluene or other inert solvent. Lower yields are obtained from the phenol and alkyl sulphite in presence of an anhydrous mineral acid as catalyst. Aniline is readily alkylated, and a convenient method is afforded for preparation of the higher alkylanilines. Thus from 1 mol. of aniline and 3 mols. of *iso*amyl sulphite mono- (p-*toluenesulphonyl* derivative, m. p. 76—77°) and di-*iso*amylanilines were obtained in yields of 74% and 15%, respectively. The *benzenesulphonyl* derivative of ethylaniline has b. p. 188·5°/1·5 mm. Carboxylic acids are esterified by warming with an alkyl sulphite (1·1 mols. for each carboxyl group) in presence of a little mineral acid, but the method is not applicable to acids that are not esterified by the alcohol in presence of a catalyst.

Interaction of methyl sulphite (2 mols.) with dimethylaniline (1 mol.) at 135 140° gives *phenyltrimethylammonium methanesulphonate*, m. p. 188—189°, in 99% yield (75% with 1·1 mols. of sulphite), identified by synthesis from dimethylaniline and methyl methanesulphonate. Equimolecular quantities of the reagents on long keeping at the ordinary temperature, however, give (probably) *phenyltrimethylammonium methosulphite*, m. p. 120—121° to a turbid liquid (sinters at 90°); this is recovered unchanged after heating at 135°, and evolves sulphur dioxide when treated with acids. N-*Methylpyridinium methanesulphonate*, m. p. 117—118°, and *methosulphite*, m. p. 104—107°, are similarly prepared.

II. Acetals are produced by interaction of the carbonyl compound (1 mol.) with the alcohol (2—3 mols.) and an alkyl sulphite (1·1 mols.) in presence of an acid catalyst. In common with orthoformates and orthosilicates, the sulphites are considered to act merely as dehydrating agents, thereby disturbing the equilibrium $CORR'+2R''{\cdot}OH \rightleftharpoons C(OR'')_2RR'+H_2O$. This view is based on (1) the need of a minimum amount of alcohol, (2) the relative order of ease of acetal formation, which is also the order of ease of hydrolysis, (3) the velocity coefficients for the acid hydrolysis of sulphites and orthoformates, (4) formation of the acetal corresponding with the alcohol used and not with the sulphite (if derived from a different alcohol), and (5) the fact that acetals which are more readily hydrolysed by acid than is benzophenone dimethylacetal (*e.g.*, acetone diethylacetal) may be used in place of sulphites etc. in preparation of the latter, but such as are more slowly hydrolysed (*e.g.*, benzaldehyde dimethylacetal) are inactive. Methyl carbonate is also inactive. The following are described: n-*butaldehyde dimethyl-* and *diethyl-acetals* and *benzaldehyde* n-*butylacetal*, b. p. 149—150°, d_4^{14} 0·9289, n_D^{19} 1·4790.

Methyl- and ethyl-glucosides are similarly prepared from sugars, but the method is not applicable to the higher members on account of solubility difficulties. The product is a mixture of the α- and β-forms, of which the former preponderates. On account of the use of an acid catalyst, the method is not available for the alkylbiosides, but for the same reason it offers a convenient route to α-methylglucoside from starch.

H. A. PIGGOTT.

Formation of sulphonium chlorides and unsaturated substances by the action of water and aqueous-alcoholic potassium hydroxide on ββ′-dichlorodiethyl sulphide. J. S. H. DAVIES and A. E. OXFORD (J.C.S., 1931, 224—236).—ββ′-Dihydroxydiethyl sulphide (I), b. p. 130°/2 mm., d_4^{20} 1·1821 [*diphenylcarbamate*, m. p. 128·5—129·5°; p-*toluenesulphilimine* ($+H_2O$), m. p. 86—87°], reacts with 1, 2, or 3 mols. of aqueous ethylene chlorohydrin to give *tri-β-hydroxyethylsulphonium chloride*, m. p. 125—126°, and an oil, both being soluble in water, their solutions containing ionisable chlorine. With ββ′-dichlorodiethyl sulphide (II) I yields *sulphidobis-β-hydroxydiethyl sulphide* 1 : 3-*di-β-hydroxyethochloride*, $S[C_2H_4S(C_2H_4{\cdot}OH)_2\}Cl]_2$, m. p. 101·5—103° (*mercurichloride*, an oil; *chloroplatinate*, m. p. 133—134°), which reverts to II with hydrogen chloride at 100°. No additive compounds of II with ethyl sulphide, sulphidobis-β-hydroxydiethyl sulphide, ethylenebis-β-hydroxyethyl sulphide, 1 : 4-dithian, or

1 : 4-thioxan are obtained when mixtures of the components are heated at 80° for 6 hrs. Sulphidobis-β-hydroxydiethyl sulphide reacts with ethylene chlorohydrin at 100° to give substances presumed to be *sulphidobis-*β*-hydroxydiethyl sulphide* 1 : 2-*di*-β-*hydroxyethochloride*, m. p. 120—121·5°, 1 : 4-*dithian* 1-β-*hydroxyethochloride* (III), m. p. 175° (*mercurichloride*, m. p. 95—96°), the latter also being formed rationally from 1 : 4-dithian and ethylene chlorohydrin and from ethylenebis-β-hydroxyethyl sulphide and ethylene chlorohydrin. Hydrogen chloride and I at 100—106° give II (56%) and an undistillable residue which probably mainly consists of *oxidobis-*β*-chlorodiethyl sulphide*, $(C_2H_4Cl\cdot S\cdot C_2H_4)_2O$, since it gives a *diphenoxy*-derivative, m. p. 55—57°. Hydrolysis of II with the minimum quantity of boiling water during 6 hrs. leads to the formation of III and traces of thiodiglycol and dithian. Hydrolysis with 4 volumes of water, followed by treatment of the crude syrup with a little concentrated hydrochloric acid, leads to II and a little ethylenebis-β-chloroethyl sulphide. Treatment of the syrup with excess of concentrated hydrochloric acid leads only to II. Boiling dilute hydrochloric acid and I give a mixture of sulphonium chlorides from which III can be isolated. Hydrolysis of II with 4 mols. of 20% aqueous-alcoholic potassium hydroxide gives a mixture of divinyl sulphide (*sulphilimine*, m. p. 91—93°), β-*ethoxyethyl vinyl sulphide*, b. p. 65°/8 mm., d_4^{20} 0·9532 (*mercurichloride*, m. p. 152—153°), ββ′-diethoxydiethyl sulphide, and β-ethoxy-β′-hydroxydiethyl sulphide, but with 1 mol. of aqueous-alcoholic alkali, β-*chloroethyl vinyl sulphide* (IV), b. p. 71—72°/50 mm., 151·5—152·5/764 mm. (*sulphilimine*, m. p. 101·5—103°; ill-defined *mercurichloride*), is obtained in good yield. Hydrogen chloride converts IV into αβ′-*dichlorodiethyl sulphide* (not pure), b. p. 68—69°/9 mm. The formation of β-chloro-β′-hydroxydiethyl sulphide on hydrolysis of II (Bales and Nickelson, J.C.S., 1923, **123**, 2486) is not confirmed, the substance isolated by these authors being most probably IV. A mechanism is suggested whereby the formation of the sulphonium chlorides by hydrolysis of II may be explained.

J. D. A. JOHNSON.

Behaviour of certain thiophanes in heptane and naphtha solutions. R. W. BOST and M. W. CONN (Ind. Eng. Chem., 1931, **23**, 93—95).—The action of various reagents on tetramethylene and pentamethylene sulphides, ethyl sulphide, and thiophen in pure *n*-heptane and in three naphtha solutions has been studied. Mercuric chloride, potassium permanganate, hydrogen peroxide, and methyl iodide react with the thiophanes to form definite products which are easily purified and identified. Bromine and mercuric iodide form unstable products. Nitric acid gives the sulphone when *n*-heptane solutions of the sulphides are used, but no definite product when the naphthas are employed as solvents. In general, the thiophanes resemble the alkyl sulphides more than thiophen. The following *compounds* appear new: $Et_2S,2HgCl_2$, m. p. 119·5°; Et_2S,HgI_2, m. p. about 52°; Et_2SO_2, m. p. 70°; Et_2SO, m. p. 4—6°; $(CH_2)_4S,HgCl_2$, m. p. 124·5°; $(CH_2)_4S,xHgI_2$, m. p. about 78°; $(CH_2)_4SO_2$, m. p. 8—10°; $(CH_2)_4S,MeI$, m. p. 185—190°; $(CH_2)_4SBr_2$, m. p. 80°; $(CH_2)_5S,HgCl_2$, m. p. 137·5—138·5°; $(CH_2)_5S,xHgI_2$, m. p. about 79·5°; $(CH_2)_5SO_2$, m. p. 99°; $(CH_2)_5S,MeI$, m. p. 192·5°; $(CH_2)_5SBr_2$, m. p. 69·5°.

H. S. GARLICK.

Methanetetrasulphonic acid. F. B. KIPPING (J.C.S. 1931, 222—223).—Attempts to prepare potassium methanetetrasulphonate by the interaction of potassium sulphite and potassium di-iodomethanedisulphonate or potassium diazomethanedisulphonate (Pechmann, A., 1896, i, 14) yielded, respectively, potassium methionate and potassium methanetrisulphonate. The sulphonation of acetamide with fuming sulphuric acid containing less than 10% of sulphur trioxide yielded only potassium methionate, more concentrated acid giving potassium methanetrisulphonate. The results of Fantl and Fisch (A., 1930, 320) and of Backer and Claassens (*ibid.*, 1556) on the non-existence of hydroxymethanetrisulphonic acid are confirmed.

G. DISCOMBE.

Electrolysis of salts of *n*-butyric acid. F. FICHTER and A. BÜRGIN (Helv. Chim. Acta, 1931, **14**, 90—101).—*iso*Propyl alcohol, but not *n*-propyl alcohol, appears amongst the products of the electrolysis of potassium butyrate solutions under various conditions, and its formation is ascribed to the hydrolysis of *iso*propyl butyrate formed by the action of the primary electrolytic product, propylene, on butyric acid. By heating a solution of propylene in butyric acid for 50 hrs. at 130—140° in sealed tubes followed by hydrolysis a 50% yield of *iso*propyl alcohol was obtained. The electrolytic formation of the alcohol, even when the electrolyte is alkaline, is ascribed to the presence of free butyric acid at the anode.

The thermal decomposition of dibutyryl peroxide proceeds mainly as follows: $(Pr\cdot CO\cdot O)_2 = C_6H_{14} + 2CO_2$, a 62·6% yield of *n*-hexane being obtained. Exposure of the peroxide to ultra-violet light also causes decomposition in this manner, but the yield of hexane is smaller. The explosive decomposition of perbutyric acid takes place as follows: $C_4H_8O_3 = C_3H_6 + CO_2 + H_2O$. Propylene and carbon dioxide were also found among the products of decomposition of the peracid by ultra-violet light. It is considered, therefore, that in the electrolysis of *n*-butyrates the dibutyryl peroxide is hydrolysed at the anode to butyric and perbutyric acids; the latter is then decomposed into carbon dioxide and propylene, which reacts as shown above with butyric acid. Measurements have been made of the velocity of hydrolysis of dibutyryl peroxide.

O. J. WALKER.

Acetoacetic ester condensation. II. Reaction of aliphatic esters with sodium. J. M. SNELL and S. M. MCELVAIN (J. Amer. Chem. Soc., 1931, **53**, 750—760).—The reaction between sodium (2 atoms) and 1 mol. of ethyl acetate, propionate, butyrate, *iso*butyrate, and trimethylacetate has been studied in ether and benzene at the b. p. The resulting sodium salts are decomposed with 35% sulphuric acid and the products fractionated. The appropriate acylalkylcarbinols are obtained usually in 50—75% yield, together with small amounts of the corresponding diketones, higher-boiling products, and acids; the yield of diketone from ethyl trimethylacetate is

much higher than from the other esters. When the ester is used as solvent, the acetoacetic ester condensation takes place with ethyl acetate and propionate; no diketone or acylalkylcarbinol results in these cases. The yields of carbinol from ethyl butyrate, *iso*butyrate, and trimethylacetate are 7, 56, and 98%, respectively, on the sodium used; diketones, acids, and high-boiling products are also formed. There is no appreciable difference in the rates of reaction of the last three esters, and there is no necessity for special mechanisms to account for the slowness of reaction of an ester which cannot enolise. The suggestion that reaction proceeds, when possible, through the enol form (Scheibler and Emden, A., 1924, i, 42) is unnecessary. The diketone is probably an intermediate in the formation of the carbinol (cf. Egorova, A., 1929, 49). The following changes probably occur in the above reactions: $2Na + 2R\cdot CO_2Et \longrightarrow [\dot{C}R(ONa)(OEt)]_2 \xrightarrow{2Na} (\ddot{C}R\cdot ONa)_2 + 2NaOEt$.
H. Burton.

Degradation of the salts of organic acids by *Aspergillus fumaricus*. W. Thies (Ber., 1931, 64, [*B*], 214—218).—The action of the mould on the calcium salts of gluconic, saccharic, citric, succinic, tartaric, malic, fumaric, and lactic acids, on sodium gluconate, citrate, fumarate, and lactate, potassium succinate and malate, and ammonium tartrate has been investigated. Whereas the calcium salts yield calcium carbonate, the degradation of the alkali salts terminates with the production of oxalate. A modifying influence of acidity could not be established and acidity or neutrality of the culture medium is without effect. No support is afforded to the hypothesis that the degradation of sugar to citric or fumaric acid occurs through other acids as intermediate products.
H. Wren.

Supposed asymmetry of *meso*-tartaric acid. K. Scheringa (Pharm. Weekblad, 1931, 68, 143—145).—The configuration suggested by Böeseken (Chem. Weekblad, 1922, 207) should be associated with optical activity; this is probably compensated externally, since for every asymmetric molecule of a given orientation molecules possessing the image configuration must be present in a solution.
S. I. Levy.

Compound uronic acids. Structure of aldobionic acid from gum arabic. S. W. Challinor, W. N. Haworth, and E. L. Hirst (J.C.S., 1931, 258—265).—The aldobionic acid from gum arabic has the biose linking through the side-chain of galactopyranose. Complete methylation leads to *methyl heptamethylaldobionate* (*methyl* ester of *hexamethyl*-6-*glycuronosido*-β-*methylgalactoside*) (I), m. p. 86°, $[\alpha]_D^{20}$ −21° in water, $[\alpha]^{20}$ −43° in chloroform, mixed with the α-form (mixture, b. p. about 185°/0·02 mm.); the mixture when hydrolysed by 7% hydrochloric acid gives 2 : 3 : 4-*trimethylgalactose* (II) (crude, n_D^{16} 1·4727, $[\alpha]_D^{20}$ +83° in water) and 2 : 3 : 4-*trimethylglycuronic acid* (III) [crude, n_D^{16} 1·4709, $[\alpha]_D^{15}$ +58° (equilibrium value in water)]. The latter on methylation gives 2 : 3 : 4-*trimethyl* β-*methylglycuronide*, m. p. 133°, $[\alpha]_D^{23}$ −38° in water, $[\alpha]_D^{21}$ −63° in chloroform, identical with the completely methylated product of the lactone of the glycuronic acid obtainable from gum arabic. Methylation of II gives 2 : 3 : 4 : 6-tetramethyl-β-methylgalactoside, whilst oxidation with bromine water leads to 2 : 3 : 4-trimethyl δ-galactonolactone (IV), characterised by its *phenylhydrazide*, m. p. 165—167°. Oxidation of IV with nitric acid (*d* 1·42) gives, after esterification of the product, the *dimethyl* ester of 2 : 3 : 4-*trimethylmucic acid*, m. p. 98°, $[\alpha]_D^{20}$ +35° in water, which is proof that II possesses a free $\cdot CH_2\cdot OH$ group, and since I is non-reducing, establishes the fact that the union with the glycuronic acid residue is through the reducing group of the latter.
J. D. A. Johnson.

Highly-polymerised compounds. XLIX. Action of bases on formaldehyde solutions. H. Staudinger, R. Signer, and O. Schweitzer (Ber., 1931, 64, [*B*], 398—405; cf. this vol., 202).—The action of 0·05 equivalent of alkali, alkaline-earth, or thallous hydroxide on 30% formaldehyde solution yields precipitates which, after washing and electrodialysis, contain metal in amount indicating polymerisation to an extent far greater than that observed with the polyoxymethylene dimethyl ethers. Treatment of 40% formaldehyde with lithium, sodium, potassium, and rubidium hydroxide and with calcium, barium, and magnesium oxide gives precipitates increasing in quantity with increasing strength of the base, showing that polymerisation and precipitation depend on the hydroxyl-ion concentration. Marked difference in the solubility of the salts is not observed. The formaldehyde content of the precipitates lies between 98 and 99·5%, the metal oxide content between 0·1 and 0·2%. The precipitates therefore contain 0·5—1·5% of water. They are not polymerically uniform and it is not possible to determine the mol. wt. from the metal content even on the supposition that the latter is united chemically. Since the precipitates are decomposed by hydrochloric acid or sodium hydroxide at the same rates as polyoxymethylene, there is no evidence of the chemical union of the metals. With 40% formaldehyde and 0·5—1 mol. of solid potassium hydroxide, a vigorous Cannizzaro reaction occurs; with smaller quantities, polymerisation predominates, the best yields of precipitate being obtained with 1 mol. of hydroxide to 20—100 mols. of formaldehyde. Even with much smaller amounts polymerisation is observed. The precipitates have the same properties and composition whatever the amount of hydroxide used, so that a polymeric homologous series is not thus obtained.

The constitution of β-polyoxymethylenes is discussed in detail. The conclusion is reached that the ester-like union of sulphuric acid in these compounds is not firmly established.
H. Wren.

Absorption and reactivity of the ketone group. (Mme.) Ramart-Lucas and (Mme.) Bruzau (Compt. rend., 1931, 192, 427—429).—Absorption spectra measurements of some polyalkyl ketones indicate "mutual influence" between the ketone group and α-alkyl substituents. The decreased reactivity of the ketone group when the α-positions are fully alkylated is attributed to a similar cause.
A. A. Levi.

Enolisation of ketones. V. Grignard and H. Blanchon (Bull. Soc. chim., 1931, [iv], 49, 23—42).—

Determinations of the enolisation of ketones by a modification of Zerevitinov's method, in which the ketone is treated in ethereal solution with a large excess of the magnesium alkyl halide and the hydrocarbon liberated on heating to 40° to initiate this reaction, measured in a Bunte burette, indicate that all ketones which are structurally capable of enolisation can be enolised even if under ordinary conditions there is no evidence of a keto–enol equilibrium. The enolic form is obtained when the keto–enol equilibrium is displaced in this direction by certain reagents, particularly by Grignard reagents, which produce varying degrees of enolisation and fix the enolic form as a mixed magnesium organo-enolate. Negative groups and ethylenic linkings, especially when conjugated with the enolic linking, promote enolisation, but the latter is not dependent on the presence of anomaly, although no relation has been established between the constitution of the ketone and its tendency to enolise or the stability of the enolic form. The figures in parentheses give the percentage of enolisation with magnesium *tert.*-butyl chloride for the following ketones: pulegone (100) (cf. Grignard and Savard, A., 1926, 92, 408), dibutyl ketone (20), carvone (20·5), mesityl oxide (60), dibenzyl ketone (24), acetone (30), acetophenone (31), *cyclo*pentanone (32·5), thujone (41), 4-methyl*cyclo*hexanone (46), butyrone (49), *cyclo*hexanone (50·5), menthone (51). The enolisation is generally increased about 10% by rise of temperature, but with thujone and menthone the enolisation may thus attain or exceed 60%. The effect of the Grignard reagent depends both on the nature of the halogen and on the organic radical. With dibutyl ketone at 13—14°, primary magnesium alkyl halides produce 6—8·5% enolisation, secondary, 13·5—16%, and tertiary, *e.g.*, magnesium *tert.*-butyl chloride, 19·7—20·4%. The enolising action of the chlorides is inferior to that of bromides and iodides, the latter being usually a little inferior to the bromides. Determinations of the keto–enolic equilibrium of the following ketones by Job and Reich's method (A., 1924, i, 24) has given the percentage of enol indicated: *cyclo*hexanone 8·2, 4-methyl*cyclo*hexanone 6·3, mesityl oxide 6·3. Acetone, butyrone, dibutyl ketone, dibenzyl ketone, acetophenone, *cyclo*pentanone, menthone, carvone, and thujone initially contained no enol.

The enolic forms have been isolated by conversion into the magnesium alkyl enolenate by treatment with magnesium *iso*propyl bromide in ether, initiating the reaction by warming at 40° for ½ hr., conversion of the enolenate into the acetyl derivative by treatment with acetyl chloride in ether at —5°, and hydrolysis with ice-water, using sodium hydrogen carbonate to neutralise the acetic acid liberated.

After distillation of the ether, *cyclo*hexanone yields a small fraction, 30% of enol, b. p. 60—62°/12 mm., a fraction, b. p. 75°/12 mm., n_D^{13} 1·4867, *cyclo*hexanonenyl acetate, and a fraction, b. p. 132°/12 mm., *iso*propyl*cyclo*hexyl acetate, hydrolysed to *iso*propyl*cyclo*hexanol, b. p. 125°/12 mm. Hydrolysis of the *cyclo*hexanonenyl acetate with 10% oxalic acid yields on ether extraction a 70—75% enol, n_D^{12} 1·4601 falling to 1·45451 in 10 hrs. Benzoquinone and phthalic anhydride do not stabilise the enol.

Similarly, thujone, b. p. 83—85°/12 mm., d_4^{15} 0·905, n_D^{15} 1·4471, yields a fraction, 89·5% of thujonenol, b. p. 84—86°/12 mm., d_4^{15} 0·9010, n_D^{15} 1·45401, falling to 69·9% enol, n_D^{15} 1·45261, in 1 hr. and to 4·1%, n_D^{15} 1·44731, in 15 hrs., stabilised by phthalic anhydride and oxalic acid, and a larger fraction, iso*propylthujyl acetate*, b. p. 124°/12 mm., hydrolysed to iso*propylthujol*, b. p. 115°/12 mm.

Carvone, b. p. 222°, d_4^{15} 0·965, n_D^{15} 1·503, with magnesium ethyl bromide gives a fraction, 96·5% of carvonenol, b. p. 114—115°/12 mm., d_4^{15} 0·957, n_D^{15} 1·5151, falling to 82·3% enol, n_D^{15} 1·51, in 1 hr. and to 1·5%, n_D^{15} 1·5033, in 25 hrs., the transformation being accelerated by sunlight alkali, ammonia, bromine, and mineral acids, and retarded only 5 hrs. by 1% of phthalic anhydride, together with a larger fraction, *ethylcarveol acetate*, b. p. 142°/12 mm., hydrolysed to ethylcarveol, b. p. 135°/12 mm. Mesityl oxide with magnesium *iso*propyl bromide similarly yields a fraction, 70% of enol, b. p. 134°, d_4^{12} 0·861, n_D^{12} 1·45001, falling to 50·1% enol in 1 hr., and to 6·4% in 5 hrs., phthalic anhydride and oxalic acid having no stabilising effect, a fraction, b. p. 140—145°, consisting of the enol acetate, and a fraction, b. p. 172°, containing the acetate of βγε-*trimethyl*-Δ^{δ}-*hexen*-γ-*ol*, b. p. 163°.

An alternative method of preparing the enols is from the chlorohydrins through the acetates. Thus pulegone, d_4^{12} 0·93, n_D^{12} 1·47392, is converted by phosphorus pentachloride into the enolic chlorohydrin, b. p. 88—89°/12 mm., d_4^{12} 0·995, n_D^{13} 1·49889 (cf. Klages, A., 1900, i, 44), which with alcoholic potassium acetate and decomposition with water affords the pure enol, b. p. 79—81°/3 mm., d_4^{12} 0·9130, n_D^{12} 1·48115, in 50% yield on the pulegone. Similarly, acetophenone in light petroleum with phosphorus pentachloride yields the enolic chlorohydrin, b. p. 195°/740 mm., converted in boiling alcoholic potassium acetate in 12 hrs. and treatment with ice-water into a mixture of the enol and its acetate, yielding when boiled with aqueous oxalic acid an oil, b. p. 205°, 75% hydroxyl. Acetophenonenol is completely tautomerised in 10 hrs. in the dark and in 5 hrs. in direct daylight.

The substances previously described as stabilisers, quinone, phthalic anhydride, and oxalic acid, do not appreciably retard the tautomerisation of this enol, and sunlight, sodium carbonate, ammonia, bromine, alkali hydroxides, strong acids, and sometimes even sodium hydrogen carbonate have a pronounced and even instantaneous accelerating action.

R. BRIGHTMAN.

***cis*- and *trans*-Forms of *iso*butylideneacetone and the isomeric βγ-unsaturated ketone.** R. HEILMANN (Bull. Soc. chim., 1931, [iv], 49, 75—80).—The results obtained by Eccott and Linstead (A., 1930, 893) indicating that the semicarbazones, m. p. 126° and 160°, correspond with *trans*- and *cis*-forms of *iso*butylideneacetone appear to weaken the view previously advanced (A., 1930, 325) that the semicarbazone, m. p. 164°, is derived from β-methyl-Δ^{β}-hexen-ε-one. The formation of the hexenone from the residues in the preparation of 3-methyl-5-*iso*propylpyrazoline is now attributed to spontaneous oxidation of the latter to the ketazine of *iso*butylideneacetone, hydrolysis of the latter to a mixture of *cis*- and *trans*-*iso*butylideneacetone, and isomerisation of the *trans*-form to β-methyl-Δ^{β}-hexen-ε-one. Hydrolysis of the oxidation products of 3-methyl-5-*iso*propylpyrazoline and of the residues obtained in the preparation of this pyrazoline does not, however, yield identical results, the latter affording larger quantities of β-methyl-Δ^{β}-hexen-ε-one. It is concluded that this ketone corresponds at least in part with an initial βγ-unsaturated ketazine formed by the action of hydrazine on β-methyl-Δ^{β}-hexen-ε-one present in the *iso*butylideneacetone and that in the condensation of *iso*butaldehyde with acetone some β-methyl-Δ^{β}-hexen-ε-one is always formed with the *iso*butylideneacetone. R. BRIGHTMAN.

Constitution of homomesityl oxide. S. G. POWELL and C. H. SECOY (J. Amer. Chem. Soc., 1931, **53**, 765—768; cf. Becker and Thorpe, J.C.S., 1922, **121**, 1303).—Homomesityl oxide (improved method of preparation given) is ethyl β-methyl-Δ^{α}-butenyl ketone, since it is reduced catalytically (Adams) to ethyl β-methylbutyl ketone, b. p. 158°, d_4^{24} 0·829, n_D^{24} 1·412 [semicarbazone, m. p. 96° (lit. 102°)], which is oxidised by sodium dichromate and dilute sulphuric acid to acetic and β-methylvaleric acids. Reduction of homomesityl oxide with sodium and moist ether gives ethyl-β-methylbutylcarbinol, b. p. 155°, d_4^{24} 0·8425, n_D^{24} 1·433, obtained also from magnesium β-methylbutyl bromide and propaldehyde, which is oxidised to the above saturated ketone.

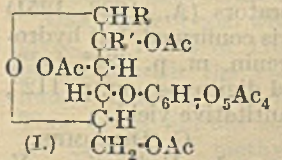
Methyl αβ-dimethylbutyl ketone, b. p. 158°, d_4^{22} 0·8295, n_D^{22} 1·412 (semicarbazone, m. p. 124—126°), is obtained by hydrolysis of ethyl methyl*sec.*-butylacetoacetate with 15% sodium hydroxide solution. H. BURTON.

Preparation of organic reagents. III. Diacetyldioxime. K. H. SLOTTA and K. R. JACOBI (Z. anal. Chem., 1931, **83**, 1—5).—An ice-cold mixture of methyl ethyl ketone (72 g.), ether (200 c.c.), and 20% methyl-alcoholic hydrochloric acid (30 c.c.) is treated with a slow stream of ethyl nitrate for 1½ hrs. The resulting diacetylmonoxime solution is treated with 1000 c.c. of water and a solution of sodium hydroxylaminodisulphonate, prepared as described below, and heated at 65—75° on the water-bath for 10 hrs., whereby the ether and excess of ethyl nitrite are slowly evaporated and diacetyldioxime separates in white crystals, which, after washing, are suitable for use without further purification. The sulphonate solution is prepared by treating 260 g. of sodium carbonate crystals in 50 c.c. of water with an excess of sulphur dioxide, adding the solution to an ice-cold solution of 138 g. of sodium nitrite in 500 c.c. of water, and saturating the mixture with sulphur dioxide at below 5°. A. R. POWELL.

Reactive form of glucoseoxime. M. L. WOLFROM and A. THOMPSON (J. Amer. Chem. Soc., 1931, **53**, 622—632).—Oximation of aldehydoglucose penta-acetate (A., 1929, 1043) gives *aldehydoglucoseoxime penta-acetate*, m. p. 99—99·5°, $[\alpha]_D^{24}$ +57·2° in chloroform, acetylated by acetic anhydride in pyridine at 0° to *aldehydoglucoseoxime hexa-acetate* (I), m. p. (labile form) 79°, resolidifying with m. p. about 119°, m. p. (stable form) 119·5°, $[\alpha]_D^{5}$ +45·9° in chloroform. Crystallographic data are given for I. Acetylation of glucoseoxime, m. p. 142—143° (lit. 138°), $[\alpha]_D^{25}$ in water −8·9⟶−1·9°, by Wohl's method (A., 1893, i, 292; cf. Behrend, A., 1907, i, 481) affords a glucoseoxime hexa-acetate, m. p. 113—115°, $[\alpha]_D^{25}$ +7·3° in chloroform (cf. *loc. cit.*), which must have the ring structure; it is designated the β-form. Deacetylation of the above penta-acetate by cold methyl-alcoholic ammonia gives β-glucoseoxime. When I is heated at 135—140° or boiled with acetic anhydride and sodium acetate, acetic acid is eliminated and penta-acetylgluconbackslash nitrile, m. p. 83—84°, $[\alpha]_D^{20}$ +47·8° in chloroform, is obtained. Similar treatment of the β-hexa-acetate gives none of the nitrile. Treatment of β-glucoseoxime with acetic anhydride and sodium acetate at 75—80° (cf. Wohl, *loc. cit.*) gives penta-acetylgluconbackslash nitrile and a small amount of I; it is presumed that ring fission occurs during acetylation and nitrile formation occurs by way of I. *Penta-acetylmannononitrile*, m. p. 92—93°, $[\alpha]_D^{3}$ −1·8° in chloroform, prepared from mannoseoxime, acetic anhydride, and sodium acetate at 85—90°, is not formed during any of the above reactions, indicating that ψ-oxime formation does not take place. H. BURTON.

Fall of rotatory power of solutions of polysaccharides under the action of alkali. J. EFFRONT (Compt. rend., 1931, **192**, 529—532).—The optical rotation of a 4—5% starch solution is decreased by 16% in 5·5 hrs. (no further change after 24 hrs.) by addition of an equal volume of *N*-sodium hydroxide. The rotations of solutions of maltose and dextrose are similarly reduced by 25·2% and 48·2%, respectively, in 5·5 hrs., and by 50% and 91%, respectively, in 24 hrs. These values vary only slightly with the specimen of starch used and the concentration of the solutions. Thus a decrease in optical rotation, under such conditions, of more than 52% in a solution containing dextrin, maltose, and dextrose, indicates the presence of the last-named, and in solutions of maltose and dextrose the decrease in rotation beyond the 48·2% given by maltose alone is directly proportional to the dextrose content of the mixture. The method also serves to determine approximately the amount of free maltose in the presence of soluble starch and reducing dextrins obtained by enzymolysis of malt extracts with diastase. J. W. BAKER.

Crystalline acetates of cellobiosone and the question of the formation of the γ-pyrone ring from disaccharides. K. MAURER and K. PLÖTNER (Ber., 1931, **64**, [*B*], 281—289; cf. A., 1930, 1412).—2-Hydroxycellobial hepta-acetate, m. p. 125°, is readily hydrogenated in presence of palladium and glacial acetic acid to 1 : 4-*glucosidostyracitol hepta-acetate*, m. p. 187°, $[\alpha]_D^{22}$ +7·0° in chloroform, hydrolysed by methyl-alcoholic ammonia to 1 : 4-*glucosidostyracitol*, m. p. 173°, $[\alpha]_D^{22}$ +29·01° in water. Treatment of 2-hydroxycellobial hepta-acetate suspended in ether with dry chlorine gives a mixture of products from which a solid *dichloride* (I; R=R′=Cl), m. p. 158°, $[\alpha]_D^{20}$ −5·74° in chloroform,



(I.)

is isolated. It is re-converted by zinc dust and 50% acetic acid into 2-hydroxycellobial hepta-acetate and transformed by an excess of silver acetate in glacial acetic acid into *cellobiosone hydrate nona-acetate* (I; R=R′=OAc), m. p. 122—124°, $[\alpha]_D^{22}$ +38·92° in alcohol, re-converted into the hepta-acetate by pyridine and acetic anhydride. The crystalline dichloride is not affected by silver carbonate in cold or warm, moist ether, but one or more of the non-crystalline isomerides which are formed during its preparation are transformed into *cellobiosone hydrate hepta-acetate* (I; R=R′=OH), m. p. 121—138°, $[\alpha]_D^{21}$ +43·88° to +32·60° in aqueous alcohol. Treatment of this substance with acetic anhydride yields *cellobiosone hepta-acetate*, m. p. 172°, $[\alpha]_D^{20}$ +2·40° in chloroform; formation of a hydroxy-4-pyrone is not observed. Confirmation of the structure of cellobiosone hepta-acetate is deduced from its formation from cellobiosone hydrate nona-acetate and an excess of acetic anhydride. The cellobiosone acetates resemble cellobiosone in their reducing action towards cold Fehling's solution and potassium permanganate at 20°. They do not yield an osazone with phenylhydrazine. Hydrolysis with warm sodium hydroxide converts them into products which do not reduce Fehling's solution or form an osazone. A similar effect is produced by cold sodium hydroxide or methyl-alcoholic ammonia except that the syrups reduce boiling Fehling's solution. Fischer's cellobiosone behaves similarly. Hydrolysis with acids involves the glucosidic linking.

2-*Hydroxygentiobial hepta-acetate*, m. p. 130° after softening at 126°, $[\alpha]_D^{22}$ −29·04° in chloroform, prepared from acetobromogentiobiose and diethylamine in chloroform, is hydrogenated in presence of palladium to 1 : 6-*glucosidostyracitol hepta-acetate*, m. p. 152°, $[\alpha]_D^{22}$ +17·21° in chloroform, hydrolysed by methyl-alcoholic ammonia to 1 : 6-*glucosidostyracitol*, m. p. 223° (decomp.), $[\alpha]_D^{20}$ +2·44° in water. Treatment of 2-hydroxygentiobial hepta-acetate with chlorine in ether affords a non-crystalline *dichloride*, converted by silver carbonate in moist ether into a syrupy *osone hydrate*, from which kojic acid is obtained by means of pyridine and acetic anhydride.

H. Wren.

Effect of ethylene on the hydrolysis of salicin by emulsin. D. T. Englis and F. A. Dykins (J. Amer. Chem. Soc., 1931, **53**, 723—726).—Ethylene has no influence on the hydrolysis of salicin by emulsin, as determined polarimetrically and by the amount of reducing sugar formed. H. Burton.

Digitalis glucosides. III. Glucosides of *Digitalis lanata*. S. Smith (J.C.S., 1931, 23—25).—Leaves of *D. lanata* contain digoxin (A., 1930, 583), gitoxin, $[\alpha]_{5461}^{30}$ +3·5° in pyridine, identical with that from *D. purpurea*, and other glucosides. The work of Windaus and his collaborators (A., 1928, 1251) and of Cloetta (A., 1926, 755) is confirmed, but hydrolysis of gitoxin gives gitoxigenin, m. p. 234°, $[\alpha]_{5461}^{20}$ +38·5° in methyl alcohol, and digitoxose, m. p. 112°, $[\alpha]_{5461}^{20}$ +55·7° in water, in quantitative yield.

G. Discombe.

Digitalin of Nativelle and digitoxin. V. Hasenfratz (Compt. rend., 1931, **192**, 366—368; cf. Raymond-Hamet, A., 1929, 613).—Digitalin, probably $C_{41}H_{64}O_{13}$, m. p. (block) 263°, is hydrolysed by aqueous-alcoholic hydrochloric acid to digitoxose and a genin, $C_{23}H_{34}O_4$, m. p. (block) 256°, $[\alpha]_D^{23}$ +18·5° in methyl alcohol. Digitalin appears to be identical with digitoxin (Windaus and Stein, A., 1929, 71).

H. Burton.

Synthesis of glucosides. VIII. 6-Bromoindican. A. Robertson and R. B. Waters (J.C.S., 1931, 72—76).—The synthesis of 6-bromoindican by the author's general method (A., 1927, 960) is described. The interaction of *O*-tetra-acetyl-α-glucosidyl bromide and *methyl* 6-*bromo*-3-*hydroxyindole*-2-*carboxylate* (I), m. p. 192° (*diacetyl* derivative, m. p. 151°), prepared by the action of sodium and sodium methoxide on a benzene suspension of *dimethyl* 5-*bromophenylglycine*-2-*carboxylate*, m. p. 101°, yields *methyl* 6-*bromo*-3-O-*tetra-acetyl*-β-*glucosidoxyindole*-2-*carboxylate*, m. p. 171°, $[\alpha]_D^{20}$ −59·7° in acetone, converted by hydrolysis and acetylation into 6-*bromo*-1-*acetyl*-3-O-*tetra-acetyl*-β-*glucosidoxyindole*, m. p. 151°, $[\alpha]_D^{20}$ −48·8° in acetone, which is hydrolysed by methyl-alcoholic ammonia at 0° to 6-*bromo*-3-β-*glucosidoxyindole* (6-*bromoindican*) *tetrahydrate*, m. p. 64°, $[\alpha]_D^{20}$ −6·4° in acetone. The latter is hydrolysed by hydrochloric acid and by emulsin to dextrose and 6-bromoindoxyl, which on oxidation yields 6 : 6′-dibromoindigotin. On hydrolysis in presence of isatin or of *p*-nitrobenzaldehyde, 6-*bromoindirubin*, m. p. above 340°, and p-*nitrobenzaldehyde*-6-*bromoindogenide*, respectively, are formed.

Attempts to prepare 6-bromoindoxyl by the acetylation of 6-bromoindoxylic acid obtained by the hydrolysis of I gave 6-bromo-1-acetyl-3-acetoxyindole (*hydrate*, m. p. 150—152°) in small yield.

G. Discombe.

Para*iso*dextran. A. Kiesel and M. Znamenskaja (Ber., 1931, **64**, [*B*], 378—383).—Successive extractions of *Polyporus betulinus* with 1·5, 3, and 6% sodium hydroxide followed by acidification of the extracts gives a material much less homogeneous than that obtained by Winterstein (A., 1895, i, 323). The fractions have $[\alpha]_D$ +219·4°, +259·6°, and +81·4° in 5% sodium hydroxide. They give reddish-brown colorations with iodine and sulphuric acid or zinc chloride and iodine. The presence of pentoses is established in the first two fractions by the orcinol reaction. Hydrolysis of all the fractions affords mannose in addition to dextrose. Acetylation and subsequent regeneration of the carbohydrate causes the three fractions to approximate more closely to one another in composition. Since the pentose content of the initial fractions remains almost unchanged, the simultaneous participation of hexose and pentose groups in the structure of the complete molecule must be assumed. The product obtained by means of 6% sodium hydroxide retains its initial properties almost unchanged and is more uniform than the other fractions; apart from its lower optical activity, it coincides most closely with Winterstein's para*iso*dextran. Treatment of the fractions with acetic anhydride and pyridine yields the corresponding triacetates; determinations of mol. wt. in freezing glacial acetic acid give results in harmony with the simple formula $C_6H_7O_5Ac_3$. H. Wren.

Starch. J. Effront (Ann. Soc. Zymol., 1930, 2, 27 pp.; Chem. Zentr., 1930, ii, 2886).—Maquenne and Roux' hypothesis that starch is composed of amylopectin and amylose is contested; these substances are, however, produced by natural starch by depolymerisation followed by repolymerisation. The polymerised product is more sensitive than natural starch to chemical and physical attack.

A. A. Eldridge.

Cellulose. XXXVIII. Morphology and chemistry of cellulose fibres. Purification of fibres in connexion with swelling, tenacity of fibre, size of crystallite, and viscosity of solutions. II. K. Hess, C. Trogus, L. Akim, and I. Sakurada (Ber., 1930, 64, [*B*], 408—427; cf. A., 1930, 1417).—A review of the literature leads the authors to the conclusion that there is at present no established method for the identification of cellulose, so that the course of purification of natural cellulose can be followed only by observation of as many properties as possible of the material at its different stages and comparison of the data thus obtained among themselves.

The crude fibre of *Boehmeria nivea* is subjected to four successive extractions with 2% sodium hydroxide in the absence of air, then bleached three times with neutral hypochlorite solution of progressively decreasing concentration, and finally treated with chlorine dioxide and sodium sulphite. The considerable loss of material during the last stage of the operations is remarkable. The fibres remain intact and exhibit no damage under the microscope. The final product cannot be regarded as 100% cellulose, but further purification is possible only through dissolution and reprecipitation. Morphological examination shows that the treatment with 2% sodium hydroxide and dilute hypochlorite removes a non-cellulose material localised on the outer layers of the fibre and that a component probably lying between the micelle series is removed by exhaustive treatment with chlorine dioxide. The extent to which this component is affected by the sodium hypochlorite cannot be stated, but the great decrease in the viscosity of the solutions after the first bleaching indicates that the treatment penetrates beyond the primary lamellæ.

As the purification progresses, the tenacity and extension of the fibres pass through a maximum which is reached with the removal of the primary lamellar material by dilute sodium hydroxide. Subsequent treatment with hypochlorite causes a considerable diminution of tenacity, which is not further affected greatly by chlorine dioxide. Röntgenographic examination shows that degradation of the crystallites does not take place during purification. Products of the nitration of the preparation according to the method of Trogus (following abstract) retain their fibrous form and yield well-defined Röntgen diagrams. The relative viscosity of solutions of the nitrated compounds in acetone diminishes very markedly as the purification progresses, as does also the dependence of viscosity on pressure. In these respects a similar behaviour is shown by ramie in ammoniacal copper solution. It is considered doubtful whether the fibre properties have the expected relationship to the constitution of cellulose.

H. Wren.

Preparation of fibrous cellulose nitrates. C. Trogus (Ber., 1931, 64, [*B*], 405—407; cf. Berl and Rueff, this vol., 203).—Highly-nitrated cellulose nitrate is produced by the addition of air-dried ramie fibre to a mixture of nitric acid (*d* 1·52), glacial acetic acid, and acetic anhydride or phosphoric oxide. After 2—4 hrs. the fibre is well washed with water and stabilised with boiling 50% acetic acid. For the preparation of products containing 11—12·5% of nitrogen, a mixture of nitric acid (*d* 1·52) and glacial acetic acid is used.

H. Wren.

Composition and formation of cellulose acetate soluble in acetone. S. Iwasaki (J. Soc. Chem. Ind. Japan, 1931, 34, 9—10B).—Fractions precipitated from a cellulose acetate soluble in acetone were found to have widely different physical properties, although their acid content was practically the same. A theory of the ripening of cellulose acetate is based on these observations and on the micellar theory of Meyer and Mark.

H. Ingleson.

Lignin. V. Distillation of alkali lignin with zinc dust in an atmosphere of hydrogen. M. Phillips (J. Amer. Chem. Soc., 1931, 53, 768—774).—When lignin is heated with zinc dust in a current of hydrogen up to 400°, carbon dioxide, oil, and an aqueous distillate are obtained. The aqueous distillate contains acetone (0·36%), methyl alcohol (1·48%), and acid (as acetic, 0·24%), and gives characteristic reactions for pyrocatechol. The oil (16% of lignin used) contains guaiacol and an unidentified methoxyphenol (3 : 5-*dinitrobenzoate*, m. p. 110°). Lignin probably contains an aromatic nucleus. The production of carbon dioxide suggests the presence of a free or combined carboxyl or lactone group.

H. Burton.

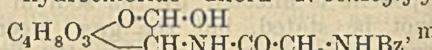
Lignin, humic acids, and humins. W. Fuchs (Z. angew. Chem., 1931, 44, 111—118).—A lecture. The following appears to be new. The β-methoxyethyl alcohol derivative ("methylin," cf. A., 1929, 1282) prepared direct from pine-wood by an improved method is degraded by fusion with potassium hydroxide at 250—295° to protocatechuic acid and small amounts of pyrocatechol, *m*-hydroxy-aromatic acids, and oxalic acid. The methylin derivative may be separated by solvents into two principal and two subsidiary fractions; of the former the more readily soluble has mol. wt. about 1000, and the other about 2000. Their solubility in organic solvents is improved by methylation and still further by acetylation of the methyl derivatives, which occurs by replacement of methyl groups. The methylin residues are removed by hydrochloric acid, giving products with the properties of the original lignin. Tentative lignin and humic acid structures are formulated.

Oxidation of coal with nitric acid (*d* 1·4) at 90—95° gives, in yields of 110—120% of starting material, products with the characteristics of the dehydrohumic acids prepared from lignite (cf. B., 1928, 555). They are somewhat soluble in organic solvents, and are capable of methylation to products with the properties of ether-esters. Alcoholic potassium acetate converts them into definite potassium salts, which are either soluble in water or may be obtained in water-soluble forms; the potassium is almost quantitatively replaced by treatment with ammonium chloride. H. A. Piggott.

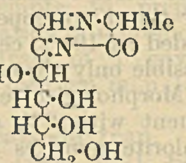
Action of formaldehyde on amino-acids. Formation of amines. L. Zeleny and R. A. Gortner (J. Biol. Chem., 1931, **90**, 427—441).—Hydrolysis of alanine, cystine, glutamic acid, and tyrosine by 20% hydrochloric acid in presence of formaldehyde results in the appearance of 12—40% of the total nitrogen as volatile amines (including a little ammonia). Casein after removal of amide nitrogen by preliminary hydrolysis behaves similarly. The distribution of primary, secondary, and tertiary amines in the volatile distillates is essentially the same as is found when ammonium chloride is boiled with 20% hydrochloric acid in presence of formaldehyde. The non-volatile amino-nitrogen reaches a minimum value after several hours' boiling, but the non-volatile non-amino-nitrogen steadily decreases, showing that, after a few hours at least, the latter is the progenitor of the volatile nitrogen, which, except in the case of tyrosine, continually increases. Trimethylamine is the final product of the hydrolysis and no evidence of the formation of amines by decarboxylation was obtained. J. D. A. Johnson.

***n*-Aminobutenes.** E. Galand (Bull. Soc. chim. Belg., 1930, **39**, 529—538).—Fuming hydrobromic acid converts γ-ethoxybutylamine (Luchmann, A., 1896, i, 544) into γ-bromobutylamine hydrobromide, converted by quinoline at 100° into Δ^{β}-butenylamine, b. p. 82—83°/757 mm., d_4^{20} 0·7771, n_D 1·43016, which could not be separated into geometrical isomerides either by careful fractional distillation or by fractional crystallisation of its *phenylthiourethane*, m. p. 106° (crystallographic data), or its *phenylurethane*, m. p. 130°. The same unsaturated amine is obtained by reduction of crotononitrile with zinc–copper couple in acetic acid. Similar reduction of vinylacetonitrile affords Δ^{γ}-*butenylamine*, b. p. 81—82·5°/748·5 mm., d_4^{20} 0·7735, n_D 1·42734, which differs from the amine to which Luchmann (*loc. cit.*) assigned this structure. Silver nitrite converts Δ^{β}-butenylamine into crotyl alcohol. J. W. Baker.

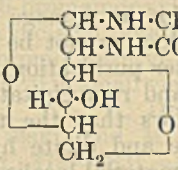
Thiocholine halides. II. Thiocholine chloride and its derivatives. I. Harada (Bull. Chem. Soc. Japan, 1931, 6, 25—28).—*Chlorocholine chloride*, m. p. 242° (decomp.) after becoming discoloured at 163°, is obtained by the interaction of trimethylamine with ethylene chloride. It reacts with 2-thiouracil at 150° to form *thiocholine chloride*, m. p. 238° (decomp.) after softening at 200°, isoelectric point at p_H 7·0, which forms a *complex* with silver chloride, m. p. about 228° (decomp.) after darkening at 70°. G. Discombe.

Synthesis of peptide-like substances from amino-sugars and amino-acids. I. Glucosamine as a component. A. Bertho, F. Hölder, W. Meiser, and F. Hüther (Annalen, 1930, **485**, 127—151).—The synthesis of various simple derivatives of the type of the products of enzymolysis of glucoproteins is described. Condensation of chloroacetyl chloride with glucosamine hydrochloride in the presence of sodium hydroxide gives a 5% yield of N-*chloroacetylglucosamine*, m. p. 168—169°, $[\alpha]_D^{25}$ +24·8° in methyl alcohol. The corresponding α-bromopropionyl derivative [which with benzoyl chloride and 50% potassium hydroxide gives a *tetrabenzoyl* derivative, m. p. 189°, $[\alpha]_D^{20}$ +73·75° in chloroform (crystallisation affords a sample $[\alpha]_D^{18}$ +86·7°, which, however, is not optically pure), together with a *substance*, m. p. 238°, $[\alpha]_D^{25}$ +25·87° in chloroform, possibly tetrabenzoyl *N*-(α-hydroxypropionyl)glucosamine] and α-bromo*iso*hexoylglucosamine (*tetrabenzoyl* derivative, m. p. 189°, $[\alpha]_D^{15}$ +103·1° in chloroform) (cf. Weizmann and Hopwood, A., 1913, i, 958), exhibit mutarotation and fractional crystallisation separates a specimen of higher initial rotation. The failure to obtain carbonyl derivatives with phenylhydrazine and semicarbazide is ascribed to steric effects and not to betaine formation (cf. Irvine and Hynd, J.C.S., 1913, **103**, 41). Prolonged action (3 months) of cold methyl-alcoholic ammonia on *N*-α-bromopropionylglucosamine affords, in addition to *N*-alanylglucosamine (obtained by Weizmann and Hopwood, *loc. cit.*, by similar action of aqueous ammonia), N-*alanylanhydroglucosamine anhydride*, m. p. 199°, $[\alpha]_D^{20}$ −89·8° in water, to which the structures I and II, respectively, are assigned. The latter is almost the only product when concentrated methyl-alcoholic ammonia at 100° in a sealed tube is used, and is also obtained in very small yield when aqueous ammonia is employed. These two products reduce Fehling's solution only very slowly and are formed independently in the reaction, since they could not be interconverted. By the action of benzoylated amino-acid azides on glucosamine benzamidoacylglucosamines are obtained. Thus hippurazide and glucosamine hydrochloride afford N-*benzoylglycylglucosamine*,  $C_4H_8O_3{<}\begin{matrix}O\cdot CH\cdot OH\\ CH\cdot NH\cdot CO\cdot CH_2\cdot NHBz\end{matrix}$, m. p. 200° (decomp.), together with a trace of a *substance*, m. p. 263—265° (decomp.), but with *p*-bromohippurazide only an amorphous *substance*, m. p. 214°, containing two bromohippuryl residues could be obtained. With benzoylalanine azide is obtained N-*benzoylalanylglucosamine*, m. p. 222° (decomp.), $[\alpha]_D^{20}$ +59·0° in water, which is a mixture of optical isomerides. The structure of these glucosamine derivatives and others in the literature is discussed. J. W. Baker.

(I.)



(II.)



Resolution of synthetic *iso*leucine into four optically active components, namely, *l*(+)- and *d*(−)-*iso*leucines and *d*(−)- and *l*(+)-*alloiso*leucines. E. Abderhalden and W. Zeisset (Z. physiol. Chem., 1931, **195**, 121—131).—Treatment of α-bromo-β-methylvaleric acid with saturated aqueous ammonia during 4—5 days at 37°, evaporation of the resulting solution in a vacuum until crystallisation begins, admixture of this with alcohol whereby crystalline material is obtained, and crystallisation of this from water gives *dl-iso*leucine (α-amino-β-methylvaleric acid). The mother-liquors from this crystallisation contain *dl-alloiso*leucine (*formyl* derivative, m. p. 117—118°), isolated by way of the ethyl ester, b. p. 85—88°/15 mm., which is hydrolysed to the free acid by boiling water. Resolution of both *dl*-acids is effected by Locquin's method (A., 1907, i, 593). The following data (amongst others) are recorded for the optically active acids and their derivatives: *l*(+)-*iso*leucine, m. p. (sealed tube) 285—286° (decomp.) (lit. 280°), $[\alpha]_D^{20}$ +10·7° in water, +40·8° in 20% hydrochloric acid [formyl, m. p. 155°, $[\alpha]_D^{20}$ +26·6° in alcohol; benzenesulphonyl, m. p. 153° (lit. 149—150°), $[\alpha]_D^{20}$ +25·3° in alcohol; phenylcarbimide, m. p. 121°, $[\alpha]_D^{20}$ +37·5° in alcohol, and α-naphthylcarbimide, m. p. 178—179°, $[\alpha]_D^{20}$ +30·1° in alcohol, derivatives]; *d*(—)-*iso*leucine, m. p. (sealed tube) 283—284° (decomp.) (lit. 280—290°), $[\alpha]_D^{20}$ —10·7° in water, —41·6° in 20% hydrochloric acid (formyl, m. p. 156°, $[\alpha]_D^{20}$ —26·8° in alcohol; *benzenesulphonyl*, m. p. 153—154°, $[\alpha]_D^{20}$ —25·5° in alcohol; *phenylcarbimide*, m. p. 119—121°, $[\alpha]_D^{20}$ —36·3° in alcohol, and α-*naphthylcarbimide*, m. p. 177—178°, $[\alpha]_D^{20}$ —29·5° in alcohol, derivatives); l(+)-alloiso*leucine*, m. p. (sealed tube) 278° (decomp.), $[\alpha]_D^{20}$ +14·0° in water, +38·1° in 20% hydrochloric acid (*formyl*, m. p. 126°, $[\alpha]_D^{20}$ +24·2° in alcohol; *benzenesulphonyl*, m. p. 147—148°, $[\alpha]_D^{20}$ +30·7° in alcohol; *phenylcarbimide*, m. p. 151°, $[\alpha]_D^{20}$ +30·8° in alcohol, and α-*naphthylcarbimide*, m. p. 165—166°, $[\alpha]_D^{20}$ +25·1° in alcohol, derivatives); *d*(—)-*alloiso*leucine, m. p. (sealed tube) 274—275° (decomp.), $[\alpha]_D^{20}$ —14·2° in water, —38·0° in 20% hydrochloric acid (*formyl*, m. p. 126°, $[\alpha]_D^{20}$ —25·2° in alcohol; *benzenesulphonyl*, m. p. 147—148°, $[\alpha]_D^{20}$ —30·7° in alcohol; *phenylcarbimide*, m. p. 151°, $[\alpha]_D^{20}$ —30·6° in alcohol, and α-*naphthylcarbimide*, m. p. 168°, $[\alpha]_D^{20}$ —25·5° in alcohol, derivatives). H. BURTON.

Ethyl aminomalonate. Action of acyl chlorides on ethyl aminomalonate. *N*-Acyl derivatives of ethyl aminomalonate. R. LOCQUIN and V. CERCHEZ (Bull. Soc. chim., 1931, [iv], **49**, 42—47).—When ethyl aminomalonate is treated with acyl chlorides in pyridine ethyl *N*-acylaminomalonates are obtained in 60—80% yields. The same derivatives are obtained when the sodium derivative of ethyl aminomalonate is treated with acyl chlorides in ether and the yields are higher. Acetyl cyanide and ethyl sodioaminomalonate also yield the *N*-acetyl derivative and it is concluded that the amino-group prevents the fixation of an acyl radical on the central carbon atom. Attempts to obtain such a compound by previously blocking the amino-group failed, since ethyl *N*-formamidomalonate yields no sodium derivative.

Ethyl *N*-acetamidomalonate, m. p. 95°, b. p. 185°/20 mm., is obtained quantitatively from ethyl sodioaminomalonate and acetyl chloride in ether, or in lower yield from acetyl cyanide. Ethyl *N*-*iso*butyramidomalonate, m. p. 74°, *ethyl* N-*isovaleramidomalonate*, m. p. 49°, b. p. 185—190°/17 mm. (*diamide*, m. p. 250°); *ethyl* N-*nonoamidomalonate*, m. p. 66° (*diamide*, m. p. 229—230°), and *ethyl* N-*benzamidomalonate*, m. p. 61°, are similarly obtained by the pyridine method. R. BRIGHTMAN.

Action of carbonyl chloride on ethyl aminomalonate. Preparation of ethyl carbamidodimalonate and its hydrolysis to carbamidodiacetic acid and hydantoin-3-acetic acid. R. LOCQUIN and V. CERCHEZ (Bull. Soc. chim., 1931, [iv], **49**, 47—54).—When a 20% solution of carbonyl chloride (0·5 mol.) in toluene is added to a mixture of ethyl aminomalonate (1 mol.) and pyridine (2·5 mols.) in ether and the pyridine hydrochloride removed with water, *ethyl carbamidodimalonate*, m. p. 167°, is obtained in 80% yield; with ethyl sodioaminomalonate the yields are much lower. On hydrolysis with aqueous *N*-sodium hydroxide ethyl carbamidodimalonate is converted into carbamidodiacetic acid, m. p. 230° (decomp.), and with 10% hydrochloric acid (*d* 1·015) into hydantoin-3-acetic acid, m. p. 196°.

R. BRIGHTMAN.

Optical activity of cystine preparations used for animal experiments. J. R. HAAG (J. Amer. Chem. Soc., 1931, **53**, 808—809).—The specific rotations of cystine preparations (from human hair) vary from —185·9° to —216·6° in *N*-hydrochloric acid. The majority of the samples have $[\alpha]_D^{11}$ about —210°. The variations in rotation are partly due to prolonged washing of some of the samples with hot water to remove tyrosine. H. BURTON.

Action of magnesium ethyl halides on ethyl diethylcyanoacetate. A. MAVRODIN (Compt. rend., 1931, **192**, 363—365; cf. this vol., 205).—When ethyl diethylcyanoacetate is treated with magnesium ethyl bromide or iodide, part of the ester is converted into β-*cyano*-ααβ-*triethyl*-n-*butyl alcohol*, b. p. 132—133°/20 mm., which reacts further with the Grignard reagent, forming some triethylcarbinol (*allophanate*, m. p. 182—183°) and α-ethylbutyronitrile. The remainder of the ester reacts as previously described (*loc. cit.*), giving, after hydrolysis, diethyl ketone, ethyl α-ethyl-*n*-butyrate, and ethyl ααγγ-tetraethylacetoacetate. These results confirm the hypothesis that in ethyl cyanoacetate and ethylcyanoacetate (A., 1929, 796) enolisation of the carbonyl group occurs. The above cyano-compound is dehydrated by thionyl chloride to δ-*cyano*-γδ-*diethyl*-Δ^β-*hexene*, b. p. 105°/16 mm. H. BURTON.

Diethyl dicyanoglutaconate. Y. URUSHIBARA (Bull. Chem. Soc. Japan, 1931, **6**, 29—31).—Methods are described by which *diethyl dicyanoglutaconate* (I), and not the semihydrate (A., 1927, 345, 1059), is prepared. The presence of the free ester is proved by the precipitation of the semihydrate from an alkaline extract of the reaction mixture. Ethyl hydroxymethylenecyanoacetate condenses with ethyl cyanoacetate in presence of acetic anhydride to yield I. *Ethyl chloromethylenecyanoacetate*, b. p. 105°/12 mm., condenses with ethyl chlorocyanoacetate in presence of copper and with ethylcyanoacetate in presence of pyridine to give I, whilst ethyl ethoxymethylenecyanoacetate failed to react with ethyl cyanoacetate in presence of acetic anhydride and zinc chloride.

G. DISCOMBE.

Mechanism of the conversion of nitriles into amides by sulphuric acid. J. VERHULST (Bull. Soc. chim. Belg., 1930, **39**, 563—567).—The action of concentrated sulphuric acid below 25° on the cyanohydrins of acetone, methyl propyl ketone, methyl ethyl ketone, and diethyl ketone, exact neutralisation of the solution with potassium (or sodium) carbonate, evaporation to dryness, and extraction of the residue with hot alcohol furnishes the crystalline *potassium* (or *sodium*) salts of the type $\mathrm{OH\cdot CRR'\cdot(C{:}NH)\cdot OSO_3K}$. These give no ionic reaction for sulphate in aqueous solution, but when boiled with barium chloride in dilute hydrochloric acid solution barium sulphate is precipitated and rapid cooling of the solution affords the corresponding hydroxy-acid amide more or less contaminated with the hydroxy-acid. An almost quantitative yield of the amide is obtained if the initial reaction between the sulphuric acid and the nitrile is carried out at 80—100°. The intermediate imino-sulphates from the cyanohydrins of methyl *iso*propyl and ethyl *n*-propyl ketones are less stable and could not be obtained pure, but the *amides*, m. p. 89°, and m. p. 72·2—73·2°, respectively, of α-hydroxy-αβ-dimethylbutyric and of α-hydroxy-α-ethyl-*n*-valeric acids were similarly obtained. The cyanohydrins of di*iso*butyl ketone affords the *amide*, m. p. 101—102°, of α-hydroxy-γ-methyl-α-*iso*butyl-*n*-valeric acid. The mechanism of the hydrolysis of nitriles by sulphuric acid is therefore $\mathrm{OH\cdot CRR'\cdot CN \xrightarrow{H_2SO_4} OH\cdot CRR'\cdot C({:}NH)\cdot O\cdot SO_3H \rightarrow OH\cdot CRR'\cdot C({:}NH)\cdot OH \rightarrow OH\cdot CRR'\cdot CO\cdot NH_2}$. J. W. Baker.

Carbamidosulphonic acids. P. Baumgarten and I. Marggraff (Ber., 1931, **64**, [*B*], 301—309).—Carbamide is converted by a molecular proportion of *N*-pyridiniumsulphonic acid (cf. A., 1926, 844) at 120° into *pyridinium carbamidosulphonate*, m. p. 130° (also *monohydrate*), transformed by alkali hydroxide into the corresponding *sodium* and *potassium* salts, $\mathrm{NH_2\cdot CO\cdot NH\cdot SO_3K(Na)}$. In acid solution the salts undergo rapid and quantitative hydrolysis to carbamide and sulphuric acid, so that the free acid could not be prepared. In neutral or alkaline solution, hydrolysis occurs more slowly with formation of ammonia, carbon dioxide, and alkali aminosulphonate. The *barium* salt is converted by an excess of barium hydroxide into the *dibarium* salt, $\mathrm{(NH_2\cdot CO\cdot N\cdot SO_3)Ba,3H_2O}$. The hygroscopic *dipotassium* salt, $\mathrm{NH_2\cdot CO\cdot NK\cdot SO_3K}$, is analogously prepared. Treatment of carbamide (1 mol.) with *N*-pyridiniumsulphonic acid at 140—150° yields *pyridinium carbamidodisulphonate*, $\mathrm{CO(NH\cdot SO_3H,C_5H_5N)_2}$, m. p. 146°; the corresponding *monohydrated potassium*, *dihydrated sodium*, and *monohydrated barium* salts are described. In acid solution, the disulphonates are rapidly hydrolysed, mainly to carbamide and sulphuric acid, but partly to carbon dioxide and aminosulphonic acid. In neutral solution they are rapidly decomposed when heated, giving exclusively carbon dioxide and aminosulphonate if the solutions are dilute, but yielding carbamide and hydrogen sulphate in minor amount if the solutions are more concentrated. In alkaline solution (as tetra-salts) they are remarkably stable. *Tetrapotassium carbamidodisulphonate*, $\mathrm{CO(NK\cdot SO_3K)_2,H_2O}$, and the corresponding *tetrahydrated barium* salt are described. H. Wren.

***cis–trans*-Isomerism of unsaturated aliphatic nitriles and amides.** P. Bruylants (Bull. Soc. chim. Belg., 1930, **39**, 572—580).—A theoretical paper in which it is emphasised that the configurations assigned to ethylenic nitriles and amides on the basis of their ultra-violet absorption spectra are untrustworthy and often opposed to chemical evidence (cf. A., 1930, 1276). J. W. Baker.

ββ′-Diethylacrylonitrile. P. Colmant (Bull. Soc. chim. Belg., 1930, **39**, 568—571).—Magnesium ethyl bromide reacts with ethyl chloroacetate at −10° (Fourneau and Tiffeneau, A., 1907, i, 817) to give a 50% yield of a mixture containing 86% of the chlorohydrin, $\mathrm{CH_2Cl\cdot CEt_2\cdot OH}$, converted by alcoholic potassium cyanide into β-*hydroxy*-β-*ethyl*-n-*valeronitrile*, b. p. 231—232°/766 mm., d_4^{20} 0·9562, n_D^{20} 1·45086 (50% yield), which is converted by distillation under atmospheric pressure with a few drops of concentrated sulphuric acid into a mixture of β-ethyl-Δ^{α}- and -Δ^{β}-pentenonitriles, which are only partly separated by fractional distillation (physical data of fractions recorded). Isomerisation with alcoholic sodium ethoxide affords a fraction, b. p. 177·4—178·4°, d_4^{20} 0·84248, n_D^{20} 1·44755, which contains 97% of the Δ^{α}-form, hydrolysed to the corresponding *amide*, m. p. 90—91°. J. W. Baker.

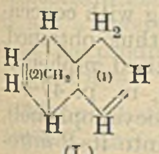
Aliphatic compounds of arsenic. W. J. C. Dyke, G. Davies, and W. J. Jones (J.C.S., 1931, 185—188).—Tri-*n*-propylarsine has b. p. 84°/17 mm., 92°/27 mm., and 113°/79 mm., connected by the expression $10{\cdot}2378 - \log_{10} p = 3215/(t + 273)$. The arsines were prepared by the interaction of arsenic trichloride and the appropriate Grignard reagent, and purified by distillation. On oxidation in air, the oxide is formed. *Tri*-n-*butylarsine oxide* and *tri*-n-*amyl arsine oxide* are described. The sulphides (A., 1907, i, 496) *tri*-n-*propyl sulphide* and *triï*so*butyl sulphide* form needles. By interaction of carbon tetrachloride solutions of the arsine and chlorine or bromine, the dichlorides or dibromides are formed, the di-iodides being obtained from solutions of the components in light petroleum. *Tri*-n-*propylarsine dichloride*, m. p. 84°; *tri*-n-*butylarsine dichloride*, m. p. 40°; *triï*so*butylarsine dichloride*, m. p. 130°; *tri*-n-*amylarsine dichloride*, liquid. *Tri*-n-*propylarsine dibromide*, m. p. 95°; *tri*-n-*butylarsine dibromide*, m. p. 55°; *triï*so*butylarsine dibromide*, m. p. 135°; *tri*-n-*amylarsine dibromide*, liquid. *Tri*-n-*propylarsine di-iodide*, m. p. about 130°; *tri*-n-*butylarsine di-iodide*, m. p. 124°; *triï*so*butylarsine di-iodide*, m. p. 117—119°. The dibromides react with silver sulphate to give the arsine sulphate; *tri*-n-*propylarsine sulphate*, m. p. 84°. With mercuric chloride in alcohol the arsines give double salts, $\mathrm{R_3As,HgCl_2}$. *Tri*-n-*propylarsine mercurichloride*, m. p. 106°; *tri*-n-*butylarsine mercurichloride*, m. p. 70°; *triï*so*butylarsine mercurichloride*, m. p. 158°. Methiodides, from methyl iodide and the arsine in ether: *methyltriethylarsonium iodide*, m. p. 270°, *cadmi-iodide*, m. p. 283°, *mercuri-iodide*, m. p. 61°; *methyltri*-n-*propylarsonium iodide*, m. p. 204°, *chloroplatinate*, m. p. 219° (decomp.), *cadmi-iodide*, m. p. 279°, *mercurichloride*, m. p. 141°, *mercuri-iodide*, m. p. 61°; *methyltriï*so*butylarsonium iodide*, m. p. 254°, *chloroplatinate*, m. p. 224° (decomp.), *cadmi-iodide*, m. p. 138°, *mercuri-iodide*, m. p. 117°; *methyl tri*-n-*butylarsonium iodide*, impure, *cadmi-*

iodide, m. p. 100°, *mercuri-iodide*, m. p. 76°; *ethyltri*-n-*butylarsonium iodide*, impure, m. p. about 107°; *methyltri*-n-*amylarsonium iodide*, oil, *chloroplatinate*, m. p. 114°. G. DISCOMBE.

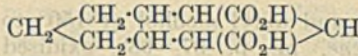
Mechanisms for the formation of organo-magnesium and other organometallic compounds. H. GILMAN and R. E. BROWN (Rec. trav. chim., 1931, 50, 184—187).—Theoretical. J. W. BAKER.

Reducing action and constitution of the Grignard reagent. C. R. NOLLER (J. Amer. Chem. Soc., 1931, 53, 635—643).—The various possibilities whereby Grignard reagents can function as reducing agents are discussed. The Grignard reagent ($c=$ about $1{\cdot}3M$) from magnesium and *iso*butyl bromide is shown by Schlenk and Schlenk's method (A., 1929, 687) to contain about 75% of magnesium di*iso*butyl. Addition of a solution of benzophenone in benzene to the Grignard reagent gives a complex, probably $(CHPh_2{\cdot}O)_2Mg,MgBr_2$, also precipitated when benzophenone is treated successively with magnesium di*iso*butyl and anhydrous magnesium bromide. Solutions of magnesium di*iso*butyl which are almost halogen-free (*i.e.*, contain little magnesium *iso*butyl bromide) reduce benzophenone to benzhydrol to at least 64% of the theoretical amount. It is considered that the constitution of the Grignard reagent is best represented by the equilibrium $R_2Mg,MgX_2 \rightleftharpoons MgR_2+MgX_2$. H. BURTON.

Polymerisation of cyclic hydrocarbons. I. Polymeric forms of *cyclo*pentadiene. K. ALDER, G. STEIN, and H. FINZENHAGEN (Annalen, 1931, 485, 223—246).—The formation by di*cyclo*pentadiene of an additive *compound*, m. p. 130—131°, with phenyl azide is in better agreement with the structure (I), tentatively suggested by Wieland (A., 1906, i, 417), than with the generally accepted formula of Krämer and Spilker (A., 1896, i, 289). This view is conclusively proved by isolation (as anhydride) of *cyclo*pentane-1 : 3-dicarboxylic acid from the products of oxidation with permanganate of the dihydro-derivative; the main product, m. p. 137° (Wieland and Bergel, A., 1926, 56, give m. p. 134°), is therefore 3 : 6-*endo*methylenehexahydrohomophthalic acid (probably *trans*), the double linking in ring 1 (formula I) being the point of attack. Further evidence in favour of formula I is afforded by the existence of the hydrocarbon in a single form only, the stability to alkalis of the "ketotribromo-compound" of Wieland and Bergel (*loc. cit.*), and the existence of a second form of the oxide. Staudinger's arguments (A., 1924, i, 274) in favour of Krämer and Spilker's formula, based on the ready thermal dissociation of the dimeride into *cyclo*pentadiene, and the comparative stability of reduction products, are rebutted by the similar behaviour of *cyclo*pentadienequinone (A., 1906, i, 674) and similar compounds. The acid $C_{10}H_{10}O_4$, m. p. 232°, isolated by Bergel and Widmann (A., 1929, 53) by oxidation of the dicyclic ketone $C_{10}H_{14}O$ with permanganate is therefore *cis*-di*cyclo*pentane-1 : 3-dicarboxylic acid



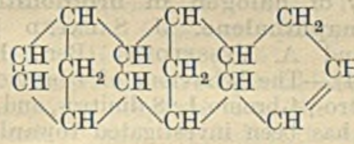
(I.)



$$CH_2{<}\begin{matrix}CH_2{\cdot}CH{\cdot}CH(CO_2H)\\ CH_2{\cdot}CH{\cdot}CH(CO_2H)\end{matrix}{>}CH_2$$

(II), derived by degradation of ring 2; it is also obtained by oxidation with nitric acid in the cold, the acid, m. p. 200°, prepared in this way by Wieland and Bergel being a mixture of II with the acid of m. p. 137°. "Di*cyclo*pentadiene monoxide" (Wieland and Bergel) is a mixture. The action of phenyl azide leads to the slow separation of an additive *compound*, m. p. 149°, presumably derived from the isomeride in which the oxygen is attached to ring 1; from the mother-liquors the isomeric *oxide*, m. p. 79—80°, may be separated, and is readily converted by palladium and hydrogen into a *dihydro*-derivative, m. p. 118—119° (the dihydro-derivative of the isomeric oxide has m. p. 98°; Bergel and Widmann give m. p. 91·5°).

It is suggested that further polymerisation occurs by 1 : 4-addition of another molecule of *cyclo*pentadiene to the reactive ethylenic linking in ring 2, proof of the structure III of tri*cyclo*pentadiene being afforded by the formation of an additive *compound*, m. p. 199—200° (decomp.), with phenyl azide. Polymerisation in this manner can continue indefinitely, on account of the highly reactive ethylenic linking (*), and accounts for the existence of each polymeride in one form only (cf. Staudinger and Bruson, A., 1926, 719). H. A. PIGGOTT.



(III.)

Aryl chlorosulphinates and aryl sulphites. M. BATTEGAY and L. DENIVELLE (Compt. rend., 1931, 192, 492—493).—The preparation of *phenyl chlorosulphinate*, b. p. 94—96°/13 mm., and of phenyl sulphite is described. A. A. LEVI.

Forced reaction between tetraphenylethylene and magnesium organohalides. H. GILMAN and S. A. HARRIS (Bull. Soc. chim., 1931, [iv], 49, 10—12).—No reaction appears to take place between tetraphenylethylene and magnesium phenyl bromide when heated in toluene at 60° for 20 hrs. or at 90—100° for 6 hrs. (cf. A., 1929, 1056), 86% of the tetraphenylethylene being recovered and a little triphenylcarbinol formed. Similarly with magnesium phenyl chloride at 60° and then at 110° for 23 hrs., 85·5% of the tetraphenylethylene is recovered unchanged. R. BRIGHTMAN.

Polarisation of the ethylenic linking. G. WITTIG (Ber., 1931, 64, [*B*], 437—444; cf. A., 1930, 762).—Examination of the criticisms of Bergmann (A., 1930, 1568) leads the authors to the conclusion that they neither prove nor disprove the interpretation of the fission of ααζζ-tetraphenylhexadiene propounded by Wittig and Leo (*loc. cit.*). Examination of ααδδ-tetraphenyl-Δ^{a}-butene, which, like ααζζ-tetraphenylhexadiene, offers two points of attack to the metal, proves that fission of the molecule occurs.

ααδδ-Tetraphenylbutadiene is converted by successive treatment with sodium–potassium alloy and methyl alcohol into ααδδ-tetraphenyl-Δ^{a}-butene, isomerised by sodium and amyl alcohol at 150° to ααδδ-*tetraphenyl*-Δ^{α}-*butene*, m. p. 97—98°, oxidised by potassium permanganate to ββ-diphenylpropionic acid, m. p. 153—154°. Alternatively, γ-phenylbutyrolactone is converted by aluminium chloride and benzene into *γγ-diphenylbutyric acid*, m. p. 105—106°. The corresponding *methyl* ester, b. p. 190—191°/12 mm., is transformed by magnesium phenyl bromide into ααδδ-*tetraphenylbutanol*, m. p. 149—150°, dehydrated by glacial acetic acid containing a little sulphuric acid to ααδδ-tetraphenyl-Δ^{α}-butene, m. p. 97—98°. With sodium–potassium alloy followed by methyl alcohol the hydrocarbon gives αα-diphenyl-Δ^{α}-propene and diphenylmethane.

s-Tetraphenylethane can be distilled unchanged under atmospheric pressure and yields only a small proportion of diphenylmethane at 400°. ααζζ-Tetraphenyl-$\Delta^{\alpha\epsilon}$-hexadiene is volatile without decomposition in a vacuum, but decomposes completely when distilled under atmospheric pressure with production of αα-diphenyl-Δ^{α}-propene. ααδδ-Tetraphenyl-Δ^{α}-butene occupies an intermediate position; at 400° it gives diphenylmethane and ααδδ-tetraphenylbutadiene. H. WREN.

Reactivity of halogen in bromonitro-derivatives of naphthalene. J. SALKIND [with E. LIFSCHITZ and A. VESSELOVA] (Ber., 1931, **64**, [*B*], 289—294).—The behaviour of 4-bromo-1-nitro-, 5-bromo-1-nitro-, 4-bromo-1 : 8-dinitro-, and 1-bromonaphthalene has been investigated towards sodium ethoxide in ethyl alcohol, benzamide in presence of copper powder and nitrobenzene, piperidine, and magnesium (with which reaction does not occur). The displaced bromine is determined titrimetrically. The nitro-group very appreciably increases the reactivity of bromine in position 4. If the halogen atom is in position 5, the effect of the nitro-group is much less pronounced and the bromine atom is little more mobile than that in 1-bromonaphthalene. In the case of 4-bromo-1 : 8-dinitronaphthalene, the influence of the second nitro-group is marked only in the reaction with piperidine; the hydrolysis with sodium ethoxide proceeds only a little more rapidly than that of 4-bromo-1-nitronaphthalene. It appears that the influence of the nitro-group extends only to substituents in the same ring and that the two rings of naphthalene are considerably independent of one another with respect to reactivity of their substituents. H. WREN.

Bromination of 4-nitro-1-methylnaphthalene. J. S. H. DAVIES and A. E. OXFORD (J.C.S., 1931, 220—221).—Bromination of 4-nitro-1-methylnaphthalene in ultra-violet light yields a nuclear-substituted *monobromo*-4-*nitro*-1-*methylnaphthalene*, m. p. 137·5—138·5°, and *tetrabromo*-4-*nitro*-1-*methylnaphthalene*, m. p. 189—190° (decomp.). α-Naphthylmethyl chloride (Wislicenus and Wren, A., 1905, i, 284) separated from alcohol at −15° as a solid, m. p. 29·5—30·5°. 2 : 4-*Dinitrobenzyl bromide*, m. p. 46—47°, is formed by the interaction of sodium bromide and 2 : 4-dinitrobenzyl chloride in methyl alcohol. G. DISCOMBE.

Sulphonation of naphthalene. C. B. RADCLIFFE and W. F. SHORT (J.C.S., 1931, 220).—Sulphonation of naphthalene with 98% sulphuric acid at 40—50° yields small quantities of naphthalene-1 : 5-disulphonic acid, contrary to the statements of Euwes (A., 1909, i, 707) and other workers, since the sodium naphthalene-1-sulphonate isolated yields on fusion with potassium cyanide small quantities of naphthylene-1 : 5-dicyanide. G. DISCOMBE.

***N*-Phenyl-*N′*-diethylaminocarbamide.** R. STOLLÉ and W. BRANDT (J. pr. Chem., 1931, [ii], **129**, 206).—The compound obtained by interaction of *as*-diethylhydrazine and phenylcarbimide is found by analysis to be N-*phenyl*-N′-*diethylaminocarbamide*, and not "phenylcarbimidediethylhydrazone" as stated by Hurd and Spence (A., 1927, 232).

H. A. PIGGOTT.

Sulphides and polysulphides of organic bases. T. G. LEVI (Gazzetta, 1930, **60**, 975—987).—The following compounds are described: phenyldiguanide hydrosulphide, $C_8H_{11}N_5,H_2S$, m. p. 143—147° (cf. Romani, A., 1924, i, 847); o-*tolyldiguanide hydrosulphide*, m. p. 123—126°; benzylamine polysulphide, $(CH_2Ph{\cdot}NH_2)_2H_2S_6$; *phenyldiguanide hexasulphide*, $(C_8H_{11}N_5)_2H_2S_6$, m. p. 130—135°; *diphenylguanidine hexasulphide*, $(C_{13}H_{13}N_3)_2H_2S,S_5$, m. p. 100—110°; *di*-o-*tolylguanidine heptasulphide*, $(C_{15}H_{17}N_3)_2H_2S,S_6$; as-*triphenylguanidine hexasulphide*, $(C_{19}H_{17}N_3)_2H_2S_6$, m. p. 108—112°.

T. H. POPE.

Nitration of *p*-thiocyanoacetanilide. J. W. DIENSKE (Rec. trav. chim., 1931, **50**, 165—183).—Nitration of *p*-thiocyanoacetanilide with absolute nitric acid at −10° affords 2 : 6-dinitro-4-thiocyanophenylnitroamine (I), decomp. (explosively) 70°, the structure of which is proved by oxidation of the thiocyano-group to a sulphonic acid by absolute nitric acid, conversion of the nitroamino-group into hydroxyl by alkali, and finally replacement of the sulphonic acid group by a nitro-group by heating with concentrated nitric acid, picric acid being thus obtained. By the Sandmeyer reaction on diazotised *p*-phenetidine is obtained p-*thiocyanophenetole*, m. p. 47·5—48° (not obtained by ethylation of *p*-thiocyanophenol), converted by nitric acid (*d* 1·4) at 50° into its 2-*nitro*-derivative, m. p. 85° (identical with a specimen obtained by the Sandmeyer reaction from 2-nitro-4-aminophenetole), together with some *p*-nitrophenetole and picric acid. Further nitration of 2-nitro-4-thiocyanophenetole with absolute nitric acid at 0° affords 2 : 6-*dinitro*-4-*thiocyanophenetole*, m. p. 77°, the constitution of which is proved by its conversion into picric acid by a method similar to that used with I (above). It is converted by warm alcoholic ammonia into 2 : 6-*dinitro*-4-*thiocyanoaniline*, m. p. 180°. By similar methods *p*-anisidine is converted into p-*thiocyanoanisole*, m. p. 35°, 2-*nitro*-4-*thiocyanoanisole*, m. p. 106° (together with *p*-nitroanisole and picric acid), and 2 : 6-*dinitro*-4-*thiocyanoanisole*, m. p. 93° (also converted into 2 : 6-dinitro-4-thiocyanoaniline). Attempted conversion of this compound into I (by absolute nitric acid at 0°) or *vice versa* (by denitrating with phenol) was unsuccessful. The m. p. of various derivatives of the type $X{\cdot}C_6H_4{\cdot}SCN$ are compared and agree with Franchimont's rules (A., 1897, ii, 542). J. W. BAKER.

3 : 5-Dimethoxyaniline. R. Seka and W. Fuchs (Monatsh., 1931, 57, 63—70).—Prolonged treatment of methyl 3 : 5-dimethoxybenzoate with liquid ammonia at the ordinary temperature gives 3 : 5-*dimethoxybenzamide*, m. p. 148—149°, converted by cold alkaline sodium hypobromite into 3 : 5-dimethoxyaniline, b. p. 177°/12 mm., m. p. 46° (*hydrochloride*, m. p. 210°; *chloroplatinate*, decomp. 223°; *picrate*, decomp. 165—170° after darkening at 150°; *picrolonate*, decomp. 230° after darkening at 220°; *benzoyl* derivative, m. p. 139°; *anisoyl* derivative, m.p. 119—120°). 3 : 5-*Dimethoxybenzhydrazide*, m. p. 168·5° (*hydrochloride*, m. p. 210°), is converted by the usual method into the azide, m. p. 50—51°, decomp. about 70°, which when heated with methyl alcohol furnishes *methyl* 3 : 5-*dimethoxyphenylcarbamate*, m. p. 43·5°.

H. Burton.

Aminodiphenylamine compounds. I. G. Farbenind. A.-G.—See B., 1931, 238.

Influence of halogens on the colour of azo-dyes. Spectral absorption of monoazo-dyes. D. G. Foster (J. Amer. Chem. Soc., 1931, 53, 654—660).—The absorption curves for solutions of sodium 1-*o*-, -*m*-, and -*p*-chloro-, 1-*o*-, -*m*-, and -*p*-bromo-, and 1-*o*-, -*m*-, and -*p*-iodo-benzeneazo-β-naphthol-3 : 6-disulphonates are all of the same type. The depth of the absorption band for the chloro- and bromo-derivatives increases in the order *m*, *o*, *p*, whilst the sequence for the iodo-compounds is *o*, *m*, *p*. The effect of position isomerism is the same as that recorded in the literature.

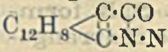
H. Burton.

***p*-Cymene. XIV. 2-*p*-Cymylhydrazine.** A. S. Wheeler and T. L. King (J. Amer. Chem. Soc., 1931, 53, 809—810).—The *acetate*, m. p. 63—64°, *lactate*, m. p. 134·5°, *oxalate*, m. p. 167°, and *benzoate*, m. p. 72·5°, of 2-*p*-cymylhydrazine are described; only the lactate is stable to water. m-*Nitrobenzaldehyde*-2-p-*cymylhydrazone* has m. p. 143°. 2-*p*-Cymylhydrazine is not a good reagent for the carbonyl group, since unstable products are obtained from many aldehydes and ketones.

H. Burton.

Monosubstituted carbohydrazides, their typical derivatives, and formation of heterocyclic compounds from them. P. C. Guha and M. A. Hye (J. Indian Chem. Soc., 1930, 7, 933—944).—Treatment of ethyl phenylcarbazinate (prepared from phenylhydrazine and ethyl chloroformate in aqueous pyridine) with hydrazine hydrate in alcohol at 120—125° gives 1-*phenylcarbohydrazide*, m. p. 154°:

$$NHPh\cdot NH\cdot CO_2Et+NH_2\cdot NH_2\longrightarrow NHPh\cdot NH\cdot CO\cdot NH\cdot NH_2.$$

1-o-*Tolyl*-, m. p. 153°, and 1-p-*tolyl-carbohydrazides*, m. p. 148—149°, are prepared similarly from *ethyl* o-*tolyl*-, m. p. 74—75°, and p-*tolyl-carbazinates*, m. p. 89—90°, respectively. Ethyl phenylcarbazinate does not react with phenylhydrazine or *o*-phenylenediamine. 1-*Phenylcarbohydrazones* and 1-o-*tolylcarbohydrazones* of the following substances are prepared (the m. p. of the latter are given in parentheses): *benzaldehyde*, m. p. 210—211° (201—202°); o-*chlorobenzaldehyde*, m. p. 212—213° (212—213°); p-*chlorobenzaldehyde*, m. p. 197—198° (198°); m-*bromobenzaldehyde*, m. p. 196—197° (216°); o-*nitrobenzaldehyde*, m. p. 208—209° (219°); m-*nitrobenzaldehyde*, m. p. 243—244° (211—212°); *salicylaldehyde*, m. p. 222—223° (218—219°); m-*phthalaldehyde*, m. p. 266—267° (236—237° [decomp.]); *acetone*, m. p. 83° (177°); *isatin*, m. p. 281° (decomp.) (251—252° [decomp.]). Phenanthraquinone and 1-phenylcarbohydrazide in boiling acetic acid give the *compound*,  $C_{12}H_8{<}\begin{smallmatrix}C\cdot CO\\ C\cdot N\cdot NHPh\end{smallmatrix}$, m. p. 285° (decomp.); reaction is presumed to occur by cyclisation of the intermediate phenylcarbohydrazone and subsequent loss of nitrogen.

1-Phenylcarbohydrazide reacts with carbon disulphide in alcoholic potassium hydroxide at the ordinary temperature, forming *potassium* 1-*phenylcarbohydrazidodithioformate*; when the mixture is boiled, potassium hydrogen sulphide is eliminated from the salt and 6-*thiol*-3-*keto*-1-*phenyl*-1 : 2 : 3 : 4-*tetrahydro*-1 : 2 : 4 : 5-*tetrazine*, m. p. 206°, results. *Ethyl* 1-*phenylcarbohydrazidoformate*, m. p. 202—203°, prepared from phenylcarbohydrazide and ethyl chloroformate, is decomposed by hydrochloric acid to hydrazine, phenylhydrazine, alcohol, and carbon dioxide. 1-*Phenylcarbohydrazidocarbonamide*, m. p. 223° (decomp.), is formed when the hydrazide is heated with carbamide at 130—135°, or treated with cyanic acid. Nitrous acid converts 1-phenylcarbohydrazide into 4-*hydroxy*-1-*phenylsemicarbazide*, NHPh·NH·CO·NH·OH, m. p. 86°.

The following 1-arylcarbohydrazidothiocarbonaryl(alkyl)amides are prepared from the requisite arylcarbohydrazide and aryl(alkyl)thiocarbimide in alcohol: 1-*phenylcarbohydrazido*-5-*thiocarbon-anilide* (I), m. p. 196° (decomp.), -o-*toluidide* (II), m. p. 175—176°, -p-*toluidide*, m. p. 196—197°, -m-4-*xylidide*, m. p. 179—180°, -*allylamide*, m. p. 196°, and -*methylamide*, m. p. 207°; 1-o-*tolylcarbohydrazido*-5-*thiocarbon-anilide*, m. p. 194—195° (decomp.), -o-*toluidide*, m. p. 189°, -p-*toluidide*, m. p. 213°, -m-4-*xylidide*, m. p. 186°, -*allylamide*, m. p. 197°, and -β-*naphthylamide*, m. p. 94—96°. 1-*Phenylcarbohydrazido*-5-*carbonanilide*, m. p. 218—219°, is unaffected by boiling hydrochloric acid, whilst I is similarly converted into 5-*anilino*-2-*keto*-2 : 3-*dihydro*-1 : 3 : 4-*thiodiazole*, m. p. 246°, also formed from I and ferric chloride solution. Potassium hydroxide solution converts I into 5-*anilo*-2-*keto*-2 : 3 : 4 : 5-*tetrahydro*-1 : 3 : 4-*oxdiazole*-2-*phenylhydrazone*, m. p. 244—245°. 5-o-*Toluidino*-2-*keto*-2 : 3-*dihydro*-1 : 3 : 4-*thiodiazole*, m. p. 220—221°, is prepared by the action of hydrochloric acid or ferric chloride on II. H. Burton.

Condensation products of phenylacethydrazide. R. Seka and S. P. Heilperin (Monatsh., 1931, 57, 45—51).—*Pyruvic acid phenylacethydrazone*, m. p. 168°, is obtained in 76·6% of the theoretical amount from aqueous solutions of pyruvic acid (1 mol.) and phenylacethydrazide (1 mol.). *Lævulic acid phenylacethydrazone*, m. p. 119°, is prepared similarly in 70% yield. Galactose and the hydrazide in boiling alcohol give 58% of *galactosephenylacethydrazone*, m. p. 192—193°. Diacetyl and the hydrazide react in aqueous solution to give a mixture of the *mono*-, m. p. 138°, and *di-phenylacethydrazones*, decomp. 254°. Benzil and the hydrazide at 120°/vac. furnish a mixture of the corresponding *mono*-,

m. p. 198—199°, and *di-phenylacethydrazones*, m. p. 236—237°. A phenylacethydrazone could not be obtained from ethyl acetoacetate. In most of the above reactions a small amount of s-*di*(*phenylacetyl*)-*hydrazine*, m. p. 236—237°, is also produced.

H. Burton.

Acyldiarylhydrazine series. II. Salt formation in the benzidine and semidine rearrangements. J. J. Ritter and F. O. Ritter (J. Amer. Chem. Soc., 1931, 53, 670—676; cf. A., 1930, 1175).—Monoacetylation of unsymmetrically substituted αβ-diarylhydrazines gives either α- or β- or mixtures of the α- and β-acetyl derivatives (cf. *loc. cit.*). The following have been prepared: α-phenyl-β-*p*-iodophenylhydrazine (α-, m. p. 135—136°, and β-, m. p. 156—157°, -*acetyl* derivatives); α-phenyl-β-*p*-carboxyphenylhydrazine (α-*acetyl* derivative, m. p. 207—208°); α-phenyl-β-*p*-ethoxyphenylhydrazine (β-*acetyl* derivative, m. p. 108°); α-*phenyl*-β-p-*acetoxyphenylhydrazine*, m. p. 117—118° (α-*acetyl* derivative, m. p. 105—106°). All m. p. are corr. Oxidation of the α-acetyl derivatives with potassium dichromate and acetic acid at the ordinary temperature gives the corresponding azo-derivatives: $\mathrm{NRAc{\cdot}NHR'} \longrightarrow \mathrm{NRAc{\cdot}NR'{\cdot}OH} \longrightarrow \mathrm{Ac{\cdot}OH + NR{:}NR'}$. Similar oxidation of the β-acetyl derivatives affords intensely coloured products (red or violet), apparently owing to the presence of the anilino-group. Various α-phenyl-β-arylhydrazines when suspended in 10% hydrochloric acid at the ordinary temperature furnish blue or violet solutions owing to atmospheric oxidation. This oxidation is parallel to the oxidation of the above acetyl derivatives, *i.e.*, the αβ-diarylhydrazines yielding β-acetyl derivatives give intensely coloured solutions, whilst those furnishing α-acetyl derivatives do not. It is assumed that salt formation occurs on either the α- or β-nitrogen atoms; the subsequent course of the reaction is the same as for the acetyl derivatives. Some of the diarylhydrazines give mixtures of salts. Analysis of the results of Jacobsen (A., 1922, i, 589, 596) suggests that similar salt formation is involved in the benzidine and semidine rearrangements. Those diarylhydrazines yielding mixtures of α- and β-acetyl derivatives give, under Jacobsen's conditions (*loc. cit.*), approximately equal amounts of diphenyl and semidine derivatives.

H. Burton.

Oxidation of propenyl derivatives by means of diazo-compounds. A. Quilico (Atti R. Accad. Lincei, 1930, [vi], 12, 341—344).—The mechanism suggested by Angeli and Polverini (A., 1930, 906) for oxidations by means of diazo-compounds (A., 1928, 997; 1929, 559; 1930, 82) is discussed. If the oxidation of a propenyl compound by a normal diazohydroxide proceeds according to the two schemes $\mathrm{CHR{:}CHMe + Ph{\cdot}N_2{\cdot}OH} \longrightarrow$ (1) $\mathrm{CHR{:}N{\cdot}NHPh + Me{\cdot}CHO}$ and (2) $\mathrm{R{\cdot}CHO + CHMe{:}N{\cdot}NHPh}$, the aromatic aldehydephenylhydrazone and acetaldehyde formed should be accompanied by the aromatic aldehyde and acetaldehydephenylhydrazone. The latter could not be found, but the formazyl compound, $\mathrm{NPh{:}N{\cdot}CMe{:}N{\cdot}NHPh}$, resulting from the interaction of the acetaldehydephenylhydrazone with the diazohydroxide present, is obtained. Similarly, free anisaldehyde is found among the products of the interaction of *p*-nitrobenzenediazonium sulphate and anethole, and free piperonaldehyde among those of the interaction of *p*-nitrobenzenediazonium sulphate and *iso*safrole.

T. H. Pope.

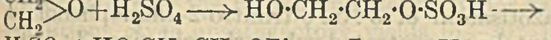
Behaviour of ketonehydrazones towards diazonium salts. M. Busch and K. Schmidt (J. pr. Chem., 1931, [ii], 129, 151—162).—The phenylhydrazones of aromatic and mixed aliphatic–aromatic ketones couple with diazonium salts in the *p*-position in the phenylhydrazone nucleus, or, if this is already substituted, in the *o*-position, but with less readiness; if both the *p*- and an *o*-position are occupied, the hydrazone residue is replaced by the diazonium salt, yielding, *e.g.*, with benzenediazonium chloride, the *p*-benzeneazophenylhydrazone and a new diazonium salt: $\mathrm{CPhMe{:}N{\cdot}NH{\cdot}C_8H_9(2:4) + Ph{\cdot}N_2Cl} \longrightarrow \mathrm{C_8H_9{\cdot}N_2Cl + HCl}$. Nitrated diazonium salts, with some exceptions, also replace the hydrazone radical, even when unsubstituted. Thus acetophenonephenylhydrazone (and also the *p*-bromophenylhydrazone) and *p*-nitrobenzenediazonium chloride give acetophenone-*p*-nitrophenylhydrazone, but acetophenonebenzylphenylhydrazone reacts normally, as also does benzophenonephenylhydrazone, which reacts only with difficulty. Deoxybenzoinphenylhydrazone behaves like the acetophenone derivative. The reaction proceeds best in all cases in alcoholic solution or in a mixture of alcohol and benzene. The presence of water is deleterious, and tends to cause hydrolysis. No reaction occurs in alkaline solution under the conditions used by von Pechmann (A., 1894, i, 457) for the aldehydehydrazones.

The following are described: *acetophenone*-p-*benzeneazophenylhydrazone*, m. p. 161° (*hydrochloride*), -4-*bromo*-2-*benzeneazophenylhydrazone*, m. p. 183°, -*benzylphenylhydrazone*, m. p. 58° (diffuse), -p-*benzeneazophenylbenzylhydrazone* (*hydrochloride*), -4-*nitro*-2-p-*nitrobenzeneazophenylhydrazone*, m. p. 300° (sinters 290°) (from the *as*-*m*-xylylhydrazone and *p*-nitrobenzenediazonium chloride; a nitrobenzenediazo-group has entered the hydrazone nucleus, thus forming an exception to the general rule), -p-*nitrobenzeneazophenylbenzylhydrazone*, m. p. 130°; *benzophenone*-p-*nitrobenzeneazophenylhydrazone*, m. p. 194—196°; *deoxybenzoin-benzeneazophenylhydrazone*, m. p. 138°, and -p-*nitrophenylhydrazone*, m. p. 160°.

H. A. Piggott.

Combustion of activated charcoal in the vapours of organic compounds containing oxygen. N. D. Zelinski and M. V. Gaverdovskaja (Ber., 1931, 64, [*B*], 435—437; cf. A., 1928, 747).—Secondary and primary alcohols are converted into hydrocarbons by passage over activated charcoal at 300°, the yields being nearly quantitative. The following examples are cited: *cyclo*hexanol to *cyclo*hexane; *o*- and *m*-methyl*cyclo*hexanol to *o*- and *m*-methyl*cyclo*hexane; *cyclo*hexylethyl alcohol to ethyl*cyclo*hexane; phenylethyl alcohol to ethylbenzene; diphenylcarbinol to diphenylmethane. Alcoholic oxygen oxidises activated charcoal more energetically and at a lower temperature than molecular oxygen attacks ordinary charcoal; the gaseous product, as with the more easily reduced oxides, is carbon dioxide. *cyclo*Hexylmethyl alcohol is not affected under the prescribed conditions. Benzyl alcohol behaves exceptionally, yielding toluene, benzaldehyde, carbon dioxide and monoxide, oxygen, hydrogen, and methane. The monoxide is a normal product of the reduction of carbon dioxide by activated charcoal. H. Wren.

Reactions of heterocyclic compounds with phenols. Reaction of ethylene oxide with phenol. R. A. Smith and J. B. Niederl (J. Amer. Chem. Soc., 1931, **53**, 806—808).—Ethylene oxide (1 mol.) and phenol (1 mol.) react in presence of sulphuric acid (0·2 mol.) at the ordinary temperature during 1 week forming *o*-vinylphenol (I), also obtained when phenyl β-hydroxyethyl ether is treated with sulphuric acid. The following reactions probably occur :



$$\begin{matrix}CH_2\\CH_2\end{matrix}\!\!>O+H_2SO_4\longrightarrow HO{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}SO_3H\xrightarrow{Ph\cdot OH}$$
$$H_2SO_4+HO{\cdot}CH_2{\cdot}CH_2{\cdot}OPh\longrightarrow I.$$

H. Burton.

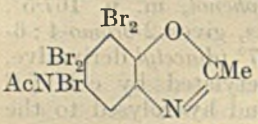
Behaviour of aceto-*p*-phenetidide towards chlorine and bromine. E. Bureš and J. Kovařovičová (Časopis Československ. Lék., 1930, **10**, 197—202, 233—239; Chem. Zentr., 1930, ii, 2775).—By the action of bromine on aceto-*p*-phenetidide 3 : 5-dibromoaceto-*p*-phenetidide is formed; dry gaseous chlorine attacks positions 2, 3, 5, and 6. The following derivatives of phenetole were prepared : 3 : 5-dibromo-4-acetamido-, m. p. 175°; 3 : 5-dibromo-4-amino-, m. p. 54° (picrate, m. p. 145°); 3 : 5-dibromo-4-dimethylamino-, m. p. 84°; 3 : 5-dibromo-4-benzamido-, m. p. 159°; 3 : 5-dibromo-4-ethylamino-, m. p. 91°; 3 : 5-dibromo-4-diacetamido-, m. p. 108°; 3 : 5-dibromo-, b. p. 267°; 3 : 4 : 5-tribromo-, m. p. 72°; 3 : 5-dibromo-4-iodo-, m. p. 99°; 4-chloro-3 : 5-dibromo-, m. p. 42—44°; 3 : 5-dibromo-4-nitro-, m. p. 128°; 3-bromo-5-nitro-4-amino-, m. p. 108°; 3 : 4 : 5-tribromo-2-nitro-, m. p. 52—53°; 3 : 5-dibromo-4-amino-, m. p. 53—54°; 2 : 3 : 5 : 6-tetrachloro-4-acetamido-, m. p. 226°; 2 : 3 : 5 : 6-tetrachloro-4-amino-, m. p. 96°; 2 : 3 : 5 : 6-tetrachloro-, m. p. 56°; 2 : 3 : 4 : 5 : 6-pentachloro-, m. p. 75°; 2 : 3 : 5 : 6-tetrachloro-4-bromo-, m. p. 81°; 2 : 3 : 5 : 6-tetrachloro-4-iodo-, m. p. 79°. 2 : 3 : 5 : 6-Tetrachlorobenzoquinone sublimes without melting. A. A. Eldridge.

Action of bromine on phenols. G. Heller [with W. Dietrich, T. Hemmer, H. Kätzel, E. Rottsahl, and P. G. Zambalos] (J. pr. Chem., 1931, [ii], **129**, 211—256).—Phenols and their derivatives are classified according to their behaviour with bromine in glacial acetic acid. The following general types of behaviour are observed : (1) no action (usually where the hydroxyl group is protected), (2) simple substitution which may or may not involve the displacement of other substituents, and, if it proceeds to completion, finally gives pentabromophenol, (3) bromination of acetamido-groups with the consequent formation of stable glyoxaline and oxazole derivatives, (4) oxidation to a quinone, sometimes followed by bromination to bromoanil, and (5) formation of tetrabromodiketo*cyclo*pentene or polybromoacetones by ring-fission. The last reaction seems characteristic of derivatives of *o*-aminophenol, corresponding derivatives of *m*- and *p*-aminophenols showing no tendency to ring-fission under the conditions employed.

4 : 6-Dinitro-3-acetamidophenyl acetate, prepared by nitration of diacetyl-*m*-aminophenol in acetic anhydride, is unaffected by bromine in acetic acid at 100°, but the corresponding *phenol*, m. p. 167·5°, obtained by alkaline hydrolysis, gives 2-*bromo*-4 : 6-*dinitro*-3-*aminophenol*, m. p. 207° (*diacetyl* derivative, m. p. 222°, completely deacetylated by cold [?] concentrated sulphuric acid, and hydrolysed to the -*acetamidophenol*, m. p. 223·5°, by dilute sodium hydroxide). This is converted by nitric acid (*d* 1·42), or by diazotisation and decomposition of the diazo-compound, into 2-*bromo*-4 : 6-*dinitroresorcinol*, m. p. 192·5—193°. Bromination of 4-nitro-2-acetamidoresorcinol gives the 6-*bromo*-derivative, m. p. 173—174°. 6-Nitro-3-acetamidophenol is converted at 100° into 2-*bromo*-, m. p. 230°, and 2 : 4-*dibromo*-6-*nitro*-3-*aminophenol*, m. p. 199—200°, bromination ceasing at the dibromo-stage; the products were identified by elimination of the amino-group (diazo-reaction). The preparation of 4 : 6-dibromo-2-nitrophenol, m. p. 117°, by Goldstein's method (J. Russ. Chem. Soc., 1878, **10**, 354) presented difficulties, but it was readily formed by bromination of *o*-nitrophenol in the usual way. Bromination of 3 : 5-dinitro-4-acetamidophenol at the ordinary temperature gives 2 : 6-*dibromo*-3 : 5-*dinitro*-4-*acetamidophenol*, decomp. 274·5°; the corresponding *aminophenol*, m. p. 138°, obtained by deacetylation with concentrated sulphuric acid at 100°, gives on further bromination bromoanil. From 4-nitro-3-acetamidophenol, the 6-*bromo*-derivative, m. p. about 295° (decomp.), is readily produced; it is hydrolysed by aqueous-alcoholic potassium hydroxide to 6-*bromo*-4-*nitro*-3-*aminophenol*, m. p. 244° (decomp.) (*potassium* salt), identified by conversion into 2-bromo-4-nitrophenol. More drastic bromination of the original substance gives 2 : 6-*dibromo*-4-*nitro*-3-*acetamidophenol*, m. p. 192—195°, and -3-*aminophenol*, m. p. 162·5°; the latter is produced from the former by alkaline hydrolysis, and from 6-bromo-4-nitro-3-aminophenol by bromination, and is readily converted into 2 : 6-dibromo-4-nitroresorcinol by the diazo-reaction. Exhaustive bromination of 4-nitro-3-acetamidophenol gives tetrabromophenol, m. p. 140° (Benedict, A., 1880, 246), which in presence of ferric chloride at 60° may be brominated to pentabromophenol.

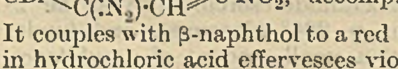
5-Bromo-, m. p. 192°, and 6-*bromo*-2 : 4-*dinitroresorcinol*, m. p. 89°, and 2-bromo-4 : 6-dinitroresorcinol are the products of bromination of the corresponding nitroresorcinols, accompanied by tetrabromoresorcinol in the case of the 2 : 4-dinitro-compound. 6-Nitro-4-acetamidoresorcinol gives the 2-*bromo*-derivative, m. p. 226° (decomp.), and (under vigorous conditions) a small amount of a *substance*, m. p. 82—84°. The preparation of *tetrabromopyrocatechol* and *tetrabromo*-o-*benzoquinone* from 3- and 4-nitropyrocatechol is described. 3-Nitro-4-acetamidophenol and its acetate are similarly brominated to pentabromophenol, but 3-nitro-4-aminophenol gives bromoanil.

By graduated bromination of 2 : 4-diacetamidophenol 6-*bromo*-, m. p. 215° (I), and 5 : 6-*dibromo*-2 : 4-*diacetamidophenol* (II), m. p. 208° (+2H_2O, m. p. 188·5°), 3 : 5 : 6-*tribromo*-2-*acetamidobenzoquinone*, golden-yellow, m. p. 198° (readily reduced by sulphurous acid to the corresponding *quinol*, m. p. 212°), the *substance* III, decomp. indef. above 180°, and tetrabromodiketo*cyclo*pentene (IV), are produced. By oxidation with dilute nitric acid I and II are converted into 6-*bromo*-, m. p. 183°, and 5 : 6-*dibromo*-2-*acetamidobenzoquinone*, m. p. 213°, the former of which is oxidised smoothly by an excess of bromine in acetic acid to IV. The compound III gives with 2*N*-sodium hydroxide at the ordinary temperature 5 : 6-*dibromo*-4-*acetamido*-1-*methylbenzoxazole*, m. p. 245°, which is readily reconverted into III by bromine in acetic acid, is hydrolysed by fuming hydrochloric acid to II, and is oxidised by nitric acid (*d* 1·4) to 5 : 6-dibromo-2-acetamidobenzoquinone. A similar series of changes is undergone by 2 : 6-*diacetamidophenol*, m. p. 170° (from the diaminophenol hydrochloride, sodium sulphite, and acetic anhydride), the following being isolated: 3 : 5(?)-*dibromo*-2 : 6-*diacetamidophenol*, m. p. 208°, a *monobromo*-compound, m. p. 215° (decomp.), and 3 : 4 : 5-*tribromo*-6-*acetamido*-1-*methylbenzoxazole*, m. p. 226° [*perbromide* (analogous to III), m. p. about 161—163° (decomp.)]. 2 : 6-*Diacetamidobenzoquinone*, orange, m. p. 270° (decomp.) (*anilide*, bluish-black, m. p. 202°), is produced by oxidation either of 2 : 6-diacetamido- or 2 : 4 : 6-*triacetamido-phenol*, m. p. 265°, with nitric acid (*d* 1·5) at a low temperature. 2 : 4 : 6-Triacetamidophenol gave no halogen derivative on bromination. 6-Nitro-2 : 4-diacetamidophenol gives 3 : 5 : 6-tribromo-2-acetamidobenzoquinone (above) and, under more vigorous conditions, IV.


(III.)

6-*Bromo*-2 : 4-*dinitro*-3-*aminophenol* (*mono*-, decomp. 221°, and *di-acetyl* compounds, m. p. 161°) is converted by further bromination into bromoanil, by diazotisation or by nitric acid (*d* 1·5) in the cold into 6-bromo-2 : 4-dinitroresorcinol (above), and by nitric acid (*d* 1·42) in the warm into styphnic acid. Bromoanil is the sole bromination product of 2 : 6-dinitro-4-acetamidophenol and 2 : 5-dinitroquinol.

Nitration of 2-nitro-4-acetamidophenol according to the directions of Meldola and Hay (J.C.S., 1909, 95, 1381) gave, not a dinitro-, but 2 : 3 : 5-*trinitro*-4-*acetamidophenol*, m. p. 171° [+β-naphthol, m. p. 181° (*loc. cit.*)]. The corresponding free aminophenol, obtained by hydrolysis with concentrated sulphuric acid, is converted by bromination into 5-*bromo*-2-*nitro*-4-*diazo*-1-*keto*-1 : 4-*dihydrobenzene*,


$\mathrm{CBr}{<}\begin{matrix}\mathrm{CH}\text{——}\mathrm{CO}\\ \mathrm{C(:N_2)\cdot CH}\end{matrix}{>}\mathrm{C\cdot NO_2}$, decomp. 186° (explodes).

It couples with β-naphthol to a red dye, and a solution in hydrochloric acid effervesces violently when boiled with cuprous chloride, and deposits a *substance*, m. p. 80°. A similar substance, exploding at 170°, is obtained from the acetyl compound; it appears to be different from the above, giving a *substance*, m. p. 122°, when boiled with cuprous chloride and hydrochloric acid. With a large excess of bromine the acetyl compound gives bromoanil. A similar behaviour appears to be shown by 3 : 5 : 6-*trinitro*-2-*aminophenol*, decomp. explosively about 167° (the *acetamido*-compound, m. p. 151°, is prepared by nitration of 5-*nitro*-2-*acetamidophenol*, m. p. 258—259°), the *diazo-keto*-compound exploding at 180°, and forming a cherry-red dye with alkaline β-naphthol; the acetyl derivative, however, appears to decompose on bromination, a *bromo*-compound, m. p. 218° (decomp.), being isolated in small amount.

Bromination of 4-*nitro*-2-*acetamidophenol*, decomp. 267°, gives the 6-*bromo*-derivative, m. p. 206° (decomp.), which, on further bromination, gives 3 : 5 : 6-*tribromo*-2-*aminobenzoquinone* 4-*dibromide* (?), m. p. 216° (decomp.) (*acetyl* derivative, m. p. 208°), and IV. The first is synthesised by partial reduction of 6-bromo-2 : 4-dinitrophenol, and acetylation of the 6-*bromo*-4-*nitro*-2-*aminophenol*, m. p. 162° (*ammonium* salt), thus produced. 4 : 6-Dinitro-2-acetamidophenol (by nitration of *o*-acetamidophenol) is decomposed by bromine to IV.

Diazotisation of 3 : 5 : 6-trinitro-2-aminophenol in moderately concentrated sulphuric acid gives 3 : 5 : 6-*trinitro*-2-*diazo*-1-*keto*-1 : 2-*dihydrobenzene* (explosive), which is decomposed by boiling alcohol to 3 : 5 : 6-trinitrophenol, and forms a reddish-violet crystalline dye with β-naphthol: short heating with alcohol gives 5 : 6-*dinitro*-3-*ethoxy*-2-*diazo*-1-*keto*-1 : 2-*dihydrobenzene*, m. p. 166° (decomp.), which gives a red dye with β-naphthol. Bromination of 5-nitro-2-acetamidoquinol (cf. this vol., 488) gives 5 : 6-dibromo-2-acetamidobenzoquinone (above), *tribromo*-2-*acetamidobenzoquinone*, m. p. 189—190° (decomp.), and IV. 2 : 5-*Diacetamidotetra-acetoxybenzene*, m. p. 216° (decomp.), gives 2 : 5-diacetamidodihydroxybenzoquinone (A., 1888, 943), whilst 3 : 4-diacetamidophenol gives successively the 6-*bromo*-, decomp. 258°, and 2 : 6-*dibromo*-derivative, m. p. 223° (decomp.), and 4 : 6-*dibromo-5-hydroxy-2-methylbenziminazole* (*hydrobromide*).

2 : 6-*Diacetamidobenzoquinone*, m. p. 295°, is obtained by oxidation with air in alkaline solution, or with ferric chloride, of the *quinol*, m. p. 240° (decomp.), itself prepared by acetylation of the reduction product of 2 : 6-dinitroquinol. Both it and the quinol give 3-*bromo*-, m. p. 225° [*quinol*, m. p. 198° (decomp.)], and 3 : 5-*dibromo*-2 : 6-*diacetamidobenzoquinone*, m. p. 201° [*quinol*, m. p. 213° (decomp.)], and, with a large excess of bromine, hexabromoacetone. Nitroaminotetrahydroxybenzene (cf. A., 1885, 779) (*di*-, decomp. about 214°, and *penta-acetyl* derivative, m. p. 194°) gives with bromine in acetic acid a yellow additive *compound*, from which it is readily regenerated; an excess of bromine yields a *substance*, $C_6H_3O_4NBr_2$, and ammonium bromide, and, under still more drastic conditions, dibromotetrahydroxybenzene, polybromoacetone, and bromoform.

Improved methods for the preparation of *o*-acetamidophenyl acetate and 3-nitro-2-aminophenol are given. From the latter by bromination in the usual way 6-*bromo*-, m. p. 233°, and 4 : 6-*dibromo*-3-*nitro*-2-*aminophenol*, m. p. 182°, 4 : 5 : 6-*tribromo*-3-*nitro*-1-*dibromomethyl*-, m. p. 233°, and -1-*tribromomethylbenzoxazoles*, m. p. 172°, are obtained; the last two compounds may also be prepared by bromination of 3-nitro-1-methylbenzoxazole and 3-nitro-2-acetamidophenyl acetate, respectively. A new aniline derivative of IV, probably 4 : 5-*dibromo*-2 : 2-*dianilino*-3-*anilino*cyclo*pentan*-1-*one*, m. p. 261° (decomp.), is described.

H. A. PIGGOTT.

4-Nitro-4′-methoxystilbene. A correction. J. T. Hewitt and W. Lewcock (J.C.S., 1931, 444).—This compound has m. p. 132° and not 162° as previously stated in error (Hewitt and others, J.C.S., 1912, 101, 608). J. W. Baker.

Naphthalene series. III. Preparation of 3-amino-2-naphthyl methyl ether. G. B. Jambuserwala, S. Holt, and F. A. Mason (J.C.S., 1931, 373—377).—Methyl sulphate and 20% sodium hydroxide convert 2-hydroxy-3-naphthoic acid into the 2-methoxy-acid (96% yield), from which by treatment with thionyl chloride the acid chloride is obtained, and the latter converted by dry ammonium carbonate in dry benzene into 2-methoxy-3-naphthoamide. Conversion of this into 3-amino-2-naphthyl methyl ether by the Hoffmann reaction under various conditions gives unsatisfactory yields (5—20%), but satisfactory results are obtained by the Curtius method. Ethyl 2-methoxy-3-naphthoate, b. p. 298°/18 mm. (Auwers and Frühling, A., 1921, ii, 230, give b. p. 208°/18 mm.), is converted by hydrazine hydrate into the *hydrazide*, m. p. 121—124°, converted by 2-methoxy-3-naphthoyl chloride in benzene into *di*(2-*methoxy*-3-*naphth*)*hydrazide*, m. p. 248—250° (corr.), and by the appropriate aldehyde into *benzylidene*-, m. p. 222·5° (corr.), m-, m. p. 223—224° (corr.), and o-, m. p. 185—186° (corr.), -*nitrobenzylidene*-, and 4′-*hydroxy*-2 : 2′-*dimethoxybenzylidene*-, m. p. 211—212° (corr.), -3-*naphthhydrazide*. The original monohydrazide is converted by ethyl nitrite and anhydrous hydrogen chloride in warm absolute alcohol into *ethyl* 2-*methoxy*-3-*naphthylcarbamate*, m. p. 104—105° (corr.), which is hydrolysed by boiling 40% aqueous potassium hydroxide to 3-amino-2-naphthyl methyl ether in 92% yield. The last-named is converted by the Sandmeyer reaction into 3-*chloro*-2-*naphthyl methyl ether*, m. p. 78·5°, hydrolysed by hydriodic acid to 3-chloro-β-naphthol. J. W. Baker.

Naphthalene series. IV. Preparation and properties of β-naphthol-3-sulphonic acid. S. Holt and F. A. Mason (J.C.S., 1931, 377—381).—Diazotisation of 3-amino-β-naphthyl methyl ether and treatment of the diazonium solution with an excess of sulphur dioxide and chemically prepared copper affords 2-*methoxynaphthalene*-3-*sulphinic acid*, m. p. 133—134°, which condenses in warm alcoholic solution with 2 : 4-dinitrochlorobenzene to give 2 : 4-*dinitrophenyl*-2-*methoxy*-3-*naphthylsulphone*, m. p. 213—214°, which is oxidised by potassium permanganate in acetone suspension to 2-*methoxynaphthalene*-3-*sulphonic acid* (*potassium* salt; *sulphonyl chloride*, m. p. 137—138°; *amide*, m. p. 113°; and *anilide*, m. p. 173—174°). This does not couple with diazonium salts, but is readily hydrolysed by dilute hydrochloric acid (1 : 1) to β-*naphthol*-3-*sulphonic acid* [*sodium* $+H_2O$, *aniline*, m. p. 241—242°, and α-*naphthylamine*, m. p. 247—248°, salts; *amide*, m. p. 110°, and *anilide*, m. p. 112° (decomp.), not obtained pure], which with nitrous acid affords 1-*nitroso*-β-*naphthol*-3-*sulphonic acid*, decomp. 268°. β-Naphthol-3-sulphonic acid couples with diazotised amines and thus are obtained the *azo*-dyes from aniline, *p*-nitroaniline, *m*-xylidine, α-naphthylamine, and dianisidine, which dye wool somewhat deeper shades than does the corresponding 2 : 6-sulphonic acid, the peaks of the absorption curves being shifted a little in the direction of longer wave-lengths compared with those in the latter acid. J. W. Baker.

Preparation of *iso*eugenol from clove oil. R. Priester (Riechstoffind., 1930, 5, 83—85, 108—109; Chem. Zentr., 1930, ii, 3206).—Glycerol and ethylene glycol are suitable diluents. Eugenol (30 g.), water (50 g.), potassium hydroxide (15 g.), and glycerol (10 g.) are heated for 45 min. at 180° and then for 15 min. not above 186°; only 1 g. of resin is produced and good conversion is effected, the product having n_D^{20} 1·5744. A. A. Eldridge.

Bromo*iso*vanillin. H. Pauly (Ber., 1931, 64, [*B*], 503; cf. A., 1916, i, 150).—A reply to Henry and Sharp (A., 1930, 1602). H. Wren.

Relative directive powers of groups of the forms RO and RR′N in aromatic substitution. IX. Nitration of *p*-cetyloxyanisole and *p*-benzyloxyanisole. J. C. Smith (J.C.S., 1931, 251—258).—The action of methyl-alcoholic sodium methoxide on a boiling acetone solution of cetyl iodide and quinol monomethyl ether gives 4-*cetyloxyanisole*, m. p. 67·9°, nitrated with nitric (*d* 1·42) and acetic acids at 0° or 25° to a mixture of 2- (dimorphous), m. p. 62·5° (prisms) and 63·9° (needles), and 3-, m. p. 49·5°, -*nitro*-4-*cetyloxyanisole*, containing 67·9% of the latter. The composition of the product was determined by thermal analysis, the 2- and 3-nitro-compounds being synthesised by similar methods from 3- and 2-nitro-4-methoxyphenol, respectively. They are resistant to alkaline hydrolysis and form a complex binary system, the curve indicating the existence of a compound of the type AB. 4-*Benzyloxyanisole*, m. p. 69·7° (plates, unstable) and 71·5° (needles), is similarly prepared, using benzyl chloride at 90°, and by nitration under similar conditions affords a mixture of 2-, m. p. 59·8°, and 3-, m. p. 61·3°, -*nitro*-4-*benzyloxyanisole* (similarly synthesised) containing 51% (at 28°) and 51·4% (at 14°) of the 3-nitro-isomeride. These nitro-compounds give a normal m.-p. curve. On the basis of these data the values of the relative directive powers of the cetyloxy- and benzyloxy-groups are, respectively, 210 and 107 (OMe=100 : cf. Robinson and Smith, A., 1926, 397), and the results are in agreement with the requirements of the theory of Allan, Oxford, Robinson, and Smith (*ibid.*, 397). J. W. Baker.

Phenyl ethers. M. Oesterlin (Monatsh., 1931, 57, 31—44).—*p*-Bromoanisole and potassium phenoxide condense in presence of copper-bronze (Naturkupfer *C*) at 200—210° to give *p*-methoxydiphenyl ether, b. p. 163—165°/14 mm., which is brominated with a bromide–bromate mixture in presence of dilute sulphuric acid and carbon disulphide to 4-*bromo*-4′-*methoxydiphenyl ether*, m. p. 85°, and demethylated by aluminium chloride in benzene to p-*hydroxydiphenyl ether*, m. p. 84°. This condenses (as above) with *p*-bromoanisole, forming 4-*phenoxy*-4′-*methoxydiphenyl ether*, m. p. 82°, demethylated by the above method to 4-*hydroxy*-4′-*phenoxydiphenyl ether*, m. p. 87°. Quinol monomethyl ether and *p*-bromoanisole afford 4 : 4′-*dimethoxydiphenyl ether*, m. p. 102°, demethylated by aluminium chloride in xylene to the 4 : 4′-dihydroxy-derivative, m. p. 160°. Quinol monomethyl ether and *p*-dibromobenzene furnish *quinol di*-p-*methoxyphenyl ether*, m. p. 136—137° (also formed from quinol monomethyl ether and 4-bromo-4′-methoxydiphenyl ether), convertible into *quinol di*-p-*hydroxyphenyl ether*, m. p. 188°. 4 : 4′-*Di*-p-*methoxyphenoxydiphenyl ether*, m. p. 164°, is prepared from 4 : 4′-dibromodiphenyl ether and quinol monomethyl ether. *p*-Nitrodiphenyl ether, prepared from potassium phenoxide and *p*-chloronitrobenzene in presence of copper powder at 130—160°, is reduced by iron powder and acetic acid to *p*-aminodiphenyl ether. The acetyl derivative, m. p. 131° (lit. 127°), of this gives with nitric (*d* 1·52) in acetic acid 3-*nitro*-4-*acetamidodiphenyl ether*, m. p. 104°, hydrolysed by aqueous-alcoholic barium hydroxide to 3-*nitro*-4-*aminodiphenyl ether*, melts partly at 47—48° and resolidifies with m. p. 81°, and reduced by sodium hyposulphite in 50% alcohol to 3-*amino*-4-*acetamidodiphenyl ether*, m. p. 124°. 3 : 4-*Diaminodiphenyl ether*, m. p. 67° (*hydrochloride*, m. p. 216°), and 3 : 3′-dinitrobenzil in alcohol give 6-*phenoxy*-2 : 3-*di*-p-*nitrophenylquinoxaline*, m. p. 195—196°. *p*-Hydroxydiphenyl ether and *p*-chloronitrobenzene afford 4-*nitro*-4′-*phenoxydiphenyl ether*, m. p. 194°, reduced by stannous chloride and hydrochloric acid to 4-*amino*-4′-*phenoxydiphenyl ether*, m. p. 84° (*acetyl* derivative, m. p. 148°). 3-*Nitro*-4-*acetamido*-4′-*phenoxy*- and 3 : 4-*diamino*-4′-*phenoxy-diphenyl ethers* have m. p. 124° and 95°, respectively. 4-*Nitro*-4′-*methoxydiphenyl ether*, m. p. 111—112° (from quinol monomethyl ether and *p*-chloronitrobenzene), is reduced by iron powder and acetic acid to 4-*amino*-4′-*methoxydiphenyl ether*, m. p. 81—82° (*hydrochloride*, m. p. 212°; *sulphate*, m. p. 220°), convertible by way of its *acetyl* derivative, m. p. 131°, into 3-*nitro*-4-*acetamido*-4′-*methoxydiphenyl ether*, m. p. 106° (free *base*, m. p. 76—77°). 3 : 4-*Diamino*-4′-*methoxydiphenyl ether* has m. p. 105°. 4 : 4′-Dihydroxydiphenyl ether and *p*-chloronitrobenzene (2 mols.) afford 4 : 4′-*di*-p-*nitrophenoxydiphenyl ether*, m. p. 136°, reduced by iron powder and acetic acid to 4 : 4′-*di*-p-*aminophenoxydiphenyl ether*, m. p. 109° (*diacetyl* derivative, m. p. 265—266°).

Phenol and *p*-hydroxydiphenyl ether could not be condensed with 4-bromo-2-nitroaniline at low temperatures; at higher temperatures, resinification occurred. H. Burton.

Nitrogen derivatives of primary phenylethyl alcohol. S. Sabetay, J. Bléger, and (Mme.) Y. de Lestrange (Bull. Soc. chim., 1930, [iv], 49, 3—7).—Nitration of β-phenylethyl alcohol in acetic anhydride in presence of a few drops of sulphuric acid with nitric acid (*d* 1·49) at 35—40°, and hydrolysis of the mixed β-nitrophenylacetates with 2% methyl-alcoholic hydrogen chloride affords a mixture of β-*p*-nitrophenylethyl alcohol and β-o-*nitrophenylethyl alcohol*, b. p. 144—147°/1·3 mm., d^{22} 1·253, n_D^{22} 1·562 (*benzoate*, m. p. 55°). The latter is separated by vacuum distillation of the oil filtered from the solid *p*-isomeride. Reduction with zinc dust in presence of calcium chloride gives an 83% yield of β-o-*aminophenylethyl alcohol*, b. p. 147—148°/3·5 mm., n_D^{19} 1·5849 [*hydrochloride*, m. p. 126·5° (+H_2O, m. p. 80°); N-*acetate*, m. p. 103—103·5°, hydrolysed quantitatively by 0·5*N*-benzyl-alcoholic potassium hydroxide], which when dehydrated with potassium hydroxide yields *o*-aminostyrene, b. p. 104—105°/15 mm., d_{20}^{20} 1·019, n_D^{20} 1·6101 (*N*-acetyl derivative, m. p. 94·5°; lit. 129°). R. Brightman.

Halogenation of optically active phenylmethylcarbinol in the presence and in the absence of pyridine, by thionyl chloride and the chlorides and oxychloride of phosphorus. J. Kenyon, H. Phillips, and F. M. H. Taylor (J.C.S., 1931, 382—389).—As in the case of ethyl *l*-mandelate (Kenyon, Lipscomb, and Phillips, A., 1930, 598), *l*-phenylmethylcarbinol, $[\alpha]_{5461}$ −51·7°, which is converted by thionyl chloride in the absence of pyridine into *l*-α-chloroethylbenzene, $[\alpha]_{5461}$ −63·3° (McKenzie and Clough, J.C.S., 1910, 97, 2564), affords a product of opposite sign when the reaction is carried out in the presence of pyridine or quinoline. When the chlorides or oxychloride of phosphorus are used in the presence of pyridine, the signs of rotation of the α-chloroethylbenzene obtained are the same as in its absence, but the magnitudes of the rotations are greater. Potassium carbonate is without effect. Thus pyridine facilitates the occurrence of the reactions which lead to change of sign of rotation which are considered (*loc. cit.*) to be indicative of a change of configuration. Thus *l*-phenylmethylcarbinol with 2 mols. of phosphorus trichloride and 1 mol. of pyridine affords *d*-α-chloroethylbenzene, $[\alpha]_{5461}$ +64°, and hence, if the reaction with thionyl chloride (above) is unattended by racemisation, the reaction with phosphorus trichloride and pyridine occurs with complete inversion of configuration. These results, which are discussed in detail, are consistently explained by the mechanism previously suggested in the case of ethyl *l*-mandelate (*loc. cit.*). In the absence of pyridine the decomposition of the intermediate compound $CHMePh{\cdot}O{\cdot}\overset{+}{P}Cl_2{\cdot}\overset{-}{O}$ is initiated by the separation of a phenylmethylcarbonium cation with simultaneous production of a chlorine anion, and thus accounts for the observed formation of styrene, optically active αα-diphenyldiethyl ether, and almost inactive α-chloroethylbenzene. *dl*-α-Chloroethylbenzene has n_D 1·5280, 1·5269, 1·5264, 1·5253, and 1·5230 at 20°, 22·0°, 22·8°, 24·8°, and 28°, respectively. J. W. Baker.

Derivatives of optically active triarylcarbinols and their halochromic salts. E. S. Wallis (J. Amer. Chem. Soc., 1931, 53, 812—813).—*l*-Phenyldiphenylyl-α-naphthylmethylthioglycollic acid (I), $[\alpha]_D^{20}$ −13·63° in carbon tetrachloride (cf. A., 1930, 773), forms halochromic compounds with sulphuric and perchloric acids and mercuric chloride, which are decomposed by water to phenyldiphenylyl-α-naphthylcarbinol. The coloured compound from I and titanium tetrachloride in chloroform is decomposed by water to the *dl*-acid, whilst that from ferric chloride is similarly converted into the original optically active acid. The last observation is evidence against quinonoid formulation for the explanation of colour. H. Burton.

Reduction of triphenylmethane dyes and related substances with the formation of free radicals. J. B. Conant and N. M. Bigelow (J.

Amer. Chem. Soc., 1931, **53**, 676—690).—Short treatment of *p*-dimethylaminotriphenylcarbinol with chromous or vanadous chloride in acetic acid in an atmosphere of nitrogen and addition of the reaction mixture to aqueous sodium acetate gives *s-pp'*-tetramethyldiaminohexaphenylethane, readily oxidised in ethereal solution to p-*dimethylaminotriphenylmethyl peroxide*, m. p. 145—150° (decomp.) according to the rate of heating. The ethane and 1% sodium amalgam in ether give the unstable sodium *p*-dimethylaminotriphenylmethyl, converted by carbon dioxide into *p*-dimethylaminotriphenylacetic acid (*methyl* ester, m. p. 141°). Prolonged reduction of the carbinol with chromous or titanous chloride in acetic acid affords *p*-dimethylaminotriphenylmethane, also formed when the above ethane is reduced with titanous chloride or when an acetic acid solution is kept in absence of air. These results are readily understandable by postulating the intermediate formation of the free radical *p*-dimethylaminotriphenylmethyl, which subsequently dimerises to the ethane or undergoes the change $2R\cdot + H^{\cdot} \longrightarrow R\cdot H + R^{\cdot}$. Reduction of the carbinol by chromous chloride in acetone and hydrochloric acid affords the *compound* $C_{42}H_{40}N_2$, m. p. 165°, which probably possesses a constitution of the type of *p*-benzhydryltetraphenylmethane (substances of this type are termed Tschitschibabin compounds). Malachite-green is reduced rapidly by vanadous or titanous chloride in acetic acid and sodium acetate in nitrogen, forming *s-ppp'p'*-octamethyltetra-aminohexaphenylethane, which with sodium amalgam in ether gives only a transient coloration (*pp'*-tetramethyldiaminotriphenylmethane is isolated from the reaction mixture), is readily decomposed by acids, and is reduced by titanous chloride to *pp'*-tetramethyldiaminotriphenylmethane. The last-named compound is also produced when malachite-green is reduced by vanadous chloride in acetic acid and sodium acetate for a long time. The Tschitschibabin *compound*, $C_{46}H_{50}N_4$, from malachite-green has m. p. 231—232°.

p-Dimethylaminobenzhydrol is reduced by chromous chloride in acetone and hydrochloric acid to a mixture of αβ-*diphenyl*-αβ-*di*-p-*dimethylaminophenylethane*, m. p. 206—207° (also prepared by the action of sodium-potassium alloy on the corresponding ethylene), and an *isomeride*, m. p. 264—267°. *p*-Dimethylaminophenyl*iso*propylcarbinol is similarly reduced to two isomeric *compounds*, $C_{24}H_{36}N_2$, m. p. 174° and 239—240°, whilst *pp'*-tetramethyldiaminobenzophenone chloride and tetra-*p*-dimethylaminophenylethylene glycol are reduced to tetra-*p*-dimethylaminophenylethylene. H. Burton.

Cholesterol. XIII. Action of phosphorus pentasulphide. E. Montignie (Bull. Soc. chim., 1931, [iv], **49**, 73—75).—When refluxed with phosphorus pentasulphide in carbon disulphide, cholesterol is converted into *thiocholesterol*, $C_{27}H_{45}\cdot SH$, m. p. 191°, $[\alpha]_D$ −39° (in ether) (*bromide*, m. p. 152—153°; *nitro-derivative*, m. p. 125°). With white phosphorus in benzene in a current of oxygen at 60°, cholesterol yields a *phosphorate*, $C_{27}H_{46}O_5P_2$, m. p. 120—123°, which is decomposed by boiling water, yielding an *acid*, $C_{27}H_{50}O_7P_2$ (*acetate*, m. p. 250°, decomp. about 200°; *salts*). R. Brightman.

Preparation of aromatic acid amides. C. H. Kao and S. Y. Ma (J.C.S., 1931, 443—444).—The method used for the preparation of benzamide (this vol., 220) is applied with satisfactory results to the preparation of the amides of *m*- and *p*-nitro- and *p*-chloro-benzoic, benzilic, phenylacetic, and β-phenylpropionic acids (some dehydration to the nitrile in the last two cases), and succinimide. Poor yields are obtained with *o*-nitrobenzoic and cinnamic acids, and none with salicylic acid. J. W. Baker.

***N*-Acyl derivatives of alanine. Resolution of externally compensated *m*-nitrobenzoylalanine.** W. M. Colles and C. S. Gibson (J.C.S., 1931, 279—285).—Condensation of *dl*-alanine with *m*- and *o*-nitrobenzoyl chloride affords dl-m-, m. p. 163—164° (*ethyl*, m. p. 89°, and *methyl*, m. p. 110—111°, esters; *amide*, m. p. 189—190°; *silver* salt) (91), and dl-o-, m. p. 165—166° (47), -*nitrobenzoylalanine*, reduced by ferrous sulphate and barium hydroxide (Simonsen) to dl-o-*aminobenzoylalanine*, not melting at 270°, and dl-m-*aminobenzoylalanine hydrochloride*, m. p. 150—152° (decomp.), respectively. By similar methods are obtained dl-p-*toluoyl*-, m. p. 188—189° (95); dl-m-*nitrobenzenesulphonyl*-, m. p. 158·5—159° (21); dl-4-*nitrotoluene-2-sulphonyl*-, m. p. 125·5—126·5° (2), and dl-*cinnamoyl*-, m. p. 196—197° (92), -*alanine*. The figures in parentheses give the percentage hydrolysis by constant b.-p. hydrochloric acid in 3 hrs., the corresponding values for benzoyl-, phthalyl-, *p*-nitrobenzoyl-, benzenesulphonyl-, α- and β-naphthalenesulphonyl-, and *p*-toluenesulphonylalanine being 96, 76, 97, 14, 66, 18, and 17, respectively. Resolution of *dl-m*-nitrobenzoylalanine is effected by the half-molecule method, addition of quinine to a boiling solution of the sodium salt affording crystals of the *quinine* salt, $+2H_2O$ and anhydrous, converted into a glass at 125°, $[\alpha]_{5461}^{20}$ −137·1° in alcohol, of l-m-*nitrobenzoylalanine*, m. p. 158°, $[\alpha]_{5461}^{20}$ −44·7° (as its ammonium salt in water), and +5·87° in ethyl alcohol (*ethyl* ester, m. p. 104—105°, $[\alpha]_{5461}^{20}$ +6·91° in alcohol). The acid recovered from the original mother-liquor contains 90·4% of the *d*-acid and is converted by brucine into the *brucine* salt, $+3\cdot5H_2O$ and anhydrous, $[\alpha]_{5461}^{20}$ −9·1° in alcohol, of d-m-*nitrobenzoylalanine*, m. p. 158°, $[\alpha]_{5461}^{20}$ +44·7° (as ammonium salt in water), −5·62° in alcohol (*methyl* ester, m. p. 126°, $[\alpha]_{5461}^{20}$ −12·7° in alcohol; *amide*, m. p. 193—194°, $[\alpha]_{5461}^{20}$ +24·2° in alcohol). The relative rotatory powers of the acids and their derivatives in water and alcohol are discussed.

J. W. Baker.

Esters of 2 : 4 : 6-trinitrobenzoic acid. I. Phenyl and nitrophenyl esters. P. P. Schorigin and M. S. Belenki (J. Russ. Phys. Chem. Soc. 1930, **62**, 2027—2032).—The *phenyl* ester, m. p. 170·5—171·5°, is prepared by heating 2 : 4 : 6-trinitrobenzoyl chloride with phenol in pyridine. Nitration of the phenyl ester under different conditions gives the p-*nitrophenyl*, m. p. 186—187°, 2 : 4-*dinitrophenyl*, m. p. 168—169·5°, and 2 : 4 : 6-*trinitrophenyl*, m. p. 224—225°, esters. E. B. Uvarov.

Esters of orthophenylacetic acid. P. P. T. Sah, S. Y. Ma, and C. H. Kao (J.C.S., 1930, 305—307).—By prolonged action of the appropriate alcohol on phenylacetimido-ethyl and *-methyl* ether hydrochlorides (prepared in usual manner) at the ordinary temperature the following orthophenylacetates, $CH_2Ph\cdot C(OR)(OR')_2$, have been prepared in 40—45% yields: trimethyl, b. p. 216—218°, d_4^{20} 1·0651, n_D^{20} 1·5075; dimethyl ethyl, b. p. 217—219°, d_4^{20} 1·0640, n_D^{20} 1·5080; *diethyl methyl*, b. p. 224—226°, d_4^{20} 1·0356, n_D^{20} 1·5000; *triethyl*, b. p. 225—227°, d_4^{20} 1·0308, n_D^{20} 1·4997; *di*-n-*propyl methyl*, b. p. 239—242°, d_4^{20} 1·0109, n_D^{20} 1·4950; *diiso*p*ropyl methyl*, b. p. 227—229°, d_4^{20} 1·0079, n_D^{20} 1·4913; *di*-n-*propyl ethyl*, b. p. 238—241°, d_4^{20} 1·0094, n_D^{20} 1·4967; *diisopropyl ethyl*, b. p. 228—230°, d_4^{20} 1·0030, n_D^{20} 1·4908; *di*-n-*butyl methyl*, b. p. 254—257°, d_4^{20} 0·9953, n_D^{20} 1·4911; *diisobutyl methyl*, b. p. 245—248°, d_4^{20} 0·9929, n_D^{20} 1·4898; *di*-n-*butyl ethyl*, b. p. 254—257°, d_4^{20} 0·9974, n_D^{20} 1·4916; *diisobutyl ethyl*, b. p. 248—251°, d_4^{20} 0·9867, n_D^{20} 1·4883; *diisoamyl methyl*, b. p. 260—265°, d_4^{20} 0·9880, n_D^{20} 1·4900, and *ethyl*, b. p. 260—265°, d_4^{20} 0·9867, n_D^{20} 1·4887, *orthophenylacetates*.
J. W. Baker.

Asymmetric induction, in particular the optical activity of cinnamic acid. L. Ebert and G. Kortüm (Ber., 1931, 64, [*B*], 342—358).—A critical review of the literature leads the authors to the conclusion that, although asymmetric induction must be recognised as fundamentally probable and necessary in theory, almost all the quantitative measurements point to an action of very small magnitude. A marked effect of asymmetric induction appears to be found most convincingly in Erlenmeyer's observations of the activation of cinnamic acid, whereas other investigations have yielded results which are either negative or capable of explanation in another manner.

Measurements are recorded of the solubility of potassium hydrogen *d*- and *l*-tartrate in water and in a 0·5*N*-solution of *d*-mannitol and of *d*- and *l*-camphorsulphonic acid in benzene and in 0·25*N*-solutions of *d*- and *l*-camphor in benzene. Within the limits of experimental error, *d*-mannitol has the same influence on the *d*- and *l*-tartrate and the effect of the camphor antipodes is the same for either camphorsulphonate. Changes in the relative surface tensions of *N*- and 0·5*N*-aqueous solutions of sodium *d*- and *l*-camphorsulphonate are not observed when these solutions are saturated with strychnine nitrate, *d*-pinene, *d*-camphor, menthol, menthone, menthene, methyl camphorate, propyl *d*-tartrate, or menthyl acetate.

Repetition of Erlenmeyer's work confirms the observation that the cinnamic acids produced by heating storax or synthetic cinnamic acid or their anhydrides with *d*-tartaric acid at 168—170° are optically active. Crystallisation of the activated acids from much water at 75° results in the separation of optically inactive crystals and concentration of the activity in the residue obtained by evaporation of the filtrates to dryness. Fractional extraction of the activated acid with water shows that the solubility of the active component varies between fairly wide limits and that the material is probably not homogeneous. The residues obtained from the various fractions evolve cinnamic acid at about 130°, become brown between 130° and 140°, form brown drops of liquid at 143—148°, and finally melt indefinitely at 152—155°. When heated in a vacuum at 100° they give a sublimate of cinnamic acid and a compound, m. p. above 160°. The ratio C : H in them is invariably much lower than in cinnamic acid. Repeated fractional extraction of the activated acid until optical activity has ceased to appear in extract or residue yields further extracts which give a residue in which the percentage of carbon is much less than that in cinnamic acid, thus indicating the presence of inactive or feebly active impurities. It is regarded as established that the observed activity is not associated with a substance with the analytical composition of cinnamic acid. The presence of tartaric acid in the active component of the preparations is established by prolonged treatment of the residues from the aqueous extracts with sodium hydroxide. The residues obtained by evaporation of the solutions to dryness are feebly dextrorotatory in aqueous solution and exhibit the very characteristic small dispersion of the tartrates and increased magnitude after addition of boric acid. The existence of an optically active cinnamic acid in preparations from molten tartaric acid is regarded as extremely improbable.
H. Wren.

Derivatives of salicylic acid. II. 3-Nitro-5-sulpho- and 5-nitro-3-sulpho-salicylic acids. A. N. Meldrum and N. W. Hirve. **III. 3-Sulphosalicylic acid.** N. W. Hirve (J. Indian Chem. Soc., 1930, 7, 887—892, 893—897).—II. Salicylic acid (20 g.) is dissolved in sulphuric acid (*d* 1·8, 100 g.) and after 1 hr. the mixture is treated with nitric acid (*d* 1·4, 21 g.) below 20°; 3-*nitro*-5-*sulphosalicylic acid* (+$4H_2O$) [*barium* (+H_2O), *barium hydrogen* (+$2·5H_2O$), *potassium hydrogen* (+H_2O), *potassium* (+H_2O), and *tripotassium* (+H_2O), salts] is thereby produced. The acid is also prepared by nitrating 5-sulphosalicylic acid with a mixture of nitric acid (*d* 1·4) and acetic anhydride and by the method of Sakellarios (A., 1922, i, 1144) (in this case, some dinitrosalicylic acid is also produced); it could not be prepared by Hirsch's method (A., 1901, i, 84) or by sulphonation of 3-nitrosalicylic acid. *Methyl* and *ethyl* 3-*nitro*-5-*sulphosalicylates* (*potassium* salts; *barium* salts; *dibarium* salts) are prepared by the usual methods. 5-*Nitro*-3-*sulphosalicylic acid* (+$2H_2O$) [*barium*, *silver*, *potassium hydrogen*, *potassium* (+$2·5H_2O$), and *tripotassium* (anhydrous and +$3H_2O$) salts] is obtained when 5-nitrosalicylic acid is sulphonated with fuming sulphuric acid (19% SO_3). *Methyl* and *ethyl* 5-*nitro*-3-*sulphosalicylates* (*potassium* salts; *barium* salts; *dibarium* salts) are also described.

III. 5-*Amino*-3-*sulphosalicylic acid* (+1 and $3H_2O$), decomp. 353° *sodium* ([+$3H_2O$) and *barium* salts], prepared by sulphonating 5-aminosalicylic acid with fuming sulphuric acid (20% SO_3) or reducing 5-nitro-3-sulphosalicylic acid with iron powder and hydrochloric acid, is converted by way of 5-*diazo*-3-*sulphosalicylic acid*, decomp. 166° (rapid heating) or 216° (slow heating) [*potassium hydrogen* (+H_2O), decomp. violently at 210°; *sodium hydrogen* (+$0·5H_2O$), decomp. violently at 205°; *sodium*, and *barium* (+H_2O), salts], into 3-*sulphosalicylic acid* (+$5H_2O$; 3 mols.

are lost when it is kept in a desiccator), m. p. 152·5° [*potassium hydrogen, sodium hydrogen* (+1·5H_2O), and *barium* (+1·5H_2O) salts]. Nitration of this gives 5-nitro-3-sulphosalicylic acid, whilst bromination of the potassium salt in water affords 5-*bromo*-3-*sulphosalicylic acid*, m. p. (+4H_2O) 98—100°, m. p. (+2H_2O) 174° (*potassium hydrogen* salt, also formed when potassium hydrogen 5-diazo-3-sulphosalicylate is treated with hydrobromic acid and copper powder). Desulphonation of the last-named acid with superheated steam furnishes 5-bromosalicylic acid.
H. BURTON.

Reaction of mutual displacement of phenylacetic and salicylic acids from their compounds with β-naphthylamine. A. P. OBUCHOV (J. Russ. Phys. Chem. Soc., 1930, **62**, 1919—1931).—Salicylic acid (15%) and phenylacetic acid (85%) give a simple eutectic at 65°. Phenylacetic acid and β-naphthylamine form an equimolecular *compound*, m. p. 71·5° (decomp.); a transition point corresponds with 50% of phenylacetic acid. A eutectic point at 42° between phenylacetic acid and the compound corresponds with 33·8 mol.-% of β-naphthylamine. The ternary system consists of five surfaces, two triple transition points, and one triple eutectic. E. B. UVAROV.

Reaction of mutual displacement of β-naphthylamine and *m*-phenylenediamine from their compounds with salicylic acid. D. E. DIONISIEV (J. Russ. Phys. Chem. Soc., 1930, **62**, 1933—1946).—Both bases form equimolecular compounds with salicylic acid. Salicylic acid and β-naphthylamine form a stable binary system with a eutectic at 77°, corresponding with 24·7% of β-naphthylamine. The ternary system consists of 5 unequal surfaces meeting in 3 triple points. The binary system *m*-phenylenediamine–β-naphthylamine gives a eutectic at 54°, corresponding with 87·6 mol.-% of *m*-phenylenediamine. E. B. UVAROV.

Nitration of 6-methoxy-*m*-toluic acid. J. L. SIMONSEN (J.C.S., 1931, 444).—The neutral product obtained by nitration of the above acid is 5-nitro-*o*-tolyl methyl ether, m. p. 69—70° (not 63°), and not the 6-nitro-compound as previously stated (J.C.S., 1918, **113**, 781; 1915, **107**, 834). J. W. BAKER.

Optically active mandelonitrile. I. A. SMITH (Ber., 1931, **64**, [*B*], 427—434).—Hydrolysis of amygdalin with sulphuric acid under somewhat modified conditions (cf. Walker and Krieble, J.C.S., 1909, **95**, 1369) gives *d*-mandelonitrile, m. p. 28·5—29·5°, $[\alpha]^{15}_{5461}$ +5·27° in benzene (among other values), hydrolysed by concentrated hydrochloric acid to *l*-mandelic acid. The nitrile is readily racemised by water, very readily by alcoholic alkali hydroxide. Treatment of *d*-mandelonitrile with magnesium phenyl bromide, short boiling of the product, and its subsequent treatment with ice and concentrated hydrochloric acid affords an aqueous solution from which *l*-benzoin, $[\alpha]^{18·5}_{D}$ −119° in acetone, slowly separates (cf. McKenzie and Wren, J.C.S., 1908, **93**, 313), whilst small amounts of highly active material are isolated from the ethereal solution after removal of diphenyl. The process is applicable to the crude *d*-mandelonitrile obtained directly from amygdalin. Treatment of the homogeneous *d*-nitrile with the Grignard reagent followed by decomposition with ice and sulphuric acid and extraction of the product with ether yields a product racemised to an extent which inhibits the isolation of homogeneous *l*-benzoin. H. WREN.

Local anæsthetics. F. KONEK [with A. LOCZKA and J. DOKTAY] (Mat. Nat. Anz. Ungar. Akad. Wiss., 1929, **46**, 348—360; Chem. Zentr., 1930, ii, 2892—2893).—Methyl 3-methoxysalicylate, m. p. 64° (the acid has m. p. 148°), with *m*-nitrobenzoyl chloride at 100° affords methyl 3-methoxy-*m*-nitrobenzoylsalicylate, m. p. 45°, which on reduction with tin and hydrochloric acid gives *methyl* 3-*methoxy*-m-*aminobenzoylsalicylate hydrochloride*, m. p. 204° (decomp.), which produces local anæsthesia. 5-Nitro-3-methoxysalicylic acid, m. p. 220°, obtained by nitration of methyl 3-methoxysalicylate in acetic acid below 5° and then at 80° (red barium salt; methyl ester, m. p. 137·5—138·5°), is readily converted (as the methyl ester) into the benzoyl derivative, m. p. 112—118°, and thence into *methyl* 3-*methoxy*-5-*amino*-2-*benzoylsalicylate hydrochloride*, which is a local anæsthetic. 3-Ethoxysalicylic acid has m. p. 157°.
A. A. ELDRIDGE.

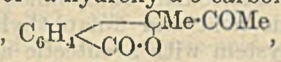
Preparation of phenylmalonic acid, *o*- and *p*-chlorophenylmalonic acids. D. IVANOV and A. SPASSOV (Bull. Soc. chim., 1931, [iv], **49**, 19—23).—When magnesium phenylacetate chloride, $CH_2Ph{\cdot}CO_2{\cdot}MgCl$, is treated with 1 mol. of magnesium ethyl bromide, and after the evolution of ethane is complete, the dimagnesium derivative is treated with carbon dioxide at 0°, phenylmalonic acid is obtained in 62·5% yield on hydrolysis. With magnesium *iso*propyl chloride the yield is 65·6%; with other Grignard reagents the yields are as follows: magnesium *iso*propyl bromide 48·9%, propyl chloride 45%, butyl bromide 42·2%, *cyclo*hexyl bromide 40%, *o*-tolyl bromide, 50·6%, α-naphthyl bromide 53·3%, benzyl chloride 3·1%. Magnesium methyl iodide gives practically no evolution of gas. Magnesium *o*- and *p*-chlorophenylacetate chlorides behave similarly. o-*Chlorophenylmalonic acid*, m. p. 139°, is obtained in 46·2% yield with magnesium *iso*propyl chloride and in 52·8% yield with magnesium phenyl bromide. p-*Chlorophenylmalonic acid*, m. p. 163°, is obtained in 56·4% yield with magnesium *iso*propyl chloride and in 48·3% yield with magnesium *o*-tolyl bromide. Phenylmalonic acid and *o*-chlorophenylmalonic acid are determined by heating in a pyrex flask with an air condenser in a current of air at 150—160° for 10—15 min. and absorbing and weighing the carbon dioxide evolved. R. BRIGHTMAN.

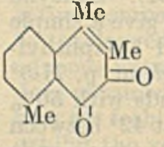
Dibenzylsuccinic acids. P. CORDIER (Compt. rend., 1931, **192**, 361—363).—Dibenzylidenesuccinic acid is reduced by Stobbe's method (A., 1904, i, 673) to a dibenzylsuccinic acid, m. p. 203°, which when treated with acetic anhydride for a short time at 100° (bath) gives the corresponding anhydride, m. p. 104°. More prolonged treatment affords the *anhydride*, m. p. 125°, of r-*dibenzylsuccinic acid*, m. p. 172°, resolved by strychnine into d-, α_D +22·8°, and *l-isomerides*, α_D —29·5°, both of which have m. p. about 130°. The dibenzylsuccinic acid, m. p. 204°, and anhydride, m. p. 155°, obtained by Stobbe (*loc. cit.*) could not be prepared. H. BURTON.

Synthesis of 2 : 4 : 5-trimethoxyphenylalanine. T. SZEKI and E. LAKOS (Acta chem. min. phys., 1929, 1, 157—166; Chem. Zentr., 1930, ii, 1539—1540).—Condensation of asarylaldehyde with hippuric acid, or with hydantoin followed by hydrogenation and fission, gives 2 : 4 : 5-trimethoxy-*N*-benzoylphenylalanine, from which free 2 : 4 : 5-trihydroxyphenylalanine could not be obtained. The following compounds are described: 2-*Phenyl*-4 : 2′ : 4′ : 5′-*trimethoxybenzylidenoxazol*-5-*one*, m. p. 210°; *α-benzamido*-β-2 : 4 : 5-*trimethoxyphenylacrylic acid*, m. p. 204°; *α-benzamido-β-asarylpropionic acid*, m. p. 191°; 2 : 4 : 5-*trimethoxyphenylpyruvic acid*, m. p. 145°; 2 : 4 : 5-*trimethoxyphenylacetic acid*, m. p. 104°; 2 : 4 : 5-*trimethoxybenzylidenehydantoin*, m. p. 274° (decomp.) [*bromo*-derivative, $C_{13}H_{15}O_5N_2Br$, m. p. 254° (decomp.)]; 2 : 4 : 5-*trimethoxybenzylhydantoin*, m. p. 234°; dl-2 : 4 : 5-*trimethoxyphenylalanine*, by hydrolysis of the foregoing substance with barium hydroxide, m. p. 217° (decomp.) (*ethyl* ester *hydrochloride*, $C_{14}H_{22}O_5NCl$, m. p. 181°). A. A. ELDRIDGE.

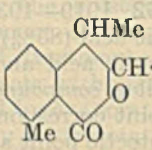
Opianic acid. I. Fission of opianic acid (and other hydroxycarboxylic acids and their ethers and esters) by heating with water under pressure. P. SCHORIGIN, V. ISSAGULIANZ, and V. BELOV (Ber., 1931, 64, [*B*], 274—280, and J. Russ. Phys. Chem. Soc., 1930, 62, 2039—2045).—Opianic acid passes when heated with water at 190—200° during 4—5 hrs. into 3-hydroxy-4-methoxybenzaldehyde (yield about 38%). The hypothesis that the mobility of one methyl group is due to the influence of the vicinal carboxyl is supported by the observations that *o*-methoxybenzoic acid passes when similarly treated into carbon dioxide, methyl alcohol, and phenol (yield about 23%), whilst methyl *o*-methoxybenzoate is produced in minor amount; *o*-dimethoxybenzene and *m*- and *p*-methoxybenzoic acid are unchanged by this treatment. Methyl salicylate is decomposed by water at 200—210° into salicylic acid and phenol; methyl *o*-methoxybenzoate yields phenol and *o*-methoxybenzoic acid, whilst salicylic acid is almost quantitatively transformed into phenol. The reaction is attributed to the intermediate formation by addition of water of an oxonium complex which decomposes into acid and methyl alcohol.

Treatment of *iso*vanillin with potassium hydroxide and ethyl *p*-toluenesulphonate in methyl alcohol yields 4-*methoxy*-3-*ethoxybenzaldehyde*, m. p. 51—52°; 3 : 4-dimethoxybenzaldehyde has m. p. 47—48°. H. WREN.

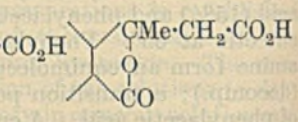
Congo copal oil. II. Oxidative degradation of the naphthalene hydrocarbon $C_{13}H_{14}$ from Congo copal oil. L. WESTENBERG and J. P. WIBAUT (Rec. trav. chim., 1931, 50, 188—199).—Oxidation of the trimethylnaphthalene obtained by catalytic dehydrogenation of Congo copal oil (Westenberg, A., 1929, 818) with chromic oxide affords 3-acetyl-*o*-toluic acid [*oxime*, m. p. 162°; methyl ester, m. p. 68° (Heilbron and Wilkinson, this vol., 80, give m. p. 47—48°)], which has also been obtained by similar oxidation of the trimethylnaphthalene obtained from squalene (Heilbron and Wilkinson, *loc. cit.*). It is also converted by further oxidation with potassium permanganate into hemimellitic acid, and by iodine and 10% sodium hydroxide into toluene-2 : 3-dicarboxylic acid identical with a specimen synthesised from *m*-toluic acid. When a smaller proportion of chromic oxide is used in the original oxidation the trimethyl-β-naphthaquinone (I), darkens at 120° (*quinoxaline*, m. p. 142°), is obtained. This is further oxidised by chromic and acetic acids to the lactonic acid, $C_{12}H_{12}O_4$, m. p. 201°, obtained by Westenberg (*loc. cit.*), to which structure II or IIa is assigned. This is further oxidised by potassium dichromate and sulphuric acid, or, better, by potassium permanganate, to an *acid*, $C_{12}H_{10}O_6$, probably by oxidation of a methyl group to a carboxyl group. The substance $(C_4H_4O)_n$, m. p. 69°, also obtained (Westenberg, *loc. cit.*) in the original chromic acid oxidation of the trimethylnaphthalene is now assigned the constitution of the *lactone* (*oxime*, m. p. 116°) of α-hydroxy-α-*o*-carboxyphenylethyl methyl ketone,  $C_6H_4<\begin{matrix}\text{——CMe·COMe}\\ \text{CO·O}\end{matrix}$, which is considered to be identical with the oxidation product, m. p. 70—71°, obtained by Heilbron and Wilkinson (*loc. cit.*) and to which these authors assigned the structure 5 : 8-diacetoxy-1 : 6-dimethylnaphthalene. This lactone is oxidised by hydrogen peroxide in alkaline solution, by iodine and methyl-alcoholic sodium hydroxide, or by dilute potassium permanganate to the *lactone* (+H_2O), m. p. 74°, of α-hydroxy-α-(*o*-carboxyphenyl)-propionic acid. These results accord well with the view that the original hydrocarbon is 1 : 2 : 5-trimethylnaphthalene. J. W. BAKER.



(I.)



(II.)

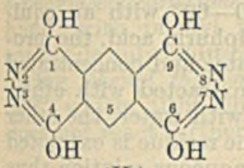


(IIa.)

Pyromellitic acid. Diketobenzohydrindene and benzodipyridazine derivatives. R. SEKA, H. SEDLATSCHEK, and H. PREISSECKER (Monatsh., 1931, 57, 86—96).—When pyromellitic anhydride is heated with 2-methylquinoline at 250°, a mixture of the *hydrindene* (I), decomp. 265°, and a *substance*, $C_{20}H_{11}O_6N$, decomp. about 125°, is produced; the former is converted by fuming sulphuric acid (50% SO_3) at 170° into a sulphonic acid (*sodium* salt), which dyes wool and silk yellow (similar to quinoline-yellow). Pyromellitic anhydride and alcoholic hydrazine hydrate give the cyclic *dihydrazide*, decomp. about 450° (*tetra-acetyl* derivative, m. p. 235—238°), of pyromellitic acid, which is considered to be

(I.)

1 : 4 : 6 : 9 - tetrahydroxybenzodipyridazine (II).



(II.)

4 : 9 - *Dihydroxy* - 1 : 6-*diphenylbenzodipyridazine*, chars at 445°, is prepared similarly from 2 : 5 - dibenzoylterephthalic acid, whilst 4 : 6-*dihydroxy*-1 : 9-*diphenyl*-, decomp. 430°, and 4 : 6-*dihydroxy*-1 : 9 - *dixylyl* - *benzodipyridazine* are obtained from 4 : 6-dibenzoyl*iso*phthalic and dixyloylbenzenedicarboxylic acid (A., 1927, 360), respectively. Pyromellitic anhydride and α-naphthylamine at 200° give *pyromellitdi-α-naphthylimide*, m. p. 431°. 2-Benzoylanthraquinone-3-carboxylic acid and alcoholic hydrazine hydrate at 120° afford the corresponding *hydrazide*, decomp. 374°. *Methyl* and *phenyl pyromellitates*, m. p. 138° and 179·5°, respectively, are prepared from pyromellityl chloride and sodium methoxide and phenoxide, respectively, in benzene. H. BURTON.

Manufacture of aromatic amino-aldehyde compounds. I. G. FARBENIND. A. G.—See B., 1931, 335.

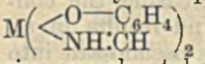
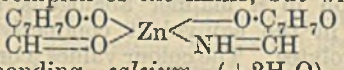
Homologues of cinnamaldehyde. I. α-Alkyl substituted homologues of cinnamaldehyde. P. SCHORIGIN, V. ISSAGULIANZ, E. SMOLIANINOVA, K. BOGATCHEVA, and S. SKOBLINSKAYA (J. Russ. Phys. Chem. Soc., 1930, 62, 2033—2038).—The following α-alkyl substituted homologues and derivatives of cinnamaldehyde are described : *ethyl*, b. p. 122—123°/13 mm., d^{20} 1·0384 (*semicarbazone*, m. p. 199—200°); iso*propyl*, b. p. 139—140°/15 mm., d^{23} 1·0112 (*semicarbazone*, m. p. 191—192°); n-*hexyl*, b. p. 174—176°/15 mm., m. p. 4°, d^{24} 0·9500 (*semicarbazone*, m. p. 111—112°). The molecular refraction of the aldehydes shows considerable exaltation.

E. B. UVAROV.

Salt-forming characteristics of doubly- and singly-linked elements of the oxygen group. II. Nitration of benzaldehyde and acetophenone in sulphuric acid solution. J. W. BAKER and W. G. MOFFITT (J.C.S., 1931, 314—318).—The conclusions reached from physical data (this vol., 486) concerning the existence of benzaldehyde and acetophenone as oxonium salts in sulphuric acid solution have been confirmed by a study of the proportions of the *m*-nitro-derivatives (determined by Flürscheim and Holmes' method, A., 1928, 403, after oxidation to the mixed nitrobenzoic acids) formed by nitration at 5° of these substances with nitric acid (*d* 1·53) in the presence of sulphuric acid of various concentrations. The presence of the positive charge on the cation $\text{Ph}\cdot\overbrace{\text{CR}\dot{:}\text{OH}}^{\oplus}$ of the salt form causes a considerable increase in the proportion of *m*-nitration observed under these conditions. Thus in sulphuric acid containing 7·3% of free sulphur trioxide benzaldehyde and acetophenone afford 90·8 and 90·0% of the *m*-nitro-isomeride, respectively. The proportion decreases gradually as the concentration of the sulphuric acid is diminished until in 80% sulphuric acid the values are 83·9 and 83·1% of *meta*, respectively. Moreover, in all cases, the addition of ammonium sulphate to the nitrating medium causes a depression in the amount of *m*-isomeride formed, comparable in both magnitude (4—5%) and type with that observed in the case of the ψ-base benzylidene-*m*-nitroaniline (Baker and Ingold, A., 1930, 594), thus proving that substitution occurs mainly through the cation of the oxonium salt. With nitric acid (*d* 1·53) alone at − 10°, benzaldehyde affords 72·1% of the *m*-nitro-isomeride, and the formation of a loose salt-like complex even in nitric acid alone is suggested by the slight fall in the proportion of *m*-nitration of acetophenone from 70% in nitric acid d^{15} 1·53 (Camps, A., 1902, i, 294, found only 55%) to 66·9% in nitric acid d^{15} 1·485, that is, as the dilution of the acid is increased.

J. W. BAKER.

Condensation of phenolic aldehydes with methyl *n*-propyl and *n*-butyl ketones. K. IWAMOTO and T. KATO (Sci. Rep. Tôhoku, 1930, 19, 689—693).—Methyl *n*-propyl and *n*-butyl ketones condense with 1 mol. of a *p*-, or with 2 mols. of a *m*-hydroxy- or -methoxy-benzaldehyde in the same way as methyl ethyl ketone (A., 1927, 566). The formation of styryl methyl or of distyryl ketone depends therefore on the position of the substituent in the benzaldehyde. The ketones are formed from the dialkyl ketone and the corresponding benzaldehyde in presence of hydrogen chloride; p-*hydroxy-α-ethylstyryl methyl ketone*, m. p. 120—121°; p-*hydroxy-α*-n-*propylstyryl methyl ketone*, m. p. 100—101° (*oxime*, m. p. 119·5—121·5°); p-*methoxy-α-ethylstyryl methyl ketone*, b. p. 171—172°/12 mm. (*oxime*, m. p. 93—94·5°); p-*methoxy-α*-n-*propylstyryl methyl ketone*, b. p. 183—184°/14 mm. (*oxime*, m. p. 91—92°). mm′-*Dihydroxy-α-ethyldistyryl ketone*, mm′-*dihydroxy-α*-n-*propyldistyryl ketone*, and the corresponding *methoxy*-compounds are brick-red or yellow amorphous solids. G. DISCOMBE.

Inner-complex salts of hydroxyaldimines and hydroxyketimines. P. PFEIFFER, E. BUCHHOLZ, and O. BAUER (J. pr. Chem., 1931, [ii], 129, 163—177).—Complex *zinc* and *nickel* compounds of *salicylaldimine* are obtained by action of ammoniacal zinc and nickel acetates on salicylaldehyde; the copper complex isolated by Ettling (Annalen, 1840, 35, 265; cf. Delépine, A., 1900, i, 177) is also of this type, which may be represented by the formula  $M\left(<{}^{O-C_6H_4}_{NH:CH}\right)_2$ (where M is a bivalent metal). The zinc complex takes up 2 mols. of pyridine on crystallisation from this solvent. *o*-Vanillin readily gives a *nickel* complex of the imine, but with zinc the *compound*  $\begin{matrix}C_7H_7O\cdot O\\CH{=\!=}O\end{matrix}\!>Zn<\!\begin{matrix}{-}O\cdot C_7H_7O\\NH{=}CH\end{matrix}$ is formed. The corresponding *calcium* (+$2H_2O$) and *magnesium* (+$2H_2O$) derivatives of salicylaldehyde, similarly prepared, appear to be the simple aryloxides.

With *o*-hydroxyacetophenone and its substitution products nickel acetate and dilute ammonia give complex salts of the ketone which are capable of combining with pyridine or aniline; these are converted by concentrated aqueous ammonia into complex compounds of the corresponding ketimines, which are also formed by use of higher concentrations of ammonia in the original preparation, and (with one exception) no longer have the power of adding solvent molecules. The *nickel* (+$2C_5H_5N$; +$1\frac{1}{2}PhNH_2$) and *copper* (+$2C_5H_5N$; +$2PhNH_2$) compounds of 2-hydroxy-

4-methoxyacetophenone in the pure state (cf. Pfeiffer and Golther, A., 1927, 362) are described, as also are the *nickel* complexes of *o*-hydroxyacetophenone ($+2C_5H_5N$), *o*-hydroxy- ($+1NH_2Ph$), 2-hydroxy-4-methoxy-, and 2-hydroxy-5-methoxy-acetophenone-imines, and 2-hydroxy-4-methoxyphenyl styryl ketimine. H. A. Piggott.

Salt-forming characteristics of doubly- and singly-linked elements of the oxygen group. I. Carbonyl group in benzaldehyde and acetophenone. J. W. Baker (J.C.S., 1931, 307—314).—By analogy with Schiff's bases (Baker and Ingold, A., 1930, 594) it is suggested that the intensely coloured solutions formed by benzaldehyde and acetophenone in concentrated or fuming sulphuric acid are due to the formation of oxonium salts of the type $\overbrace{\mathrm{Ph{\cdot}CR{:}OH}}^{\oplus}\}\overset{\ominus}{\mathrm{HSO_4}}$, the ions of which are in equilibrium with the colourless pseudo salt-form $\mathrm{Ph{\cdot}CR(OH)(OSO_3H)}$ (cf. Kendall and Carpenter, A., 1915, i, 15). When benzaldehyde is partitioned, at the ordinary temperature, between light petroleum and sulphuric acid containing 7·3% of free sulphur trioxide, 100, 90, and 80% sulphuric acid, only 0·5, 0·81, 0·83, and 1·77% of the benzaldehyde (determined as its *p*-nitrophenylhydrazone), respectively, is found in the petroleum layer, indicating that the equilibria $\mathrm{Ph{\cdot}CR{:}O+HO{\cdot}SO_3H=Ph{\cdot}CR(OH)(O{\cdot}SO_3H)} \rightleftharpoons \overset{\ominus}{\mathrm{O}}\mathrm{{\cdot}SO_3H+Ph{\cdot}}\overbrace{\mathrm{CR{:}OH}}^{\oplus}$ are displaced largely towards the right. Addition of ammonium sulphate to the acid layer causes a repression of the ionic dissociation, followed, in turn, by a further decomposition of the pseudo-salt into sulphuric acid and free benzaldehyde and in this case 1·4, 1·03, 8·7, and 30·8%, respectively, of the latter is retained in the petroleum layer. By colorimetric measurements it is shown that solutions of these two carbonyl compounds in 100% sulphuric acid do not obey Beer's law, the specific colour value (*s*) decreasing with decreasing concentration of the carbonyl compound (*c* equiv. per litre) more slowly than this law requires, whilst, in agreement with the view that decreasing the concentration of the carbonyl compound results in an increased ionisation of the colourless pseudo-salt into the coloured carbonium–oxonium ion, the molecular equivalent colour value ($1000s/c$) increases with increasing dilution in a manner analogous to the similar increase in the equivalent conductivity in solutions of electrolytes. The colour values (corrected for differences in total volume of the solutions) of solutions of benzaldehyde in 100, 90, 80, and 70% sulphuric acid in which the mol. ratio $\mathrm{Ph{\cdot}CHO/H_2SO_4}$ is constant (1/89) are, respectively, [100], 85, 45, and 21, indicating that, of the amount of oxonium salt present in 100% sulphuric acid, 15, 55, and 79%, respectively, suffers hydrolysis in the presence of the same molecular quantity of sulphuric acid, but in 90, 80, and 70% dilution, respectively. Similar results are obtained with acetophenone. J. W. Baker.

Preparation of phenylglyoxal. C. Neuberg and E. Hofmann (Biochem. Z., 1930, 229, 443—445; cf. this vol., 68).—Oximinoacetophenone dissolved in dry dioxan to which water is added is oxidised first at 0—5° and then at about 40—60° with an equimolecular amount of nitrosylsulphuric acid, the product being then diluted with water and concentrated in a vacuum. The residue is extracted with ether, the ethereal solution is washed with water, the ether is removed by distillation, and the residue is extracted with boiling water. When the aqueous solution thus obtained is filtered, concentrated in a vacuum, and cooled to 0° phenylglyoxal crystallises and can be purified by dissolution in the minimum quantity of warm ether, filtration of the ethereal solution, and addition at 0° of an equal volume of light petroleum (*d* 0·71—0·72). Yield up to 50%, m. p. 73°. W. McCartney.

Catalytic esterification of alcohols in alkaline solution. I. J. Houben and W. Fischer (Ber., 1931, 64, [*B*], 240—247).—In the presence of a small proportion of alkali metal or alkoxide, trichloromethyl ketones react with alcohols, yielding esters and chloroform: $\mathrm{R{\cdot}CO{\cdot}CCl_3+R'{\cdot}OH=[R{\cdot}C(OR')(OH){\cdot}CCl_3]\longrightarrow R{\cdot}CO_2R'+CHCl_3}$. Reaction is generally effected at the ordinary temperature or at 0° and can be applied to primary, secondary, and tertiary alcohols, hydroxy- and polyhydroxy-compounds. The following examples are cited: trichloroacetophenone into methyl, ethyl, or *iso*propyl benzoate; *p*-trichloroacetophenetole into ethyl *p*-ethoxybenzoate; trichloroacetocarvacrol into *methyl 4-hydroxy-5-methyl-2-*iso*propylbenzoate*, b. p. 153—154°/1·5 mm.; trichloroacetothymol into *methyl 4-hydroxy-2-methyl-5-*iso*propylbenzoate*, m. p. 97—98°; 4-trichloroacetyl-2-methylphenetole into *methyl 4-ethoxy-3-methylbenzoate*, b. p. 178—179°/43 mm., m. p. 33°; trichloroacetophenone into benzyl benzoate, linalyl benzoate, mono- and di-benzoylglycol, menthyl benzoate, ethyl benzoyl-lactate, glyceryl di- and tri-benzoate. H. Wren.

Preparation of cyclic non-saturated ketones with more than nine ring-members. Soc. Anon. M. Naef et Cie.—See B., 1931, 290.

4-*p*-Tolylthiosemicarbazide and its reactions with ketones. R. W. Bost and W. F. Smith (J. Amer. Chem. Soc., 1931, 53, 652—654).—4-*p*-Tolylthiosemicarbazide, m. p. 137° (*hydrochloride*, m. p. 173°), is obtained in 90% of the theoretical amount from hydrazine hydrate and *p*-tolylthiocarbimide. 4-p-*Tolylthiosemicarbazones* were prepared from the following ketones: methyl ethyl ketone, m. p. 75°; ethyl acetoacetate, m. p. 107°; *cyclo*hexanone, m. p. 125°; acetophenone, m. p. 165°; benzophenone, m. p. 158°; benzoylacetone, m. p. 126°; benzoin, m. p. 161°; benzil, m. p. 164°, and carvone, m. p. 147°. *Acetylacetone*-4-p-*tolylthiosemicarbazone*, m. p. 100°, when boiled with alcohol, gives 3 : 5-dimethylpyrazole and ethyl anilinothioformate. H. Burton.

Some reactions of phenyl propenyl ketone with semicarbazides and thiosemicarbazides. A. Y. Livingstone and F. J. Wilson (J.C.S., 1931, 335—337).—Phenyl propenyl ketone reacts with δ-phenylsemicarbazide and δ-phenylthiosemicarbazide to give only its *δ-phenylsemicarbazone*, m. p. 212°, and *δ-phenylthiosemicarbazone*, m. p. 140°, whilst *p*-methoxyphenyl propenyl ketone similarly affords only its δ-*phenylsemicarbazone*, m. p. 249°. On the other hand, with phenyl propenyl ketone and thiosemicarbazide only addition to the ethylenic linking occurs, giving *phenyl thiosemicarbazidopropyl ketone*, m. p. 140°, which, although it yields an *oxime*, m. p. 165°, does not react further with thiosemicarbazide.

J. W. Baker.

Heteropolar compounds. XIII. Effect of the nitro-group on the colour of salts of positive ions. W. Dilthey, C. Blankenburg, W. Brandt, W. Braun, R. Dinklage, W. Huthwelker, and W. Schommer (J. pr. Chem., 1931, [ii], **129**, 189—205).—The bathochromic influence on halochromism of a nitro-group as substituent in the phenyl nucleus attached to a carbonyl group (cf. A., 1929, 1300) is confirmed by observations of the colour of further chalkones, Ar·CH:CH·CO·Ar, and benzophenone derivatives in concentrated sulphuric acid. Halochromism is also shown by the former in the presence of small proportions only of acid, *e.g.*, with sulphuric acid in acetic acid, or perchloric acid in acetic anhydride, but the shades are lighter than in sulphuric acid, and deepen on warming; this difference in behaviour is still more marked with the benzophenone derivatives, presumably on account of their lower basicity. The effect of the nitro-group on shade is not, however, conditioned by the decreased basicity, as this is also shown in cases where it has a hypsochromic action. The following nitro-compounds are prepared by interaction of the appropriate acyl chloride with diphenyl, diphenyl ether, diphenyl sulphide, etc., reduction to the corresponding amino-compounds being effected by stannous chloride and hydrochloric acid in acetic acid: 4′-*nitrophenyl 4-diphenylyl ketone*, m. p. 164°; 4-p-*nitrophenylthiolacetophenone*, m. p. 119°; 4-p-*nitrobenzoyl*-, m. p. 121—122°, 4-m-*nitrobenzoyl*-, m. p. 87—88°, 4-m-*aminobenzoyl*- (isolated as *hydrochloride*, m. p. 200—206°; *benzoyl* derivative, m. p. 127°; *azo*-β-*naphthol* derivative, orange-red), 4 : 4′-*di*-p-*nitrobenzoyl*-, m. p. 226°, 4 : 4′-*di*-p-*aminobenzoyl*-, m. p. 177—178° (*hydrochloride*; *azo*-β-*naphthol* derivative), 4 : 4′-*di*-m-*nitrobenzoyl*-, m. p. 175°, and 4 : 4′-*di*-m-*aminobenzoyl-diphenyl ether*, m. p. 150—151° (*azo*-β-*naphthol* derivative); 4-m-*nitrobenzoyl*-, m. p. 128—129°, 4 : 4′-*di*-m-*nitrobenzoyl*-, m. p. 229—230°, 4 : 4′-*di*-p-*nitrobenzoyl*-, m. p. 278°, and 4′-*nitro-4-benzoyl-diphenyl sulphide*, m. p. 145°; 4 : 4′-*di*-m-*nitrobenzoyl*-, m. p. 221—222°, and 4 : 4′-*di*-p-*nitrobenzoyl-diphenyl selenide*, m. p. 267—268°. Interaction of 4-*p*-nitrophenylthiolacetophenone with the appropriate aldehyde in ethyl alcohol in presence of sodium methoxide gives 4-p-*nitrophenylthiolchalkone*, m. p. 142°, followed by resolidification and further fusion at 180°, and its 4-*methoxy*-, m. p. 154°, and 3′ : 4′-*methylenedioxy*-, m. p. 174°, -derivatives. Condensation of sodium thiophenoxide with *p*-chloronitrobenzene in alcoholic solution gives, not the expected *p*-nitrodiphenyl sulphide (cf. A., 1897, 27), but p-*azodiphenyl sulphide*, m. p. 121—122°.

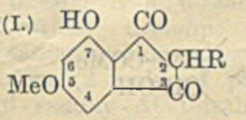
H. A. Piggott.

Stereochemical structure. II. Optically active α- and β-methylhydrobenzoins. R. Roger (Biochem. Z., 1931, **230**, 320—329).—*d*(−)-Acetylphenylcarbinol with magnesium phenyl bromide gives the *α-form* of *d*(+)-methylhydrobenzoin, m. p. 92—93°, α_{5893}^{20} +31·1° in acetone, +40·6° in ethyl alcohol. This is compared with a sample of the β-form obtained by the action of magnesium methyl iodide on *d*(−)-benzoin, which gives m. p. 80—81°, α_{5893}^{20} +30·9° in acetone, +21·3° in ethyl alcohol. Admixture of the α- with the β-form of *d*(+)-methylhydrobenzoin depresses the m. p. to 50—70°, and the m. p. of the α-form on keeping for 2 months fell from 92—93° to 84—89°. By the action of magnesium phenyl bromide on ethyl *d*(+)-lactate, β-methyl-αα-diphenylethylene glycol is obtained, m. p. 92—93°, α_{5893}^{20} +133° in acetone. The substance is therefore readily distinguished from the methylhydrobenzoins by its high rotation (cf. A., 1930, 211).

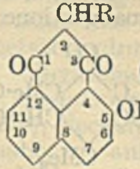
P. W. Clutterbuck.

Syntheses of antiseptic derivatives of indan-1 : 3-dione. I. Interaction of malonyl chloride and of alkylmalonyl chlorides with the methyl ethers of resorcinol and β-naphthol. R. Black, H. Shaw, and T. K. Walker (J.C.S., 1931, 272—279).—Malonyl chloride (best prepared by the action of phosphorus pentachloride on malonic acid, Staudinger and Bereza's method, A., 1909, i, 83, being unsatisfactory) and various alkylated malonyl chlorides condense with resorcinol dimethyl ether and β-naphthyl methyl ether in the presence of aluminium chloride in nitrobenzene to give indandiones of types I and II, respectively, demethylation only of the methoxy-group in the *ortho*-position to the carbonyl group occurring.

(I.)



(II.)

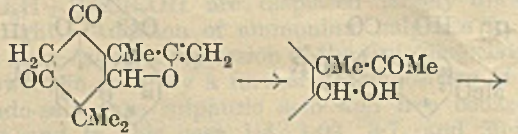


These products possess selective antiseptic properties, being without action on *B. coli communis* and *B. pyocyaneus*, but they inhibit the growth of *Bacterium C*, the values of *x*, the inhibiting concentration (1 g. in *x* c.c.), being given in parentheses after each compound. The following were prepared: 7-*hydroxy*-5-*methoxy*-, m. p. 217° (22,000); 7-*hydroxy*-5-*methoxy*-2-*methyl*-, m. p. 225—226° (10,000), -2-*ethyl*-, m. p. 192·5° (8300), and -2-n-*propyl*-, m. p. 190·5° (12,500), [the -2-n-*butyl* derivative (20,000) was not obtained pure], -*indan*-1 : 3-*dione*: 5-*hydroxy*-, m. p. 276—280° (16,600); 5-*hydroxy*-2-*ethyl*-, m. p. 215° (66,400), -2-n-*propyl*-, m. p. 181° (166,000), and 2-n-*butyl*-, m. p. 185° (277,000), -peri*naphthindan*-1 : 3-*dione*. Introduction of an alkyl group in the 2-position of the resorcinol derivative lowers the antiseptic power, but this depressing effect is counterbalanced as the length of the substituent alkyl chain is increased. The lowering effect of alkyl groups is absent in the derivatives of β-naphthol.

J. W. Baker.

Essential oil of *Backhousia angustifolia*. III. Constitution of angustione and dehydroangustione. R. S. Cahn, C. S. Gibson, A. R. Penfold, and J. L. Simonsen (J.C.S., 1931, 286—294).—Oxidation of angustione with potassium hypobromite converts it quantitatively into *l*-ααγ-trimethylglutaric acid. Oxidation with potassium permanganate in acetone at 0° affords a liquid ketonic acid, probably $CO_2H{\cdot}CMe(COMe){\cdot}CH_2{\cdot}CMe_2{\cdot}CO_2H$, since it is further oxidised smoothly to *l*-ααγ-trimethylglutaric acid with sodium hypobromite. Although only 80% of the hydrogen required for one ethylenic linking is absorbed, reduction of dehydroangustione with hydrogen and palladised norite in alcohol affords a homogeneous product of dl-*angustione*, b. p. 127°/14 mm., d_{20}^{20} 1·083, n_D^{20} 1·5087 (*copper* derivative, m. p. 203—204°), isolated by the action of ammonia on the alcoholic solution as dl-*aminoangustione*, m. p. 138—139°, and converted by hydroxylamine into dl-*anhydroangustione*-4(or 6)-*oxime*, m. p. 57—58°. Hence the original sample of dehydroangustione contained 26% of angustione, the presence of which accounts for the formation of ααγ-trimethylglutaric acid in the products of the oxidation of dehydroangustione with sodium hypobromite (A., 1930, 921). The neutral product, $C_8H_{10}O_3$, m. p. 88·5°, obtained in the latter oxidation (*loc. cit.*) is the anhydride of *cis*-ααγ-trimethylglutaconic acid (III), since it is readily hydrated to this acid [converted by bromine, not into a dibromide as stated by Perkin and Smith (J.C.S., 1904, 85, 157), but into the *lactone*, m. p. 147—148°, of β-bromo-γ-hydroxy-ααγ-trimethylglutaric acid], whilst a small yield of *trans*-β-hydroxy-ααγ-trimethylglutaric acid (II) [Perkin and Smith (*loc. cit.*); reduced by hydriodic acid (*d* 1·7) and red phosphorus at 170—180°, followed by sodium and amyl alcohol, to ααγ-trimethylglutaric acid] is also isolated. These results confirm the structure previously assigned to dehydroangustione (I) and are represented thus :

(I.)



(II.) $CO_2H\cdot CHMe\cdot CH\cdot(OH)\cdot CMe_2\cdot CO_2H$

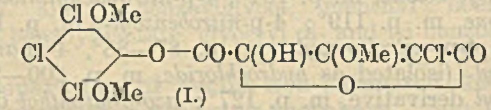
$CO_2H\cdot CMe{:}CH\cdot CMe_2\cdot CO_2H$ (III.)

Hydrobromic acid (*d* 1·5) at 100° converts natural or *dl*-angustione into 1 : 1 : 3-trimethyl*cyclo*hexane-4 : 6-dione, whilst dehydroangustione is similarly converted into 1 : 1 : 3-trimethyl-Δ^2-*cyclo*hexene-4 : 6-dione, oxidised by sodium hypobromite to *cis*-ααγ-trimethylglutaconic acid, and an unstable *substance*, $C_8H_{12}O_2$, m. p. 85—86°, probably $CMe_2{<}\begin{matrix}CO-CO\\CH_2\cdot CHMe\end{matrix}$ or its dienol, which has phenolic properties and with bromine affords a red bromide, decomposed by water into the substituted glutaconic acid. Dehydroangustione is converted by *p*-toluidine and zinc chloride at 140—150° into p-*toluidinodehydroangustione*, m. p. 63—65°.

[With O. J. EVANS and F. G. SOPER.] The parachors of *dl*-angustione and dehydroangustione at 20° are, respectively, 442, and 435, and possible explanations of the negative anomalies from the calculated values (462·1 and 439·5, respectively) are discussed. J. W. BAKER.

Quinone formation from nitroacetamidoquinol. G. HELLER and T. HEMMER (J. pr. Chem., 1931, [ii], 129, 207—210).—2 : 5-Dinitroquinol (Nietzki, A., 1883, 465) is more conveniently prepared from its diacetate by hydrolysis with 5% sulphuric acid than with alkali. It is reduced by the calculated quantity of stannous chloride in hydrochloric acid to 2-*nitro*-5-*acetamidoquinol*, decomp. 226° without melting (*diacetate*, m. p. 183—184°), readily hydrolysed to 2-*nitro*-5-*aminoquinol*, decomp. 154°. The acetyl compound is oxidised by fuming nitric acid in acetic acid to 2-*nitro*-5-*acetamido*-3 : 6-*dihydroxybenzoquinone*, m. p. 164° (decomp.), an unstable substance, decomposed by heating with the commoner solvents, but capable of recrystallisation, with care, from ethyl acetate. Careful oxidation with chromic in place of nitric acid gives a small quantity of a somewhat impure substance, decomp. indefinitely above 140°, probably 2-*nitro*-5-*acetamido*-3-*hydroxybenzoquinone*. Both of these hydroxyquinones readily give with aniline in alcohol 5-*nitro*-2-*acetamido*-3 : 6-*dianilinobenzoquinone*, decomp. 260°. H. A. PIGGOTT.

New type of oxidation product derived from quinones. W. H. HUNTER and M. M. SPRUNG (J. Amer. Chem. Soc., 1931, 53, 700—711).—The colourless compound formed during the oxidation of trichloropyrogallol 1 : 3-dimethyl ether with chromic oxide in acetic acid (A., 1926, 839) has m. p. 187·4—187·8° (decomp.), and is also formed by similar oxidation of 3 : 5-dichloro-6-methoxy-2-(3′ : 4′ : 5′-trichloro-2′ : 6′-dimethoxyphenoxy)-*p*-benzoquinone. It furnishes an *acetyl* derivative, m. p. 135—136° (decomp.), and is decomposed by boiling 6% potassium hydroxide solution to the original trichloropyrogallol dimethyl ether. Its production from the above quinone probably involves fission of the quinone ring, loss of one carbon atom, and subsequent hydroxylactone formation; the compound is given the structure I. The analogous compound, m. p. 206—206·6° (decomp.) [*acetyl* derivative, m. p. 141—144° (decomp.)] (cf. *loc. cit.*), from tribromopyrogallol 1 : 3-dimethyl ether, is also formed by oxidation of 3 : 5-dibromo-6-methoxy-2-(3′ : 4′ : 5′-tribromo-2′ : 6′-dimethoxyphenoxy)-*p*-benzoquinone. It appears to be an anhydro-compound formed by loss of 1 mol. of water from 2 mols. of an intermediate of type I (where Cl=Br); during acetylation a simpler compound (type I) is produced. The possible mechanism of formation of these colourless substances is discussed. H. BURTON.



(I.)

Reaction occurring in place of the Beckmann transformation with certain aromatic diketonemonoximes. II. R. SCHOLL, K. STEPHANI, and E. STIX. **III.** R. SCHOLL and J. DONAT (Ber., 1931, 64, [*B*], 315—318, 318—321; cf. this vol., 357).—II. Phenyl 1-anthraquinonyl ketoxime, m. p. 230° when rapidly heated, 223° after darkening when slowly heated, is converted by concentrated hydrochloric acid at 175° into anthraquinone-1-carboxylic acid, aniline, a little anhydro-oxime, and phenyl 1-anthraquinonyl ketone; under similar conditions the last-named substance is unchanged. With ethyl-alcoholic hydrochloric acid at 150° the oxime affords the corresponding *ethyl ether*, m. p. 154—156° after softening, also prepared from the oxime, alcoholic sodium ethoxide, and ethyl iodide. Antimony pentachloride in chloroform, benzenesulphonyl chloride in pyridine, and phosphorus pentachloride in acetyl chloride are without action. Phenyl 1-anthraquinonyl ketoxime is transformed into the anhydride by treatment with concentrated sulphuric acid at 100°, with glacial acetic acid at 230—240°, with boiling glacial acetic acid containing potassium iodide, or, most advantageously, by treatment with boiling nitrobenzene containing a little hydrogen chloride. *m*-Xylyl 1-anthraquinonyl ketoxime is converted into its anhydride by treatment with potassium iodide in boiling glacial acetic acid, with boiling nitrobenzene even in the absence of hydrogen chloride, and with hydrogen chloride in boiling glacial acetic acid.

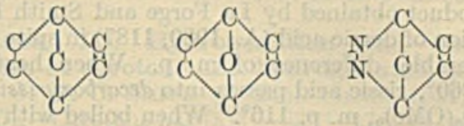
III. The possibility has been suggested (*loc. cit.*) that the anhydro-compounds are derivatives of phthalylphenanthridine, possibly formed through the *N*-aryl ethers of anthraquinone-1-aldoxime. These compounds are found to be incapable of transformation into their anhydrides and to isomerise, as expected according to Beckmann, into acid anilides. There is at present no support for the hypothesis that the anhydro-oximes are phthalylphenanthridines. Phthalic anhydride, suspended in a mixture of benzene and ether, is converted by magnesium *o*-tolyl bromide into *o*-2-toluoylbenzoic acid, m. p. 128—129°, almost quantitatively converted by fuming sulphuric acid into 1-methylanthraquinone. Oxidation of the last-named substance with manganese dioxide and sulphuric acid affords anthraquinone-1-aldehyde, transformed by β-phenylhydroxylamine into *anthraquinone*-1-*aldoxime phenyl ether*, m. p. 219—219·5°. Treatment of the ether with boiling nitrobenzene or with a mixture of glacial acetic and sulphuric acids affords, respectively, anthraquinone-1-carboxyanilide and anthraquinone-1-carboxylic acid. 4-*Chloroanthraquinone*-1-*aldoxime* N-*phenyl ether*, m. p. 214—215°, behaves analogously to the non-chlorinated compound. H. WREN.

Aminohydroxyanthraquinones and substitution products. I. G. FARBENIND. A.-G.—See B., 1931, 195.

Potentials and decomposition reactions of o-quinones in acid solution. L. F. FIESER and M. A. PETERS (J. Amer. Chem. Soc., 1931, 53, 793—805).—It is shown by potentiometric analysis that β-naphthaquinone decomposes in dilute acid solution, forming equal amounts of β-naphthaquinhydrone and 2-hydroxy-1 : 4-naphthaquinone; the reaction is unimolecular. It is suggested that slow addition of 1 mol. of water to the β-quinone occurs, forming 1 : 2 : 4-trihydroxynaphthalene, which then reacts rapidly with a further molecule of the β-quinone. Phenanthrene-3 : 4-quinone behaves similarly. The values for the normal oxidation–reduction potentials of the systems 1 : 2-dihydroxyphenanthrene–phenanthrene-1 : 2-quinone, pyrocatechol–*o*-benzoquinone, and 3 : 4 : 3′ : 4′-tetrahydroxy-1 : 1′-dinaphthyl–1 : 1′-dinaphthyl-3 : 4 : 3′ : 4′-diquinone have been redetermined using the discontinuous titration method (this vol., 172). H. BURTON.

[1-Hydroxyphenanthraquinone.] K. BRASS (Ber., 1931, 64, [*B*], 503; cf. A., 1930, 1589).—*o*-Methoxy-benzoin and -benzil have been described previously by Asahina and Terasaka (A., 1923, i, 1023). H. WREN.

Graduated additive powers of unsaturated ring systems. K. ALDER, G. STEIN, and H. FINZENHAGEN (Annalen, 1931, 485, 211—222).—Derivatives of the ring systems represented by the skeletal formulæ :



are characterised by the ready addition of phenyl azide and similar substances at the ordinary temperature. This property is not destroyed by substitution of the six-membered ring (including fusion of a saturated ring); addition does not occur, however, to unbridged *cyclo*hexene, nor when the bridge consists of more than a single atom (di*cyclo*octane). Two mols. of phenyl azide are readily taken up by bis*cyclo*pentadienequinone (Albrecht, A., 1906, i, 674), which has two 1 : 4-*endo*methylene*cyclo*hexene rings in its molecule. The underlying cause of this behaviour is regarded as stereochemical, the corresponding saturated rings being highly strained in those cases where additive power exists, but free from strain in cases where it is absent. The following additive *compounds* are described : phenyl azide with santene, m. p. 86°; Δ^4-3 : 6-*endo*methylenetetrahydrophthalic anhydride, decomp. 225°; dihydromono*cyclo*pentadienequinone, decomp. 194°; bis*cyclo*pentadienequinone (2 mols. of phenyl azide), decomp. 258°; 3 : 6 - *endo*xy - Δ^4 - tetrahydrophthalic anhydride, decomp. 200°, and *NN′*-dicarbethoxy-3 : 6-*endo*methylenetetrahydropyridazine, m. p. 126° : dihydromono*cyclo*pentadienequinone with benzyl azide, m. p. 141°, and ethyl diazoacetate, m. p. 177° (decomposition points are determined with " rapid heating "). Δ^4-3 : 6-*endo*Ethylenetetrahydro- and Δ^4-tetrahydro-phthalic anhydrides, bis*cyclo*hexadiene, dihydromono*cyclo*hexadiene-, dihydromonobutadiene-, and bisbutadiene-quinones do not react with phenylazide. H. A. PIGGOTT.

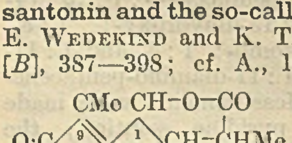
Linear pentacene series. XX. Optical absorption of pentacene derivatives. G. MACHEK (Monatsh., 1931, 57, 201—224).—Extinction curves are given for the following pentacene derivatives : pentacene-6 : 13-quinone; pentacene-5 : 7 : 12 : 14-diquinone; 1 : 8- and 6 : 13-dihydroxy-; 1 : 8-, 1 : 11-, 2 : 9-, and 6 : 13-dibromo-; 1 : 8- and 1 : 11-dinitro- and 1 : 8- and 1 : 11-diamino-pentacene-5 : 7 : 12 : 14-diquinones. Measurements were made usually in benzene and pyridine solution; the molar extinction is higher in the latter solvent. The results for the 1 : 8-disubstituted derivatives in pyridine show that the displacement towards the red is in the order nitro->amino->hydroxy->bromo-. All the compounds show the same type of curve. Substituents in the 6 : 13-positions cause the appearance of a new band, thus enabling a distinction to be made between the 6 : 13- and the 1 : 8-, 1 : 11-, and 2 : 9-derivatives. H. BURTON.

Rotenone, the active component of the *Derris* root. VI. Constitution of derric acid and rissic acid. S. Takei, S. Miyajima, and M. Ōno (Ber., 1931, 64, [*B*], 248—252; cf. A., 1930, 1044).—Rotenone is converted by a modification of Butenandt's method (A., 1928, 1017) into derrisic acid, m. p. 153°, which is oxidised by permanganate in alkaline solution to *rissic acid*, $C_9H_6O_5(OMe)_2$, m. p. 256° (decomp.) (*methyl* ester, m. p. 86°), regarded as identical with the product obtained by La Forge and Smith by the oxidation of derric acid (A., 1930, 1187) in spite of the considerable difference of m. p. When heated at 255—260°, rissic acid passes into *decarboxyrissic acid*, $C_8H_6O_3(OMe)_2$, m. p. 116°. When boiled with dilute nitric acid, rissic or decarboxyrissic acid is transformed into a *nitrodimethoxybenzoic acid*, m. p. 209° (*methyl* ester, m. p. 146°). Fusion with potassium hydroxide transforms rissic acid into quinol. Rissic acid is therefore regarded as hydroxy-2 : 5-dimethoxyphenylmalonic acid and decarboxyrissic acid as 2 : 5-dimethoxyphenylglycollic acid. Derric acid is considered to be most probably α-hydroxy-α-2 : 5-dimethoxyphenylsuccinic acid. The resolution of derric and decarboxyrissic acids into their optical antipodes has been effected. H. Wren.

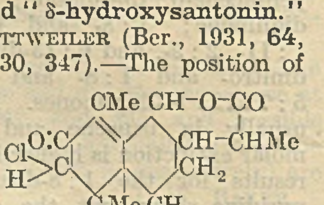
Constitution of aloins. E. Léger (Bull. Soc. chim., 1931 [iv], 47, 70—72).—A reply to Gibson and Simonsen (A., 1930, 609). Low yields in the decomposition of barbaloin into aloemodin and *d*-arabinose with sodium peroxide and alcoholic hydrogen chloride are attributed to oxidation of the products, especially arabinose, by the peroxide and to the formation of furfuraldehyde, which yields humic products or with the aloemodin gives amorphous substances. Léger's observations (A., 1917, i, 276) do not agree with the assumption that the bromobarbaloin obtained by the action of bromine water on barbaloin has the formula $C_{16}H_{15}O_7Br_3$, and the low halogen results are again attributed to loss of halogen in recrystallisation. Chlorobarbaloin, $C_{20}H_{14}O_9Cl_4$ (Cl 25·17%), gives a chloroaloemodin, $C_{15}H_6O_5Cl_4$, of correct chlorine content, and the formation of 1 mol. of the latter together with *d*-arabinose (1 mol.) from a compound $C_{16}H_{15}O_7Cl_3$ would be inexplicable. The compound $C_{20}H_{15}O_9Br_3$ may have a much greater mol. wt. than corresponds with the formula, since its solution in boiling alcohol deposits nearly insoluble crystals.

R. Brightman.

Santonin series. XV. Position of the double linkings in santonin; halogeno-derivatives of santonin and the so-called "δ-hydroxysantonin." E. Wedekind and K. Tettweiler (Ber., 1931, 64, [*B*], 387—398; cf. A., 1930, 347).—The position of the double linkings in the structure I assigned to santonin by Clemo and others (A., 1930, 919, 1442; this vol., 227) is established.



(I.)



(II.)

Re-examination of the "monochlorosantonin," $C_{15}H_{19}O_4Cl$, obtained by Wedekind and Koch (A., 1905, i, 212, 529) by the action of freshly-prepared chlorine water on powdered santonin, shows that it must be regarded as santonin chlorohydrin (II; R= OH), since it may also be obtained by the use of hypochlorous acid containing no free chlorine. The hypothesis that addition and not substitution has occurred is strengthened by the observations that α-tetrahydrosantonin is stable towards hypochlorous acid and that the chlorohydrin is hydrogenated in presence of platinum to *dihydrosantonin chlorohydrin*, $C_{15}H_{21}O_4Cl$, decomp. 214°. *Santonin bromohydrin*, decomp. 216°, is described. The hydroxyl group of the chlorohydrin cannot be detected by the usual methods except that of Zerevitinov. The chloro- or bromo-hydrin is transformed by methyl-alcoholic potassium hydroxide at 50—60° into *santonin oxide*, m. p. 214°, identical with the δ-hydroxysantonin of Wedekind and Koch (*loc. cit.*). The substance does not contain a hydroxyl group, since it does not yield methane with magnesium methyl iodide. It is hydrogenated to *α-dihydrosantonin oxide*, m. p. 142—143° (*oxime*, decomp. 225°), and small amounts of *β-dihydrosantonin oxide*, m. p. 169° [*oxime*, m. p. 189—190° (decomp.)]. When similarly treated, dihydrosantonin chlorohydrin yields α-dihydrosantonin oxide. Since the last-named substance is stable towards Caro's acid and therefore does not contain the ·CO·CH₂· group, it follows that the oxide ring is attached to the carbon atoms 6 and 7.

The action of concentrated hydrochloric acid on santonin oxide gives iso*santonin chlorohydrin*, $C_{15}H_{19}O_4Cl$, decomp. 210°, quantitatively re-converted by pyridine or boiling water into santonin oxide and catalytically hydrogenated to *dihydro*iso*santonin chlorohydrin*, m. p. 175° (decomp.), also prepared from α-dihydrosantonin oxide. The presence of the hydroxyl group is established by Zerevitinov's method, but it cannot be vicinal to the keto-group, since the compound does not yield an osazone. The *iso*-compound is probably stereoisomeric with santonin chlorohydrin. During the action of concentrated hydrochloric acid on santonin oxide, *dichlorosantonin* (II; R=Cl), decomp. 173—174°, is obtained, also prepared from dry chlorine and santonin in chloroform and regarded by Wedekind and Koch (*loc. cit.*) as a substitution product. The presence of one double linking is established by hydrogenation to *dichlorodihydrosantonin*, decomp. 145—146°, obtained also from α-dihydrosantonin oxide and concentrated hydrochloric acid. Treatment of dichlorosantonin with boiling alkali solution or, preferably, with aniline affords monochlorosantonin (I; Cl in position 7), decomp. 224° (cf. Rödiger, Diss., Tübingen, 1908), hydrogenated to *chloro-α-tetrahydrosantonin*, $C_{15}H_{21}O_3Cl$, decomp. 215°. The same product is obtained by chlorination of α-tetrahydrosantonin in chloroform. The probability that the chlorine atom is attached to a carbon atom vicinal to one of the two ketonic groups is supported by the observation that halogenation does not occur with *deoxy-α-tetrahydrosantonin*, m. p. 153—154°, and the allocation of it to position 7 follows from the inactivity of chloro-α-tetrahydrosantonin to Caro's acid. Hydrogenation of dichlorosantonin to dichlorodihydrosantonin and subsequent removal of hydrogen chloride by aniline gives a *chlorodihydrosantonin*, decomp. 160°, catalytically hydrogenated to chloro-α-tetrahydrosantonin. H. WREN.

Tephrosin. I. Composition of tephrosin and its relation to deguelin. E. P. CLARK (J. Amer. Chem. Soc., 1931, **53**, 729—732).—Deguelin, m. p. 171°, and a substance, m. p. 198° (corr.) (termed tephrosin), have been isolated from the leaves of *Cracca vogelii*, derris root, and the root of *Lonchocarpus nicou* (cf. A., 1930, 967; this vol., 357). Deguelin and tephrosin form a difficultly separable mixture, which is apparently identical with the tephrosin of Hanriot (A., 1907, ii, 292). Deguelin can be removed from such mixtures by selective oxidation with chromic and acetic acids. Tephrosin, $C_{21}H_{16}O_5(OMe)_2$, is probably a hydroxydeguelin, since, when it is warmed with sulphuric and acetic acids, dehydrodeguelin is produced. Oxidation of tephrosin with potassium permanganate in acetone at the ordinary temperature gives *tephrosindicarboxylic acid*, $C_{23}H_{22}O_{11}$, m. p. 221° (decomp.). H. BURTON.

Rotenone. XI. Relation between *iso*rotenone and rotenone. H. L. HALLER (J. Amer. Chem. Soc., 1931, **53**, 733—737).—In an attempt to isomerise rotenonic acid by treatment with acetic and sulphuric acids, the alkali-insoluble β-*dihydrorotenone*, $C_{23}H_{24}O_6$, m. p. 156°, $[\alpha]_D^{24}$ —26·5° in chloroform, was obtained. This is converted by alcoholic potassium hydroxide into β-*dihydrotubaic acid*, m. p. 175—176° (decomp.) (also formed by fusion with potassium hydroxide at 225°), and oxidised by chromic and acetic acids to a *diketone*, $C_{23}H_{20}O_7$, m. p. about 310° (decomp.). Oxidation with alkaline potassium ferricyanide gives *dehydro-β-dihydrorotenone*, m. p. 269°, converted by zinc dust and alcoholic potassium hydroxide into *dehydrodihydroxy-β-dihydorotenonic acid*, m. p. 149°, which is oxidised by alkaline hydrogen peroxide to derric acid. Treatment of β-dihydrorotenone with iodine in alcoholic potassium acetate affords β-*dihydrorotenolone*, m. p. 274° (*acetyl* derivative, m. p. 224°), dehydrated by alcoholic sulphuric acid to dehydro-β-dihydrorotenone.

The isomerisation of rotenone to *iso*rotenone (by treatment with sulphuric and acetic acids) probably involves the migration of a double linking from an *iso*propylene group to an $\alpha\beta$-position with respect to the lactone group. The double linking becomes part of a conjugated system which is reduced only with difficulty. β-Dihydrorotenone appears to be a saturated lactone; its production from rotenonic acid is accompanied by the disappearance of the double linking. H. BURTON.

Sapogenin of guaiacum bark. I. E. WEDEKIND and W. SCHICKE (Z. physiol. Chem., 1931, **195**, 132—138).—The saponin is hydrolysed with 5% sulphuric acid first at the b. p. and then at 155°. The resulting *sapogenin* (termed *guagenin*), $C_{29}H_{46}(OH)(CO_2H)$ (*methyl* ester, m. p. 196°, $[\alpha]_D^{17}$ +73·9° in chloroform), has m. p. 310° after sintering at 304°, $[\alpha]_D^{17}$ +77·4° in chloroform, when regenerated from its *acetyl* derivative, m. p. 268°, $[\alpha]_D^{17}$ +74·5° in chloroform (*methyl* ester, m. p. 220°, $[\alpha]_D^{17}$ +69·2° in chloroform). H. BURTON.

Ursolic acid. C. E. SANDO (J. Biol. Chem., 1931, **90**, 477—495).—Malol (Sando, A., 1923, i, 990), prunol (Power and Moore, J.C.S., 1910, 97, 1099), and urson (van der Haar, A., 1924, i, 643) are shown to be identical ($C_{30}H_{48}O_3$) and the name ursolic acid is proposed. The formation of already known derivatives is described in detail and the conclusion is reached that the acid is a hydroxy-acid. *Methyl phthalylursolate*, m. p. 214—215°, *phthalylursolic acid*, m. p. 264—265°, and *phenacyl ursolate*, m. p. 199—200°, are described. J. D. A. JOHNSON.

Carotene. III. Hydrogenation and optical properties of carotene and hydrogenated derivatives. J. H. C. SMITH (J. Biol. Chem., 1931, **90**, 597—605).—Carotene has $[\alpha]_D^{15}$ —63°± 17% in carbon disulphide. In ethereal solution with aluminium amalgam it gives *dihydrocarotene*, a viscous oil, $[\alpha]_D^{18}$ +41·9 in ether, $[\alpha]_D^{18}$ +38·0° in alcohol, the absorption spectrum of which is very different from that of carotene. *Octadecahydrocarotene*, b. p. 276°/1 mm., $d_4^{22\cdot2}$ 0·8828, n_D^t 1·4962—0·000367*t*, $[\alpha]_D^{14}$ +7·56° in carbon disulphide, is obtained from carotene in a mixture of acetic acid and *cyclo*hexane by catalytic hydrogenation in presence of platinum oxide. With an excess of catalyst, *eicosahydrocarotene*, b. p. 206°/10^{-4} mm., $d_4^{21\cdot2}$ 0·8748, $n_D^{21\cdot2}$ 1·4821, $[\alpha]_D^{30}$ +0·337°, was produced. The decrease in $[\alpha]$ as carotene is hydrogenated is held to show that progressive hydrogenation symmetrises the molecule, and since the linkings most difficult to hydrogenate are in such positions as to produce asymmetry, the presence of an unsaturated or a dicyclic ring is inferred. An explanation of the colour of carotene is advanced.

J. D. A. JOHNSON.

Carotenoids. III. Degradation of carotene by ozone. R. PUMMERER, L. REBMANN, and W. REINDEL (Ber., 1931, **64**, [*B*], 492—502; cf. A., 1929, 906).—Carotene has been subjected to ozonisation in carbon tetrachloride (1) with 4% ozone followed by removal of the solvent in a vacuum and hydrogenation of the ozonide in glacial acetic acid and (2) with 1·5% ozone followed by decomposition of the product with boiling water. The most characteristic substances obtained are a neutral oil, b. p. 104°/1·5 mm., also derived from β- but not from α-ionone, ε-keto-$\alpha\alpha$-dimethylheptaldehyde, ε-keto-$\alpha\alpha$-dimethylheptoic acid, and glyoxal. Considerations of the results from a quantitative viewpoint strongly support Karrer's formula for carotene with two terminal β-ionone residues.

Carotene in carbon tetrachloride is readily oxidised by oxygen with production of glyoxal. H. WREN.

Conjugated double linkings. XVI. Violaxanthin, the xanthophyll of the yellow pansy [*Viola tricolor*]. R. KUHN and A. WINTERSTEIN (Ber., 1931, **64**, [*B*], 326—332).—The dried blossoms are extracted with light petroleum at the ordinary temperature in an atmosphere of carbon dioxide and the violaxanthin ester thus obtained is hydrolysed with sodium ethoxide in a mixture of light petroleum and alcohol. *Violaxanthin*, m. p. 199—199·5° (corr., decomp.), is thus obtained in brownish-yellow prisms. On the basis of elementary analyses the formula $C_{40}H_{56}O_4$ is assigned to it. According to the Zerevitinov method, all four oxygen atoms are present in hydroxyl groups. It has $[\alpha]_{Cd}^{20}$ +35° in chloroform. The absorption spectra of zeaxanthin, lutein, and violaxanthin in carbon disulphide, chloroform, ethyl alcohol, light petroleum, and methyl alcohol are described in detail as well as the colour reactions. The behaviour of violaxanthin towards dilute mineral acids is particularly characteristic. Hydrogenation of violaxanthin in presence of alcohol and platinum oxide affords *perhydroviolaxanthin*, $C_{40}H_{78}O_4$, a colourless, viscous liquid, $[\alpha]_D^{20}$ −18° in chloroform. The alkaline, methyl-alcoholic mother-liquor from violaxanthin contains a lipochrome pigment which has not been caused to crystallise. H. WREN.

Conjugated double linkings. XVII. Polyene pigments of the azafran root. R. KUHN, A. WINTERSTEIN, and H. ROTH (Ber., 1931, **64**, [*B*], 333—341; cf. Liebermann and others, A., 1911, i, 391; 1913, i, 889; 1916, i, 56).—The powdered root is extracted with chloroform and the extracts are concentrated and cooled, whereby the bulk of the azafrin, mixed with some resin, separates. It is purified by dissolution in *N*-alcoholic potassium hydroxide, precipitation with acetic acid, and crystallisation from toluene. It has m. p. 212° (corr., decomp.), $[\alpha]_C^{25}$ −75·5° in alcohol. Elementary analyses of azafrin and many of its derivatives indicate with certainty the presence of only four oxygen atoms in the molecule and point to the formula $C_{28}H_{40}O_4$. Three active hydrogen atoms appear to be present. Azafrin is converted by sodium hydroxide and methyl sulphate into azafrin methyl ester, m. p. 192·8—193·2° (corr.), $[\alpha]_C^{20}$ −30° in chloroform, −147° in nitrobenzene; *azafrin ethyl* ester has m. p. 182° (corr., decomp.). Catalytic hydrogenation transforms azafrin into *perhydroazafrin*, a colourless, viscous liquid, $[\alpha]_D^{20}$ −6·7° in alcohol, 7 mols. of the gas being absorbed. It resembles crocetin in this respect and in its behaviour towards bromine which indicates the presence of 3·5—4 double linkings. *Perhydroazafrin methyl* ester, $C_{29}H_{56}O_4$, has $[\alpha]_D^{20}$ −9·0° in alcohol. Two of the oxygen atoms of azafrin are present in a carboxyl group, since the pigment can be titrated as a monobasic acid in alcohol in presence of thymol-blue. The remaining oxygen atoms are present in hydroxyl groups which probably are tertiary, since their acylation has not been accomplished. The optical activity of azafrin and its perhydro-derivative appears to be connected with the two hydroxyl groups, since it disappears completely when the last-named substance is treated with alcoholic hydrogen chloride and subsequently hydrolysed. Azafrin is therefore an optically active, seven-fold unsaturated, monocyclic, dihydroxymonocarboxylic acid, the colour of which is explicable by the assumption of an uninterrupted conjugation of the seven double linkings among themselves and with the carboxyl group. When the methyl ester is reduced with aluminium amalgam, a sulphur-yellow, very auto-oxidisable *dihydro*-compound, m. p. about 60°, is produced. Oxidation of azafrin with chromic acid yields acetic acid in amount pointing to the presence of five isoprene residues. The constitution $C_{10}H_{17}(OH)_2\cdot[CH\colon CH\cdot CMe\colon CH]_3\cdot CH\colon CH\cdot CO_2H$ is suggested. H. WREN.

Isoprene and caoutchouc. XXXII. Constitution of caoutchouc. H. STAUDINGER (Kolloid-Z., 1931, **54**, 129—140).—The molecular size of complex chain-like compounds is given by determination of the terminal groups if the mol. wt. does not exceed 10,000, but is too inaccurate for caoutchouc or cellulose. The mol. wt. of caoutchouc in solution, determined from the viscosity, lies between 50,000 and 200,000. The caoutchouc molecule probably consists of at least 1000 isoprene units in a chain, and is of colloidal size in one dimension only. Viscous solutions of caoutchouc and of other substances of very high mol. wt. are intermediate between gels and solutions; probably the effective volume of the long molecule is greater than the volume of surrounding liquid. The thermal and chemical sensitivity of caoutchouc is due to the unsaturation and length of the molecule. E. S. HEDGES.

Caoutchouc micelle or macromolecule? H. LOEWEN (Kautschuk, 1931, **7**, 12—14).—A reply to Staudinger (this vol., 93). The arguments in favour of the macromolecule are not convincing and rubber in solution is probably present in the form of micelles. D. F. TWISS.

Linalool from coriander oil. I. I. VANIN and A. A. TSCHERNOJAROVA (J. Russ. Phys. Chem. Soc., 1930, **62**, 2013—2017).—Linalool was prepared from coriander oil by fractionation. The *chloride*, b. p. 120—127°/8 mm., d_4^{20} 1·0304, was obtained by the action of hydrogen chloride. The action of nickel carbonate on the chloride gave a monocyclic *terpene*, b. p. 165—167°, d_4^{20} 0·8333. E. B. UVAROV.

Tribornyl borate and its use in separation of borneol from camphor. P. SCHORIGIN and Y. MAKAROV-ZEMLIANSKI (J. Russ. Phys. Chem. Soc., 1930, **62**, 2047—2049).—Borneol is converted almost quantitatively into tribornyl borate by the action of benzene or xylene and boric acid. A method for separating borneol from camphor is based on this. E. B. UVAROV.

Sesquiterpenes from the turpentines of *Pinus sylvestris*. B. A. ARBUSOV (J. Russ. Phys. Chem. Soc., 1930, **62**, 2023—2026).—A new *sesquiterpene* isolated from turpentine has b. p. 126·5—128·5°/8 mm., d^{13} 0·933, α_D −30·45° (*dioxide*, b. p. 134—136°/5·5 mm., d_4^{20} 1·0175). E. B. UVAROV.

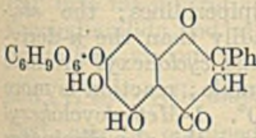
Pin*iso*sylvic acid. O. ASCHAN [with O. M. GADD] (Fenno-Chem., 1929, **1**, 18—27; Chem. Zentr., 1930, ii, 3142).—*Pinisosylvic* acid, $C_{20}H_{30}O_2$, m. p. 80° (sinters 60°) (*sodium* and *silver* salts), is obtained by heating pinabietic acid dihydrobromide with alcoholic alkali; bromination in chloroform affords the *tetrabromide*, $C_{20}H_{30}O_2Br_4$, m. p. 87°. The dihydrobromide, m. p. 192°, is identical with pinabietic acid dihydrobromide. Reduction of this with zinc and acetic acid affords *dihydropinisosylvic acid*, m. p. 92° (*hydrobromide*, m. p. 163—165°; dibromide, m. p. 92°). A. A. ELDRIDGE.

Spectrochemistry of furan and its derivatives. E. C. HUGHES and J. R. JOHNSON (J. Amer. Chem. Soc., 1931, **53**, 737—746).—The densities and refractive indices (for various wave-lengths) of furan and 20 of its derivatives are recorded. The exaltation in the molecular refraction for furan and the

2-substituted derivatives which do not contain a double linking on the atom attached to the ring is negative, whilst those compounds containing a double linking in the 2-position as part of a conjugated system give positive values. Isomeric 2- and 3-substituted furans can be distinguished from each other by von Auwers' formula (cf. A., 1921, ii, 73). Absorption spectra curves are given for 8 furan derivatives. Calculations of the wave-lengths of the absorption maxima for 5 of them by the Sellmeir dispersion formula (cf. Hunter, J.C.S., 1923, **123**, 434, 1671) gives results agreeing with those determined. Various electronic formulæ for furan are discussed. H. BURTON.

Homochromanone. S. G. POWELL and L. ANDERSON (J. Amer. Chem. Soc., 1931, **53**, 811).—Treatment of γ-phenoxybutyric acid (1 g.) with phosphoric oxide in benzene (cf. A., 1924, i, 287) gives impure homochromanone (oxime, m. p. 99°; *semicarbazone*, m. p. 228—229°). H. BURTON.

Orientation of glycuronic acid in baicalin. K. SHIBATA and S. HATTORI (Acta Phytochim., 1930, **5**, 117—118; cf. Shibata, Iwata, and Nakamura, A., 1923, i, 591).—Baicalin monomethyl ether gives a violet-brown colour with ferric chloride, indicating *ortho*-related hydroxyl and carbonyl groups in the benzopyrone nucleus. By analogy with the behaviour of primetin (Nagai and Hattori, A., 1930, 784), the green colour given by baicalin with ferric chloride, and its oxidation by pentamminocobalt salts are regarded as evidence of free 5 : 6-dihydroxy-groups. It is therefore concluded that glycuronic acid is linked through the 7-hydroxyl group of baicalein (annexed formula). A. COHEN.



Spectrography of the flavone series. III. Constitution of wogonin. S. HATTORI (Acta Phytochim., 1930, **5**, 99—116; cf. A., 1928, 1020).—Further investigation of wogonin (cf. Shibata, Iwata, and Nakamura, A., 1923, i, 591) shows that it is 5:7-dihydroxy-8-methoxyflavone (+H_2O), m. p. 201°. The ferric chloride colour reaction indicates a 5-hydroxyl group. Hydrolysis gives acetophenone and benzoic acid. It yields a *diacetyl* derivative, m. p. 152—153°, and a *dimethyl ether* (+H_2O), m. p. 167—168°, different from 5 : 6 : 7-trimethoxyflavone, m. p. 163—164° (lit. 165°), obtained by methylation of baicalein with methyl sulphate or diazomethane. Treatment of 2 : 3 : 4 : 6-tetramethoxyacetophenone (Chapman, Perkin, and Robinson, A., 1928, 183) with aluminium chloride affords a product which is identified as 2-*hydroxy*-3 : 4 : 6-*trimethoxyacetophenone*, m. p. 112—113° (*oxime*, m. p. 164°), since, on interaction with benzoic anhydride and sodium benzoate, it yields 5 : 7 : 8-*trimethoxyflavone*, m. p. 167—168°, identical with wogonin dimethyl ether. Demethylation of the latter gives 5 : 7 : 8-*trihydroxyflavone*, m. p. 226—227° (*diacetyl* derivative, m. p. 212—213°; *triacetyl* derivative, m. p. 172—173°), identical with the demethylation product of the former. These relationships are confirmed by spectrographs. A. COHEN.

Colouring matters of flowers and fruit. P. SISLEY (Bull. Soc. chim., 1931, [iv], **49**, 101—117).—A lecture.

Condensation of catechin tannin. M. BERGMANN and G. POJARLIEFF (Naturwiss., 1930, **18**, 1114).—The facility with which catechin and catechin tannins condense to form insoluble products such as tannin-red and phlobaphen is attributed to the presence of a double linking in the 2 : 3-positions of the pyran nucleus and a hydroxyl group in the 5-position, and suggests that the phenolic hydroxyl groups are not essential in this connexion, since catechin tetramethyl ether also readily undergoes analogous condensation. W. R. ANGUS.

Condensation of aldehydes and phenols. V. *m*-Chlorobenzylidenedi-β-naphthol [*m*-chlorophenyldi-2-hydroxy-α-naphthylmethane]. O. DISCHENDORFER and H. MANZANO (Monatsh., 1931, **57**, 20—30).—*m*-Chlorobenzaldehyde and β-naphthol condense in presence of acetic and hydrochloric acids at the ordinary temperature forming m-*chlorophenyldi*-2-*hydroxy*-α-*naphthylmethane* (+AcOH), m. p. (solvent-free) 178—179° after slight previous sintering (*monosodium* salt; *diacetate*, m. p. 216—217°; *dibenzoate*, m. p. 164° after sintering at 162°; *monomethyl ether*, m. p. 168°), converted by treatment with warm acetic and sulphuric acids into ms-m-*chlorophenyldinaphthopyran* (9-m-*chlorophenyl*-1 : 2 : 7 : 8-*dibenzoxanthen*), m. p. 191—192°. This pyran is also formed when the initial condensation is carried out in the warm. Oxidation of the methane with aqueous-alcoholic sodium hypobromite gives *dehydro*-m-*chlorobenzylidenedi*-β-*naphthol*, m. p. 199°, whilst oxidation of the pyran with manganese dioxide and hydrochloric acid in acetic acid and treatment of the resulting solution with ferric chloride gives ms-m-*chlorophenyldinaphthopyrylium chloride ferrichloride*, m. p. 225—226° after darkening. This is decomposed by aqueous acetone to ms-m-*chlorophenyldinaphthopyranol* (9-m-*chlorophenyl*-1:2:7:8-*dibenzoxanthhydrol*), m. p. 254—255° after darkening at 250° [*chloride mercurichloride*, m. p. 272° after darkening from 225°; *perbromide*, $C_{27}H_{16}OClBr_3$, m. p. 205—206° (decomp.) after slight previous sintering; *perchlorate*, m. p. 285° (decomp.) after darkening from 260°; *ethyl ether*, m. p. 215—216° after slight sintering, prepared by the action of alcohol on the above ferrichloride; *methyl ether*, m. p. 217—218° after slight sintering]. H. BURTON.

Third *o*-hydroxynaphthaldehyde; isomeric benzocoumarins. T. BOEHM and E. PROFFT (Arch. Pharm., 1931, **269**, 25—37).—2-Acetoxy-3-naphthoyl chloride, m. p. 99—100° (cf. Graff, A., 1909, i, 665) is hydrogenated by Rosenmund's method (A., 1918, i, 300) to 2-*acetoxy*-3-*naphthaldehyde*, m. p. 100—101° (p-*nitrophenylhydrazone*, m. p. 213—214°; *semicarbazone*, m. p. 211—212°; *oxime*, m. p. 202—203°), hydrolysed by alkali to 2-*hydroxy*-3-*naphthaldehyde*, yellow, m. p. 99—100° [*phenylhydrazone*, m. p. 246—248°; p-*nitrophenylhydrazone*, m. p. 271—273°; *semicarbazone*, m. p. above 270°; *oxime*, m. p. 207° (decomp.); *anil*, m. p. 158—159°]. This gives normal condensation *products*, m. p. 207—208°; m. p. 188—189°; m. p. 162—163°, and m. p. 112—113° (*acetyl* derivative, m. p. 142—143°), respectively, with 1 mol.

of acetone, acetophenone, βδ-diketopentane, and ethyl oxaloacetate. With acetic anhydride and sodium acetate at 180° for 3 hrs. it gives 6 : 7-*benzocoumarin*, m. p. 163—164°, which is also obtained by heating its 3-carboxylic acid (below). The compound to which von Pechmann and Welsh (A., 1884, 1346) ascribed this formula was probably 7 : 8-benzocoumarin. β-Naphthol, malic acid, and sulphuric acid yield only 5 : 6-benzocoumarin. The hydroxyaldehyde with aniline and malonic acid in alcohol affords 6 : 7-*benzocoumarin-3-carboxylic acid*, m. p. 258—259°. In presence of piperidine it gives with ethyl malonate, *ethyl* 6 : 7-*benzocoumarin-3-carboxylate*, m. p. 157—158°, with ethyl acetoacetate, 3-*acetyl*-6 : 7-*benzocoumarin*, m. p. 209—210° (p-*nitrophenylhydrazone*, m. p. 266—267°), with methyl benzoylacetate, 3-*benzoyl*-6 : 7-*benzocoumarin*, m. p. 225°, and with ethyl cyanoacetate, 3-*cyano*-4-*cyanocarbethoxymethyl*-3 : 4-*dihydro*-6 : 7-*benzocoumarin*, m. p. 158—159°. H. E. F. NOTTON.

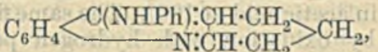
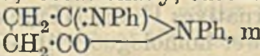
Closing of heterocyclic rings in indigoid dyes. I. S. IOFFE and R. F. MAZEL (J. Russ. Phys. Chem. Soc., 1930, **62**, 2001—2012).—The action of chlorosulphonic acid on acetylenedithiosalicylic acid produces closure of heterocyclic rings giving thioindigotin. Under analogous conditions ethylenedianthranilic and ethylenedithiophenolcarbonic acids were unchanged. E. B. UVAROV.

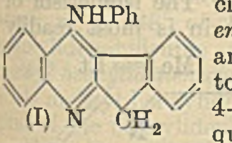
Syntheses of pyrroles and dipyrrylethanones. H. FISCHER and P. VIAUD (Ber., 1931, **64**, [*B*], 193—200).—2 : 4-Dimethylpyrrole is transformed by trichloroacetonitrile and hydrogen chloride in chloroform through the *ketimine hydrochloride* into 5-*trichloroacetyl*-2 : 4-*dimethylpyrrole*, m. p. 108—109°, stable towards boiling alcohol but converted by zinc dust and glacial acetic acid into 5-acetyl-2 : 4-dimethylpyrrole, m. p. 119—120°. 3-*Bromo*-5-*trichloroacetyl*-2 : 4-*dimethylpyrrole*, m. p. 145—146°, is described. The following compounds, including the non-analysed ketimine hydrochlorides, are analogously prepared : *ethyl* 3-*trichloroacetyl*-2 : 4-*dimethylpyrrole*-5-*carboxylate*, m. p. 173—174° ; 5-*trichloroacetyl*-2 : 4-*dimethyl*-3-*ethylpyrrole*, m. p. 101—102°, whence 5-*acetyl*-2 : 4-*dimethyl*-3-*ethylpyrrole*, m. p. 111—112° ; 5-*trichloroacetyl*-2 : 3 : 4-*trimethylpyrrole*, m. p. 114—115°, whence 5-acetyl-2 : 3 : 4-trimethylpyrrole, m. p. 135—136° ; 3-*acetyl*-5-*trichloroacetyl*-2 : 4-*dimethylpyrrole*, m. p. 145—146° ; 3-*bromo*-5-*chloroacetyl*-2 : 4-*dimethylpyrrole*, m. p. 184—186°. 2 : 4-Dimethylpyrrole is converted by ethyl cyanoformate and hydrogen chloride in chloroform into *ethyl* 2 : 4-*dimethylpyrrole*-5-*glyoxylate*, m. p. 60—61°, readily hydrolysed to the corresponding *acid*, m. p. 164—165° (decomp.). Propaldehyde and 3-acetyl-2 : 4-dimethylpyrrole in presence of a little hydrochloric acid afford *ethyldi*-3-*acetyl*-2 : 4-*dimethylpyrrylmethane*, m. p. 208—209° ; analogously, *n*-butaldehyde gives *propyldi*-3-*acetyl*-2 : 4-*dimethylpyrrylmethane*, m. p. 213—214°, whereas crotonaldehyde gives only a small amount of material, m. p. 236—238°. Addition of 2 : 4-dimethylpyrrole and 5-chloroacetyl-2 : 3 : 4-trimethylpyrrole in ether to an ethereal solution of magnesium ethyl bromide gives 3 : 4 : 5-*trimethylpyrryl*-3′ : 5′-*dimethylpyrryl*-2 : 2′-*ethan*-α-*one*, m. p. 168°. The following compounds are prepared analogously : 3 : 5-*dimethylpyrryl*-3′ : 5′-*dimethyl*-4′-*ethylpyrryl*-2 : 2′-*ethan*-α-*one*, m. p. 162—163°, and possibly a *dimeride*, m. p. 229° (corr.) ; 3 : 5-*dimethyl*-4-*ethylpyrryl*-3′ : 5′-*dimethylpyrryl*-2 : 2′-*ethan*-α-*one*, m. p. 156° ; 3 : 4 : 5-*trimethylpyrryl*-3′ : 5′-*dimethyl*-4′-*ethylpyrryl*-2 : 2′-*ethan*-α-*one*, m. p. 157° ; *di*-3 : 5-*dimethylpyrryl*-2 : 2′-*ethan*-α-*one*, m. p. 179° (corr.). According to the amount of reagent used, 5-chloroacetyl-2 : 4-dimethyl-3-ethylpyrrole is converted by sulphuryl chloride in ether into a *substance* $C_{10}H_{13}ONCl_2$, m. p. 123—125°, or 5-chloroacetyl-4-methyl-3-ethylpyrrole-2-aldehyde, m. p. 113—114°. 2 : 4-Dimethylpyrrole-3-propionic acid and chloroacetonitrile afford *chloroacetylcryptopyrrolecarboxylic acid*, $C_{11}H_{14}O_3NCl$, m. p. 212—213°. 5-*Anilinoacetyl*-2 : 3 : 4-*trimethylpyrrole*, m. p. 194—196°, 5-*anilinoacetyl*-2 : 4-*dimethylpyrrole*, m. p. 207°, 3-*bromo*-5-*anilinoacetyl*-2 : 4-*dimethylpyrrole*, m. p. 205—210° (decomp.), and 5-*anilinoacetyl*-2 : 4-*dimethyl*-3-*ethylpyrrole*, m. p. 181—183°, are described. H. WREN.

Reaction of organic halides with piperidine. I. Alkyl bromides. J. SEMB and S. M. MCELVAIN (J. Amer. Chem. Soc., 1931, **53**, 690—696).—Piperidine (2 mols.) reacts with *n*- and *sec.*-alkyl bromides and aralkyl bromides (1 mol.) in light petroleum at 90° forming usually 1-alkylpiperidines; the *sec.*-bromides react much less readily than the *n*-derivatives. *tert.*-Alkyl bromides and *cyclo*hexyl bromide undergo loss of hydrogen bromide ; reaction is more rapid at 125—135° than at 90°. 1-*Methyl*cyclo*hexyl bromide* has b. p. 65—66°/19 mm. ; this also eliminates hydrogen bromide. H. BURTON.

Hydrogenation of α-picoline under pressure in presence of pairs of catalysts. Comparative action of osmium and nickel in presence of rare earths. V. S. SADIKOV and P. I. ASTRACHANTZEV (J. Russ. Phys. Chem. Soc., 1930, **62**, 2071—2090).—Hydrogenation was carried out in autoclaves, using as catalyst osmium oxide, osmium and cerium oxides, osmium and lanthanum oxides, and osmium and zirconium oxides, and was repeated using nickel instead of osmium. The products of hydrogenation in each case were investigated, and the action of the various catalysts used is discussed. E. B. UVAROV.

Two isomeric cyanoketophenylmethylpyridines. N. TROCCOLI (Annali Chim. Appl., 1931, **21**, 41—45).—The *sodium*, *potassium*, *barium*, *copper*, *nickel*, and *cobalt* salts of 5-cyano-6-keto-4-phenyl-2-methyldihydropyridine and 5-cyano-6-keto-2-phenyl-4-methyldihydropyridine (cf. Issoglio, A., 1905, i, 609) have been prepared. T. H. POPE.

Synthesis of quinoline compounds from arylamides of carboxylic acids. II. J. VON BRAUN, A. HEYMONS, and G. MANZ (Ber., 1931, **64**, [*B*], 227—235 ; cf. this vol., 236).—It appears that every straight-chained aliphatic and fatty-aromatic acid is capable, under suitable conditions, of conversion into the 4-anilino-derivative of a 2- and 3-alkylated quinoline. Polycyclic compounds are obtained from the dianilides of pimelic and *o*-phenylenediacetic acid in good yield, whereas the reaction is less successful with adipic and hexahydro-*o*-phenylenediacetic acids and fails with sebacic and succinic acids. *n*-Butyranilide is converted by phosphorus pentachloride into *4-anilino-3-ethyl-2-propylquinoline*, m. p. 90—92° (*hydrochloride*, m. p. 234°), whilst heptanilide affords *4-anilino*-3-n-*amyl*-2-n-*hexylquinoline*, b. p. 216—220°/0·3 mm. (*hydrochloride*, m. p. 183°; *picrate*, m. p. 107°). Stearanilide gives 4-*anilino*-3-n-*hexadecyl*-2-n-*heptadecylquinoline*, m. p. 53—54° (*hydrochloride*, m. p. 107°). Adipdianilide is converted into 4-*anilino*-2 : 3-*trimethylenequinoline*,  $C_6H_4\left<\begin{matrix}C(NHPh){:}CH{\cdot}CH_2\\ N{:}CH{\cdot}CH_2\end{matrix}\right>CH_2$, decomp. 173° (*hydrochloride*, decomp. about 320° after darkening at 200°), in addition to compounds formed by condensation of several molecules. Pimeldianilide is converted with great readiness into *anilinotetrahydroacridine*, m. p. 232° (*hydrochloride*, m. p. 252°), transformed by alcohol and an excess of sodium into *as*-octahydroacridine, m. p. 83°. Treatment of the anilino-derivative with concentrated hydrochloric acid at 190—200° affords *tetrahydroacridone*, not molten below 360°, converted by distillation over lead oxide into acridone, m. p. 348°, and by subsequent treatment with zinc dust into acridine, m. p. 105°. With phosphoryl chloride and phosphorus pentachloride, tetrahydroacridone yields ms-*chlorotetrahydroacridine*, m. p. 68°, transformed by an excess of piperidine at 160° into ms-*piperidinotetrahydroacridine*, m. p. 112°. Succindianilide and sebacdianilide yield mainly non-crystalline, viscous products; occasionally, succinanil and (?) the cyclic *amidine*  $\left.\begin{matrix}CH_2{\cdot}C({:}NPh)\\ CH_2{\cdot}CO\end{matrix}\right>NPh$, m. p. 138°, can be obtained from the former compound. o-*Phenylenediacetdianilide*, m. p. 230°, gives 4-*anilino*-o-*phenylenequinolylenemethane* (I), m. p. 242—244°. cis- and trans-*Hexahydro*-o-*phenylenediacetdianilide*, m. p. 289—290° and 291—295°, respectively, appear to be converted into the same 4-anilinohexahydro-*o*-phenylene-α-quinolylenemethane, m. p. 204—206° (*hydrochloride*, m. p. 291° after darkening above 275°).


(I)

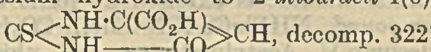
H. WREN.

Dyes derived from thiohydantoin. I. G. P. PENDSE and S. DUTT (J. Indian Chem. Soc., 1930, 7, 953—956).—Thiohydantoin condenses with aromatic nitroso- and oximino-compounds in acetic anhydride, forming readily hydrolysable acetyl derivatives of 5-aryliminothiohydantoins and 5-arylaminoiminothiohydantoins (from nitrosoamines). Thus, thiohydantoin and nitrosobenzene give 5-*anilothiohydantoin*, m. p. above 300°; with phenylmethylnitrosoamine, 5-*phenylmethylaminoiminothiohydantoin*, m. p. 156°, results. The following are described: 5-p-*hydroxyanilo*-, m. p. above 300°; 5-β-*hydroxynaphthylimino*-, m. p. 184° (from nitroso-β-naphthol), 5-4′-*hydroxy*-6′-*methyl*-3′-iso*propylanilo*-, m. p. above 300°; 5-2′ : 4′-*dihydroxyanilo*-, m. p. 278°; 5-p-*dimethylaminoanilo*-, m. p. 212°; 5-p-*diethylaminoanilo*-, m. p. 162°; 5-*phenylethylaminoimino*-, m. p. 174°; 5-*diphenylaminoimino*-, m. p. 191°; 5-*phenyl*-α- and -β-*naphthylaminoimino*-, m. p. above 300°, respectively; 5-β-*naphthylmethylaminoimino*-, m. p. above 300°; 5-N-*carbazolylimino*-, m. p. above 300°; 5-p-*dimethylamino*-o-*hydroxyanilo*-, m. p. above 300°; 5-p-*diethylamino*-o-*hydroxyanilo*-, m. p. above 300°, and 5-*phenylhydroxylaminoimino-thiohydantoins*, m. p. above 300°. Similar condensation *products*, all of which have m. p. above 300°, are prepared from thiohydantoin and oximinocamphor, oximino-1-phenyl-3-methylpyrazolone, violuric acid, benzilmonoxime, and phenanthraquinonemonoxime; it is presumed that these oximino-compounds are first converted into nitroso-derivatives. Most of the above compounds dye wool and silk from a slightly alkaline bath with a brown (light–dark) shade.

H. BURTON.

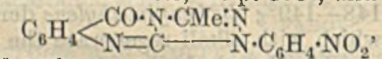
3 : 5-Diketopyrazolidine derivatives. I. T. TSUMAKI (Bull. Chem. Soc. Japan, 1931, 6, 1—9).—Hydrazobenzene on acylation gives sometimes acylhydrazobenzene and sometimes acylbenzidines (Stern, A., 1884, 1015; Bischoff, A., 1889, i, 278; Biehringer and Busch, A., 1903, ii, 296; Kaufmann, B., 1927, 155). Hydrazobenzene reacts with malonyl chloride in ether to form benzidine hydrochloride and 1 : 2-*diphenyl*-3 : 5-*diketopyrazolidine* (I), m. p. 178° (*oximino*-derivative, m. p. 163—164°; *ammonium* salt, m. p. 138—139°), hydrated by dilute hydrochloric acid to 1 : 2-*diphenyl*-3 : 4-*dihydroxy*-5-*pyrazolidone*, m. p. 160—162°, and condensing with aldehydes and ketones at 100° to form 4-alkylidene derivatives (*benzylidene* derivative, m. p. 160—165°; *furfurylidene*, m. p. 157—158°; *cinnamylidene*, m. p. 190—192°; iso*propylidene*, m. p. 113°; α-*phenylethylidene*, m. p. 148—149°; *diphenylmethylene* derivative, m. p. 269°), which with alkali regenerate the carbonyl compound and I. Hot alcoholic potassium hydroxide destroys I. Carbon suboxide and hydrazobenzene in ethereal solution give some diphenyldiketopyrazolidine.

G. DISCOMBE.

Thio-orotic [2-thiouracil-4(6)-carboxylic] acid. M. BACHSTEZ (Ber., 1931, 64, [*B*], 322—326; cf. A., 1930, 781).—Ethyl oxalacetate is condensed with thiocarbamide in the presence of alcohol containing a little hydrochloric acid and the unstable ester thus produced is immediately hydrolysed by alcoholic potassium hydroxide to 2-*thiouracil*-4(6)-*carboxylic acid*,  $CS\left<\begin{matrix}NH{\cdot}C(CO_2H)\\ NH{-}{-}{-}CO\end{matrix}\right>CH$, decomp. 322° (corr.), which is more strongly acidic than orotic acid. The *sodium*, *potassium*, and *ammonium*, *mono*-, *di*-, and *tri-silver*, *lead*, *copper*, and *mercury* salts are described. The action of hydrogen chloride on the acid suspended in methyl alcohol leads to the formation of the *O-methyl* derivative, $C_6H_6O_3N_2S$, m. p. 261° (corr., decomp.). Treatment of the disilver salt of thio-orotic acid with methyl iodide in methyl alcohol at 100° affords the *O*-methyl derivative of orotic acid, m. p. 298—300° (corr., decomp.), identical with the product described previously (*loc. cit.*), hydrolysed to orotic acid. Thio-orotic acid is unchanged by treatment with alcoholic sodium ethoxide and ethyl chloroacetate. Conversion of thio-orotic acid into its sodium salt followed by treatment with benzyl chloride gives the N-*benzyl* compound, $C_{12}H_{10}O_3N_2S$, m. p. 264° (decomp.).

H. WREN.

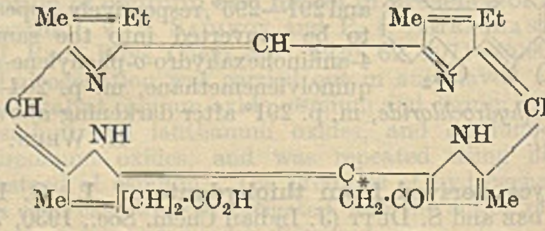
Organic catalysts. V. Fission of α-ketonic acids. W. LANGENBECK, R. HUTSCHENREUTER, and R. JÜTTEMANN (Annalen, 1931, 485, 53—61).—The catalytic decomposition of phenylglyoxylic acid in presence of aniline (cf. A., 1930, 714) is accompanied by formation of 1 : 2 : 3 : 4 : 5-*pentaphenyldihydroglyoxaline* (+$2H_2O$, not evolved at 150° in a vacuum) [*perchlorate*; *periodide* (decomp. 250° in a vacuum with evolution of iodine); *perbromide*; *hydrochloride*], the constitution of which is assumed from its formation by interaction of benzoinanilanilide with benzaldehyde; it is also formed by successive treatment of desyl chloride with aniline and benzaldehyde. By an empirical method, starting from methylamine, and studying the effects of substitution on the activity of the products as catalysts, the following series was realised: methylamine$<$glycine$<$phenylaminoacetic acid$<$3-aminoindoxyl. The last was prepared by hydrogenation of isatin-3-oxime in presence of platinum oxide (cf. Baeyer and Knop, Annalen, 1866, **140**, 37). H. A. Piggott.

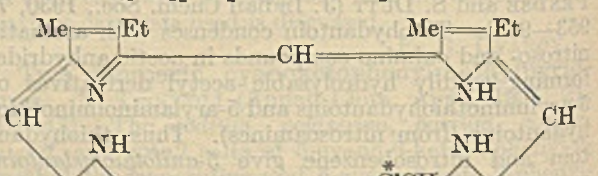
Synthesis of 1 : 2 : 4-triazoles. I. T. N. Ghosh and M. V. Betrabet (J. Indian Chem. Soc., 1930, 7, 899—903).—Ethyl acetamidoformate (acetylurethane) and *p*-nitrophenylhydrazine react in presence of xylene and phosphoric oxide at 125—130°, forming *acetylurethane*-p-*nitrophenylhydrazone*, m. p. 241° (isolated from the xylene), and 5-*keto*-1-p-*nitrophenyl*-3-*methyl*-4 : 5-*dihydro*-1 : 2 : 4-*triazole*, m. p. 259° (isolated from the phosphoric acid residue). The triazole reacts with anthranilic acid in phosphorus trichloride to give 5-o-*carboxyanilo*-1-p-*nitrophenyl*-3-*methyl*-4 : 5-*dihydro*-1 : 2 : 4-*triazole*, m. p. 308°, and the *quinazolone*,  $C_6H_4<\begin{matrix}CO\cdot N\cdot CMe\colon N\\ N{=}C\text{———}N\cdot C_6H_4\cdot NO_2\end{matrix}$, m. p. 293°. Acetylurethane and phenylhydrazine afford *acetylurethanephenylhydrazone*, m. p. 142—143°, and 5-*keto*-1-*phenyl*-3-*methyl*-4 : 5-*dihydro*-1 : 2 : 4-*triazole*, m. p. 166—167°, whilst 4-phenylthiosemicarbazide and the urethane give a mixture of α-*phenylthiocarbamido*-γ-*carbethoxyacetamidine*, m. p. 178° (corresponding α-p-*tolyl* derivative, m. p. 203°), and 5-*keto*-3-*methyl*-2 : 5-*dihydro*-1 : 2 : 4-*triazole*-1-*thiocarbonanilide*, m. p. 243° (corresponding p-*toluidide*, m. p. 228°, and *allylamide*, m. p. 201°). The first-named amidine is oxidised by ferric chloride to the *compound*, $NHPh\cdot CS\cdot N\colon N\cdot CMe\colon N\cdot CO_2Et$, m. p. 225° (decomp.). Acetylurethane and thiosemicarbazide give 5-*keto*-3-*methyl*-2 : 5-*dihydro*-1 : 2 : 4-*triazole*-1-*thiocarbonamide*, m. p. 222°, as the sole product. H. Burton.

Analogy in the chemistry of pyrazole and tetrazole. F. Konek (Math. Nat. Anz. Ungar. Akad. Wiss., 1929, 46, 340—345; Chem. Zentr., 1930, ii, 2902; cf. A., 1920, i, 880; Stollé, A., 1929, 828).—A discussion. The formation of mercuridithiobisantipyrine by shaking dithiobisantipyrine with mercury depends on radical dissociation of the sulphur atoms. A. A. Eldridge.

Complex formation between caffeine and salicylic acid. R. Labes (Arch. exp. Path. Pharm., 1930, 158, 42—52).—The constant of the reaction in which sodium salicylate and caffeine combine to form a complex is found, by a partition coefficient method, to be between 30 and 40. A. Cohen.

Chlorophyll. XV. Phyllo- and pseudo-phyllo-erythrin. H. Fischer, O. Moldenhauer, and O. Süs (Annalen, 1931, 485, 1—25; cf. this vol., 102).—ψ-Phylloerythrin (A., 1930, 1194) is identical with natural phylloerythrin in all respects except the ability to take up chloroform of crystallisation; it becomes identical in this respect also after treatment with fuming sulphuric acid. It is unaffected by heating with formic acid, or by bromine in acetic acid; chlorination with hydrogen peroxide and hydrochloric acid gives a yellow amorphous product which yields rhodoporphyrin and unchanged ψ-phylloerythrin on reduction with hydriodic acid and red phosphorus in acetic acid at 100°. The same final result is obtained by oxidation with hydrogen peroxide in sulphuric acid. Phyllo- and ψ-phyllo-erythrin have a carboxyl and a carbonyl group, which together account for all the oxygen present. They are reduced by sodium ethoxide and hydrazine hydrate at 165—170° (Wolff–Kishner) to *deoxyphylloerythrin* [*methyl* ester, m. p. 264° (*iron* and *copper* salts)], in which the carbonyl group has been completely reduced to methylene. This is also formed by heating phylloerythrinsemicarbazone with alcoholic sodium ethoxide at 165°. Of the possible structures for phylloerythrin suggested by its decomposition by alkalis (*loc. cit.*), that of 6-aldehydo-1 : 3 : 5 : 8-tetramethyl-2 : 4-diethylporphin-7-propionic acid is improbable on account of the marked differences between the spectra of 1 : 3 : 5 : 6 : 7-*pentamethyl*-2 : 4-*diethylporphin*-8-*propionic acid* (I, see below) and deoxyphylloerythrin, which should then be the isomeride in which the groups in the 7- and 8-positions are interchanged. The alternatives II and III are advanced as most probable, a lower homologue with a *cyclo*butene ring in place of the *cyclo*pentene ring of II being rejected on spatial and other considerations. It is considered that action of alkali first leads to fission between the C* and its adjacent carbonyl group. The isomerism of phylloerythrin and ψ-phylloerythrin is most readily explained on formula II, the former being assigned the ketonic and the latter the enolic structure.

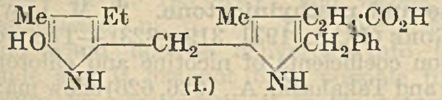

(II.)

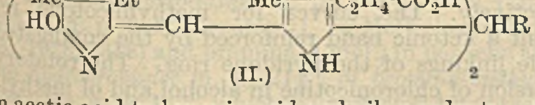

(III.)

The following derivatives of phylloerythrin are described: *potassium* salt, *semicarbazone* [*methyl* ester, m. p. 270° (decomp.)], *hydrazone*, and *oxime* (*methyl* ester). In addition to the semicarbazone and oxime (methyl ester), the *zinc* and *iron* salts of ψ-phylloerythrin are prepared (derivatives of the ester being in every case prepared from the ester). Fusion of 5-bromo-3 : 4′-dimethyl-4 : 3′-diethyl-5′-bromomethylpyrromethene and 3 : 3′ : 4′ : 5′-tetramethylpyrromethene-4-propionic acid hydrobromides (A., 1928, 76) with methylsuccinic acid at 120—160° or with succinic acid at 210° gives I (isolated as *methyl* ester, m. p. 242°), accompanied by small amounts of meso- and ætio-porphyrins. Diacetyldeuteroporphyrin dimethyl ester (*dioxime*; *disemicarbazone*) is reduced by the Wolff–Kishner method to a mixture of hæmo- and meso-porphyrins (identified spectroscopically). A green crystalline *substance* (oxime ?) obtained by interaction of chloroporphyrin e_5 with hydroxylamine is described, as also is the hydrolysis of the trimethyl ester of chlorin e to a crystalline form of the acid and a small amount of a monomethyl ester.

H. A. Piggott.

Bile pigments. X. Neo- and neoxanthobilirubic acids and partial synthesis of mesobilirubin and mesobilirubinogen (urobilinogen). H. Fischer and R. Hess (Z. physiol. Chem., 1931, 194, 193—228).—Treatment of mesobilirubin with boiling resorcinol for 30 sec. gives *neoxanthobilirubic acid* (probably *5'-hydroxy-3* : *4'-dimethyl-3'-ethyl-4-β-carboxyethylpyrromethene*), yellow, m. p. 229° {*bromo*-derivative, not melted at 350° after darkening at 171°, sintering when heated further, and then swelling at 213°; *phthalide*, m. p. 298°; *methyl* ester, m. p. 190° [*benzeneazo*-derivative *dihydrochloride*, m. p. 193° (decomp.)]}, oxidised by nitric acid (*d* 1·39) to methylethylmaleimide. Prolonged treatment of the acid with boiling hydriodic and acetic acids gives cryptopyrrole and hæmopyrrolecarboxylic acid, whilst reduction with hydriodic and acetic acids at 100°, sodium amalgam and aqueous alkali, or hydrogen in presence of colloidal palladium and dilute alkali affords *neobilirubic acid*, m. p. 184°, which is the corresponding pyrromethane (colourless). The *benzylidene* derivative, m. p. 248°, of this appears to be identical with benzylidenebilirubic acid (A., 1924, 1092), whilst *methyl benzylideneneobilirubate*, m. p. 212°, is identical with methyl benzylidenebilirubate (*loc. cit.*). Reduction of the benzylidene derivative with hydriodic and acetic acids at 100° gives *benzylneobilirubic acid* (I), m. p. 189°, identical with the compound described by Fischer and Niemann (A., 1925, i, 1198), which when treated with bromine in acetic acid is converted into benzylideneneobilirubic acid. Condensation of neoxanthobilirubic acid with benzaldehyde in presence of alkali or, better, with 25% hydrochloric acid gives the *compound* (II, R=Ph), m. p. 257°, reduced by hydriodic and acetic acids to I, and oxidised by chromic oxide in acetic acid to benzoic acid and oily products. Condensation *products*, similar to II, are also prepared from the following aldehydes : *o*-nitrobenzaldehyde, m. p. 259°; *p*-dimethylaminobenzaldehyde, m. p. 239°; ethyl 2-aldehydo-4-methylpyrrole-3 : 5-dicarboxylate, m. p. 246°, and acetaldehyde, m. p. 267°. When condensation is effected with acetone, the resultant *compound*, m. p. 250°, is formed by way of the first produced mesityl oxide. Condensation of neoxanthobilirubic acid with formaldehyde gives K-*mesobilirubin* (II, R=H), m. p. 310° (*methyl* ester *dihydrochloride*, m. p. 190°), which is probably identical with mesobilirubin. Reduction of this with sodium amalgam and water affords K-*mesobilirubinogen*, m. p. 192°, which appears to be crystallographically identical with natural mesobilirubinogen. Reduction of *K*-mesobilirubin with hydriodic and acetic acids gives bilirubic and neobilirubic acids, whilst treatment with boiling resorcinol affords neoxanthobilirubic acid.


(I.)


(II.)

H. Burton.

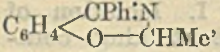
Structure of hæmocyanin. I. Isolation of "hæmocuprin," the copper-containing component of hæmocyanin from *Octopus vulgaris*. A. Schmitz (Z. physiol. Chem., 1931, 194, 232—247).—A more detailed account of work previously reviewed (A., 1930, 1304).

H. Burton.

Zerevitinov determination with hæmins and pyrrole dyes. IV. H. Fischer and P. Rothemund (Ber., 1931, 64, [*B*], 201—210; cf. A., 1928, 903).—The use of a Grignard solution more concentrated than that recommended by Zerevitinov (cf. Haurowitz and Zirm, A., 1929, 334) appears disadvantageous, since a portion of the compound separates from the solution which must then be heated before being measured, whilst eventual reseparation increases the difficulty of securing uniform conditions.

Treatment of hæmin with magnesium phenyl bromide in presence of nitrogen or oxygen yields diphenyl in amount much greater than that formed in blank experiments. Reaction is considered to occur in accordance with the scheme $2{>}Fe'''Cl+2MgPhBr=2{>}Fe''+2MgBrCl+Ph\cdot Ph$. Confirmation of this view is obtained spectroscopically, but the large quantity of diphenyl which is produced requires the assumption that the main action of the hæmin is catalytic. Deuterohæmin similarly yields diphenyl in quantity far exceeding the "blank value," whereas with ætioporphyrin I and mesoporphyrin Iα dimethyl ester only a slight excess is observed. Hæmatoporphyrin hydrochloride yields an excess of diphenyl and phæophorbid *a* behaves essentially in the same manner as hæmin. It thus appears that the Zerevitinov determination is not in a position to give constant values with hæmin and, possibly, with all hæmins. The results are more consistent with porphyrins, but variable with chlorophyll derivatives. Complex salts of the porphyrins give non-uniform results. The silver salts, which on account of their spectroscopic identity with zinc and copper salts are regarded as containing bivalent silver, yield variable results. The occasional disclosure of one active hydrogen atom instead of the theoretical none is attributed to the catalytic properties of the porphyrin molecule; this view is supported by the high value for active hydrogen obtained with chlorophyll-porphyrin copper salts.

H. Wren.

ψ-Bases in the *iso*oxazole series. IV. E. P. Kohler and W. F. Bruce (J. Amer. Chem. Soc., 1931, 53, 644—651).—The product from 3-phenylbenz*iso*oxazole and ethyl sulphate at 130—140° is converted by successive treatment with 6*N*-hydrochloric acid and ferric chloride into 3-*phenyl*-2-*ethylbenz*iso*oxazolinium ferrichloride*, m. p. 134° (corresponding *chloride*, m. p. 95—97°; *mercurichloride*, m. p. 119—120°; *picrate*, m. p. 132—133°; *perchlorate*, m. p. 183—184°). Decomposition of the initial reaction mixture with alkali hydroxide gives the ψ-*base*, $C_6H_4Bz(O{\cdot}NHEt)$-*o*, m. p. 79—80° [*oxime*, m. p. 135·6° (decomp.); *phenylcarbimide* derivative, m. p. 128° (*oxime*, decomp. 145—150° according to the rate of heating]), which can be used for the preparation of the above salts. The ψ-base passes on keeping (or when heated to 95°/vac.) into 4-*phenyl*-2-*methyl*-5 : 6-*benzometoxazine*,  $C_6H_4{<}\begin{matrix}CPh{:}N\\O{-}CHMe\end{matrix}{>}$, b. p. 175—177°/11 mm., m. p. 33—35° (*hydrochloride*, m. p. 104°, decomp. slowly at 110°; *ferrichloride*, m. p. 139—140°; *picrate*, m. p. 128—129°; *mercurichloride*, m. p. 180—181°), degraded by dilute acid or phenylhydrazine to ammonia, acetaldehyde, and *o*-hydroxybenzophenone. Methylation of I with methyl sulphate and treatment of the product with ferric chloride and hydrochloric acid gives 4-*phenyl*-2 : 3-*dimethyl*-5 : 6-*benzometoxazinium ferrichloride*, m. p. 119—120°, readily hydrolysed by water to acetaldehyde, methylamine, and *o*-hydroxybenzophenone. H. Burton.

Thiazoles. XVI. Synthesis of aminotoluthiazoles and derivatives from 2 : 5-diaminotoluene-4-thiosulphuric acid. M. T. Bogert and M. G. Sevag (J. Amer. Chem. Soc., 1931, 53, 660—669).—2 : 5-*Diaminotoluene*-4-*thiosulphuric acid*, k_{25}= $5{\cdot}56\times10^{-6}$, is prepared from 2 : 5-diaminotoluene by a slight modification of Bernthsen's method (A., 1889, 775). Condensation of the acid with *o*- and *m*-nitrobenzaldehydes gives 6-*amino*-2-o-*nitrophenyl*-, m. p. 144° (corr.), and 6-*amino*-2-m-*nitrophenyl*-5-*methylbenzthiazoles*, m. p. 233·5° (corr.). With *p*-nitrobenzaldehyde, 6-p-*nitrobenzylideneamino*-2-p-*nitrophenyl*-5-*methylbenzthiazole*, m. p. 279° (corr.), results. This is unaffected by boiling hydrochloric or 30% sulphuric acid, but is reduced by tin and hydrochloric acid to 6-*amino*-2-p-*aminophenyl*-5-*methylbenzthiazole*, m. p. 255·5° (corr.). 6-*Amino*-2-op-*dinitrophenyl*-5-*methylbenzthiazole*, m. p. 239·2° (corr.), is reduced similarly to the corresponding *triamino*-compound, m. p. 285·5°. 6-*Amino*-2-o-*aminophenyl*-5-*methylbenzthiazole*, m. p. 251° (corr.), and the isomeric *p*-aminophenyl derivative are converted by sulphonation and subsequent oxidation with sodium hypochlorite into dyes of the Columbia-yellow type. A thiosulphuric acid could not be prepared from 2 : 4-diaminotoluene. H. Burton.

Monosubstituted carbohydrazides, their typical derivatives and formation of heterocyclic compounds from them. P. C. Guha and M. A. Hye.—See this vol., 457.

Glutathione. VI. Preparation of oxidised glutathione. H. L. Mason (J. Biol. Chem., 1931, 90, 409—416).—The conclusion of Hopkins (A., 1929, 1491) that aërial oxidation of glutathione leads to loss of nitrogen and sulphur is shown to be incorrect, the low analytical figures for these elements in the product being due to the presence of alcohol (approx. 1 mol. of glutathione : 2 mols. of alcohol), which is lost with difficulty even at 111° in a vacuum. Under the latter conditions some change takes place whereby carboxyl and amino-groups (in the ratio of 2 : 1) disappear. Quantitative oxidation of glutathione with ferricyanide or iodine in excess of iodide suggests the oxidation of the thiol group to disulphide. J. D. A. Johnson.

New lead iodide double salt of trigonelline. K. Lendrich and F. Mayer (Z. Unters. Lebensm., 1930, 60, 569—575).—Trigonelline has been isolated from coffee beans as the *plumbi-iodide*, $C_7H_7O_2N,PbI_2$, m. p. 217° (decomp.). J. Grant.

Alkaloids of *Anabasis aphylla*, L. I. A. Orékhov and G. Menschikov (Ber., 1931, 64, [*B*], 266—274).—The dried plant is percolated with 95% alcohol containing 2% of ammonia. After removal of solvent the residue is treated with hydrochloric acid, from which the bases are liberated with sodium hydroxide and extracted with ether. The crude alkaloidal mixture (2·33% of the plant) is distilled under diminished pressure, giving fractions b. p. 136—138·5/12 mm. and about 200°/12 mm., of which the first has been investigated. Treatment of it with benzoyl chloride and sodium hydroxide affords lupinene, m. p. 68—69°, b. p. 265—266°/760 mm., $[\alpha]_D^{20}$ −23·62° in water (hydrochloride, m. p. 211·5—212·5°; chlorolupinan, b. p. 113°/7 mm., $[\alpha]_D^{20}$ −33·19° and its picrate, m. p. 146—147°), a little *O*-benzoyl-lupinine hydrochloride, and *benzoylanabasine*, $C_{17}H_{18}ON_2$, m. p. 82—83°, b. p. 222°/2 mm., $[\alpha]_D^{20}$ −127·23° in alcohol. *Anabasine* (probably 2-*piperidyl*-3-*pyridine*) is a pale yellow liquid, b. p. 104—105°/2 mm., 276°/760 mm., d_{20}^{20} 1·0455, n_D^{20} 1·5430, $[\alpha]_D^{20}$ −82·2°; the hygroscopic *hydrochloride*, $[\alpha]_D^{20}$ +9·23° in dilute hydrochloric acid, *picrate*, m. p. (indef.) 200—205°, and *nitrosoanabasine*, b. p. 176°/4 mm., d_{20}^{20} 1·1777, n_D^{14} 1·5698, $[\alpha]_D^{20}$ −155·0°, are described. The alkaloid is oxidised by permanganate to pyridine-3-carboxylic acid. Dehydrogenation of anabasine by silver acetate according to Tafel or by treatment with zinc dust results in the removal of six hydrogen atoms and yields a product, b. p. 292—294° (picrate, m. p. 151—152°), which appears to be identical with 2 : 3′-dipyridyl. H. Wren.

Nicotine and its derivatives. III. Chloronicotine and methylnicotone. T. M. Lowry and H. K. Gore (J.C.S., 1931, 319—323).—The molecular extinction coefficients of nicotine and chloronicotine (Karrer and Takahashi, A., 1926, 626) show maxima at log ε=3·37 at 2600 Å. and 3·55 at 2700 Å., respectively; the corresponding values for methylnicotone (Karrer and Widmer, A., 1925, i, 1084) in water and *cyclo*hexane are 3·656 at 2950 Å. and 3·445 at 3100 Å., respectively. The curves for methylnicotone represent a ketonic band reinforced by the conjugated double linkings of the pyridone ring. The rotatory dispersion of chloronicotine in alcohol and of methylnicotone in water and ethyl acetate is simple. H. Burton.

Lupin alkaloids. III. G. R. Clemo, R. Raper, and C. R. S. Tenniswood (J.C.S., 1931, 429—437).—*dl*-Lupanine and *d*-camphorsulphonic acid in acetone give d-*lupanine* d-*camphorsulphonate* (+$2H_2O$), m. p. 108—110°, $[\alpha]_D$ +45·5° in water, converted by aqueous potassium iodide into the *hydriodide* $(+2H_2O)$, m. p. 189°, $[\alpha]_D$ +45·5° in water, of *d*-lupanine, b. p. 185—186°/0·08 mm., m. p. 40° (lit. 44°), $[\alpha]_D$ +61·4° in acetone. The base from the above mother-liquors gave with *l*-camphorsulphonic acid the l-*camphorsulphonate* $(+2H_2O)$, m. p. 110—113°, $[\alpha]_D$ −45·3°, of *l*-lupanine, b. p. 186—188°/1 mm., $[\alpha]_D$ −61° in acetone [*hydriodide* $(+2H_2O)$, m. p. 190°, $[\alpha]_D$ −43·6°]. Reduction of *d*-lupanine with phosphorus and hydriodic acid gives *l*-sparteine, b. p. 130—135°/1 mm., $[\alpha]_D$ −11·3° in alcohol (cf. Willstätter and Marx, A., 1904, i, 613). Similar reduction of *l*-lupanine affords d-*sparteine*, b. p. 133—135°/1 mm., $[\alpha]_D$ +15·9° (*picrate*, m. p. 205—206°; *monohydriodide*, m. p. 229°).

Treatment of lupinine with phosphorus pentabromide in benzene yields bromolupinane, b. p. 103°/1 mm. [*methiodide*, m. p. 226—228° (decomp.)], converted by aqueous sodium acetate at 170—180° into lupinine and by boiling methyl-alcoholic alkali into a mixture of lupinine methyl ether, b. p. 84—85°/1 mm. (*methiodide*, m. p. 177—178°; *picrate*, m. p. 81—82°), and *l*-ψ-anhydrolupinine. The Hofmann degradation of ω-lupinyltrimethylammonium chloride as carried out by Karrer and Vogt (A., 1930, 1454) gives a base resembling ψ-anhydrolupinine rather than anhydrolupinine. The base, which contains some ω-*dimethylaminolupinane*, b. p. 95°/0·5 mm., $[\alpha]_D$ −37·7° in acetone (*dimethiodide*, m. p. 308°), affords a picrate, m. p. 152°, $[\alpha]_D$ −53° in ethyl acetate, the m. p. of which is not depressed by ψ-anhydrolupinine picrate; the crystalline forms of the picrates are not, however, always identical.

Chlorolupinane, potassium phthalimide, and a trace of copper powder at 210—220° give N(11)-*lupinylphthalimide*, m. p. 165°, reduced electrolytically in 20% sulphuric acid to N-*lupinyldihydroisoindole*, m. p. 88°, and hydrolysed by Ing and Manske's method (A., 1926, 1132) to 11-aminolupinane, b. p. 98°/1 mm. (*benzoyl* derivative, m. p. 131—132°). This base absorbs carbon dioxide readily, reacts with methyl succinate at 160—190°, forming *dilupinylsuccinamide*, m. p. 225—226°, and N(11)-*lupinylsuccinimide*, m. p. 137° (*methiodide*, m. p. 293—294°), and gives with methyl glutarate at 180° a mixture of *dilupinylglutaramide*, m. p. 193—195°, and *methyl* N(11)-*lupinylglutaramate*, m. p. 75—76°. The last-named compound could not be converted into lupinylglutarimide and it has not been possible to effect ring closure by elimination of water between the methylene group of the lupinyl residue and the carbonyl group of the amide or imide residue. Electrolytic reduction of lupinylsuccinimide as above gives N(11)-*lupinylpyrrolidine*, b. p. 155°/1 mm. [*dimethiodide*, m. p. 302° (decomp.)]. α-Methyloxysparteine (A., 1929, 1318) and bromine (1 mol.) in benzene afford the *hydrobromide*, m. p. 214°, of *bromo*-α-*methyloxysparteine*, m. p. 142°, which is unaffected by potassium hydroxide at 180°, hydrobromic acid, or boiling pyridine.

H. Burton.

Lupin alkaloids. IV. Synthesis of octahydropyridocoline. G. R. Clemo and G. R. Ramage (J.C.S., 1931, 437—442).—Distillation of lupininic acid with soda-lime (cf. Schöpf and others, A., 1928, 1144) gives basic and non-basic products. Reduction of the basic material (hydrogen; acetic acid; palladium) affords a *base* (I), $C_9H_{17}N$, b. p. 43—45°/0·5 mm. [*picrate*, m. p. 193—194°; *methiodide*, m. p. 333—335° (decomp.); *chloroaurate*, m. p. 166—167°], and material of b. p. 55—60°/0·5 mm. The non-identity of I with octahydropyridocoline (see below) indicates that lupinine has not the structure suggested by Karrer and others (A., 1929, 200) or that structural changes occur during the formation of I (cf. von Bruchhausen and Bersch, A., 1930, 1600; Winterfeld and Holschneider, this vol., 370).

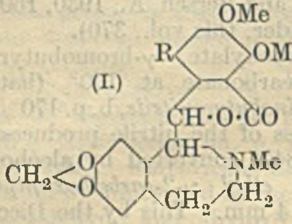
Ethyl piperidine-2-carboxylate, γ-bromobutyronitrile, and potassium carbonate at 100° (bath) give γ-2-*carbethoxypiperidinobutyronitrile*, b. p. 170°/12 mm. (the use of an excess of the nitrile produces a quaternary salt, m. p. 184°), converted by alcoholic hydrogen chloride into *ethyl* γ-2-*carbethoxypiperidinobutyrate*, b. p. 169°/14 mm. This by the Dieckmann reaction gives *ethyl* 1-*keto-octahydropyridocoline*-2-*carboxylate*, b. p. 155°/15 mm., hydrolysed by 20% sulphuric acid to 1-*keto-octahydropyridocoline*, b. p. 107°/14 mm. (*semicarbazone*, m. p. 215°; *methiodide*, m. p. 210°). Reduction of this with sodium amalgam and alcohol gives 1-*hydroxyoctahydropyridocoline*, b. p. 120°/13 mm., m. p. 65—68°, whilst Clemmensen reduction affords *octahydropyridocoline*, b. p. 43°/0·5 mm., 75°/14 mm. [*picrate*, m. p. 213° (decomp.); *methiodide*, m. p. 283°; *chloroaurate*, m. p. 170°].

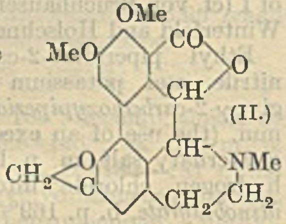
H. Burton.

Mechanism of the oxidation of laudanosine. V. K. Bhagwat, D. K. Moore, and F. L. Pyman (J.C.S., 1931, 443).—The compound $C_{14}H_8(OMe)_4$, m. p. 231° (corr.), obtained by oxidation of laudanosine with manganese dioxide and sulphuric acid (Pyman, J.C.S., 1909, **95**, 1266) or with mercuric acetate (Gadamer, A., 1916, i, 736) is 2 : 3 : 6 : 7-tetramethoxy-9 : 10-dihydroanthracene $(+0{\cdot}5H_2O$ and $+0{\cdot}5C_6H_6)$, m. p. (anhydrous) 227° (Robinson, J.C.S., 1915, **107**, 267). Gadamer's assumption that the substance is tetramethoxydibenzyl, formed by dimerisation of free dimethoxybenzyl radicals, is invalid.

H. Burton.

Synthesis of hydrastine. I. E. Hope, F. L. Pyman, F. G. P. Remfry, and R. Robinson (J.C.S., 1931, 236—247; cf. Proc. C.S., 1912, **28**, 17).—Hydrastinine and nitromeconine in boiling alcohol give 80—90% of the theoretical amount of a mixture, m. p. about 160—170°, of *anhydrohydrastininemeconines* (*nitrohydrastines*) (I, $R=NO_2$), which is rapidly decomposed by hot acetic acid, regenerating the starting materials; trituration of the mixture with 10% hydrochloric acid affords a *hydrochloride*, m. p. 137—138°. Reduction of the mixture with tin, stannous chloride, and hydrochloric acid in acetic acid below 25° yields dl-*aminohydrastine*-a, m. p. 216—217° (corr.) [dihydrochloride, m. p. 267—268°; tartrate, m. p. 201—203° (corr.); *acetyl* derivative, m. p. 208—211°], and dl-*aminohydrastine*-b, m. p. 196—197° (corr.), separable through the sparing solubility of the above hydrochloride. Reduction of the diazonium chloride from aminohydrastine-*a* with stannous chloride and hydrochloric acid gives *hydrazinohydrastine*-a, m. p. 175° (corr.) [hydrogen oxalate, m. p. 225° (decomp.); *iso*propylidene derivative, m. p. 190°], oxidised by copper acetate in dilute acetic acid to *hydrastine*-a (I, R=H), m. p. 137—138° (corr.) [hydrochloride, decomp. above 165°; *picrate*, m. p. 219° (decomp.); d-*camphorsulphonate* (+0·5H_2O), m. p. 145° (corr.; decomp.) after sintering at 135°; *hydrogen* d-*tartrate* (+3·5H_2O), m. p. 108—110° (corr.; decomp.)]. Similar oxidation of *hydrazinohydrastine*-b (+$CHCl_3$), m. p. (solvent-free) 183—184° (corr.) [iso*propylidene* derivative, m. p. 217—218° (corr.)], gives mainly *dedihydrohydrastine* (II), m. p. 183° (corr.), together with a small amount of *hydrastine*-b, m. p. 150—151° (corr.). Oxidation of hydrastines-*a* and -*b* and *l*-hydrastine (*picrate*, m. p. 184°) with manganese dioxide and 15% sulphuric acid affords, in each case, a pale greenish-brown fluorescent solution, which on successive treatment with sodium carbonate and potassium cyanide yields cyanodihydrohydrastinine. Similar oxidation of II affords an intense cherry-red solution which becomes pale brown when treated with sodium carbonate; the cyano-compound could not be isolated. Hydrastinine is formed when hydrastine-*a* or *l*-hydrastine is oxidised with dilute nitric acid at 75°; similar oxidation of II gives no hydrastinine.


(I.)

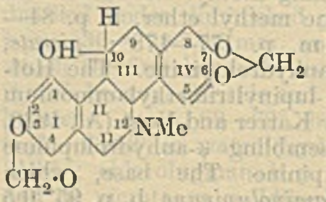

(II.)

Treatment of hydrazinohydrastine-*a* with copper chloride in dilute hydrochloric acid furnishes *chlorohydrastine*-a (I, R=Cl), m. p. 152°, which when treated with aluminium amalgam in boiling alcohol gives a small amount of hydrastine-*a*. Aminohydrastine-*a* is converted by the usual method into *iodohydrastine*-a (I, R=I), m. p., 172°, also formed together with *iodohydrastine*-b, m. p. 194—195° (corr.), from hydrastinine and iodomeconine in boiling methyl alcohol. Reduction of iodohydrastine-*a* with aluminium amalgam in boiling alcohol or 6% sodium amalgam and aqueous alcohol yields hydrastine-*a*. Hydrastinine and bromomeconine give a small amount of a bromohydrastine, m. p. 170—171° (corr.) [hydrobromide, m. p. 287—288° (decomp.)].

4-*Acetoxy*-, m. p. 127—128° (corr.); 4-*benzoyloxy*-, m. p. 135—136° (corr.); m-*nitrobenzoyloxy*-, m. p. 192—193° (corr.), and *p*-nitrobenzoyloxy-3-methoxyphthalides, m. p. 202—203°, prepared by the usual methods from normeconine methyl ether, do not condense with hydrastinine. Normeconine methyl ether and hydrastinine in boiling alcohol give the *hydrastininium salt* (?), m. p. 334° (corr.), of the ether.

H. Burton.

Constitution of chelidonine. E. Späth and F. Kuffner (Ber., 1931, 62, [*B*], 370—378).—Oxidation of *N*-acetylanhydrochelidonine with nitric acid affords benzene-1 : 2 : 4-tricarboxylic acid; the absence of benzene-tetracarboxylic or -pentacarboxylic acid shows the invalidity of the constitution assigned to chelidonine by Gadamer (A., 1924, i. 1227). Further insight into the structure of the alkaloid is sought by examination of the base, m. p. 136°, isolated by Gadamer and Stichel from crude sanguinarine to which the formula $C_{18}H_{17}N$ has been assigned. The base can be obtained from pure sanguinarine, which is closely allied to chelidonine. It has the composition $C_{17}H_{11}N$ and is identical with α-naphthaphenanthridine described by Graebe (A., 1905, i, 82). The skeleton structure of chelidonine and sanguinarine is thus established. Oxidation of chelidonine by potassium permanganate gives a mixture of hydrastic and 3 : 4-methylenedioxybenzene-1 : 2-dicarboxylic acid, isolated as the ethylimides. Each of the two methylenedioxy-groups must therefore be united to a benzene nucleus to which two carbon atoms are attached and the alcoholic hydroxyl group of chelidonine cannot be attached to either of these nuclei. The results of a study of the action of acetic anhydride and of the Hofmann degradation exclude the possibility of its presence in ring II, so that it must be assigned to ring III, as assumed by von Bruchhausen and Bersch (A., 1930, 1600). Reasons are advanced in favour of the view that it occupies position 10. The authors' experiments in conjunction with the observations of von Bruchhausen and Bersch (*loc. cit.*) and Schwarz (Diss., Marburg, 1928) allow the constitution I to be assigned to chelidonine.



On purely chemical grounds it is not possible to maintain the hypothesis of a near relationship between morphine, dionine, thebaine, and chelidonine indicated by their ultra-violet absorption spectra.

Bulbocapnine is oxidised by permanganate in feebly alkaline solution to 4 : 5-methylenedioxybenzene-1 : 2 : 3-tricarboxylic acid, m. p. 205—207° (decomp.) (*methyl* ester, m. p. 125—127°).

H. Wren.

***Strychnos* alkaloids. LVIII. Formation of diketonucine dihydrate and its reduction.** H. Leuchs and F. Kröhnke (Ber., 1931, 64, [*B*], 455—462).—Brucine can be oxidised by chromic acid to the Hanssen acid, $C_{19}H_{22}O_6N_2$, which is therefore regarded as an intermediate product of the oxidation of the alkaloid to the Wieland acid, $C_{17}H_{22}O_6N_2$ (2 : 3-diketonucine hydrate) (for nomenclature see A., 1930, 1456). The preparation of the Wieland acid from the substance $C_{17}H_{22}O_5N_2$, considered previously as 2 : 3 : 4-trihydroxynucine, is explained by the observation that 2 : 3-diketonucine dihydrate when acted on by sodium amalgam absorbs 2 atoms of hydrogen and loses 1 mol. of water, thus being reconverted into the compound $C_{17}H_{22}O_5N_2$. The last-named compound must therefore be 3-hydroxy-2-ketonucine hydrate. The alkaloid $C_{17}H_{20}O_3N_2Br_2$ (cf. A., 1929, 1320) is 2 : 2-dibromo-3-hydroxynucine or, more probably, 2 : 3-dibromo-2-hydroxynucine. It is considered that the acetyl derivative of the so-called trihydroxynucine (*loc. cit.*) is the diacetate of the monoacetylated anhydride of the compound $C_{17}H_{22}O_5N_2$ with 1 mol. of water of crystallisation.

2 : 3-Diketonucine dihydrate is transformed by acetic anhydride followed by treatment of the

product with perchloric acid in methyl alcohol into 2 : 3-*diketonucine perchlorate*, $C_{17}H_{18}O_4N_2,HClO_4$, $[\alpha]^{15}$ +53·3°/*d*, which appears to pass successively into the mono- and di-hydrate in aqueous solution.

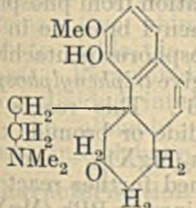
Criticism is passed on the communication of Späth and Bretschneider (this vol., 242). H. Wren.

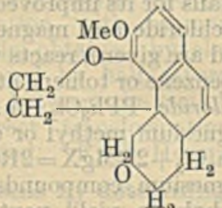
Ionisation constant of codeine. H. Baggesgaard-Rasmussen and I. Martins (Arch. Pharm., 1931, 269, 1—8).—Determinations using the quinhydrone electrode of the p_H of solutions of codeine and codeine hydrochloride give values of $6·7\times10^{-9}$ and $7·9\times10^{-7}$ for the acid and basic ionisation constants, respectively, of codeine. The activity coefficient of codeine from its solubility in 0·0—1·0*N*-sodium chloride and its partition coefficient between water and chloroform is also given. In the determination of codeine in syrups by dilution and extraction with chloroform, sodium hydroxide should be added to decrease its solubility in the aqueous phase.

H. E. F. Notton.

Sinomenine. XXIV. Degradation of sinomenine to *l*-thebenone. K. Goto, R. Inaba, and H. Shishido (Annalen, 1931, 485, 247—257).—Demethoxydihydrosinomenine methiodide (cf. A., 1930, 230) when heated with 25% potassium hydroxide gives *dl*-N-*methyldemethoxydihydrosinomenine* (I), m. p. 182°, $[\alpha]_D^{20}$ −54·94° in chloroform, the methiodide (not characterised) of which is converted by similar treatment into trimethylamine and l-*dehydrothebenone* (II), m. p. 113° (sinters at 104°), $[\alpha]_D^{18}$ −206·87° in chloroform. Reduction of II (hydrogen and palladised charcoal) gives l-*thebenone*, m. p. 134°, $[\alpha]_D^{18}$ −78·6° in chloroform (*oxime*, m. p. 204·5°).

(I.)





(II.)

Dihydrode-N-*methyldemethoxydihydrosinomenine*, m. p. 156·5°, $[\alpha]_D^{18}$ +67·82° in chloroform [the optical antipode of the dihydrode-*N*-methyldihydrothebanione of Wieland and Kotake (A., 1925, i, 1093)], prepared by reduction of I (hydrogen–palladium–charcoal) forms a *methiodide*, m. p. 226—229°, which with hot alkali gives *l*-thebenone and trimethylamine. Those compounds described above which have a double linking in the 9 : 10-position show strong halochromism, deepened by the presence of a keto-group, in concentrated sulphuric acid.

H. A. Piggott.

Arsinic acids of fluorene and its derivatives. F. E. Cislak and C. S. Hamilton (J. Amer. Chem. Soc., 1931, 53, 746—749).—The *acetyl* derivative, m. p. 250—253° (corr.), of 7-nitro-2-aminofluorene (prepared by reduction of 2 : 7-dinitrofluorene with alcoholic ammonium sulphide) is reduced by zinc dust and alcohol containing a little aqueous calcium chloride to 7-*amino-2-acetamidofluorene*, m. p. 188—192° (corr.; decomp.). This is converted into 2-*acetamidofluorene-7-arsinic acid*. *Fluorene-* and *fluorenone-2-arsinic acids* are also prepared. H. Burton.

10-Chloro-5 : 10-dihydrophenarsazine and its derivatives. XIV. Chloro-derivatives. L. A. Elson and C. S. Gibson (J.C.S., 1931, 294—305; cf. A., 1926, 1162).—The following substituted diphenylamines are prepared by (*a*) Ullmann's method (A., 1907, i, 842) and (*b*) Chapman's method (A., 1929, 550): (*a*) o-*chlorodiphenylamine* (I), b. p. 174—175°/12 mm., m. p. 15—16°; 2 : 5-*dichlorodiphenylamine* (II), b. p. 195°/17 mm.; 3 : 4-*dichlorodiphenylamine*, b. p. 218—220°/20 mm., m. p. 69° (obtained from 3 : 4-*dichlorodiphenylamine-2′-carboxylic acid*, m. p. 178°); 3 : 5-*dichlorodiphenylamine*, b. p. 200°/12 mm. (from the 2′-*carboxylic acid*, m. p. 245°); 3 : 4 : 5-*trichlorodiphenylamine*, b. p. 248°/20 mm., m. p. 85° (2′-*carboxylic acid*, m. p. 238°), and 5-*chloro-2-methyldiphenylamine*, b. p. 205—207°/23 mm. (2′-*carboxylic acid*, m. p. 200°); (*b*) 3 : 4′-*dichlorodiphenylamine*, b. p. 235°/25 mm., m. p. 63—64° (from N-3-*chlorophenylbenzimino-4-chlorophenyl ether*, m. p. 77°); 3 : 3′-*dichlorodiphenylamine*, b. p. 225—230°/18 mm.; 3′-*chloro-2-methyldiphenylamine*, b. p. 203°/20 mm. (the N-*benzoyl* derivative, m. p. 106°, is obtained by isomerisation of *N*-*o*-tolylbenzimino-3-chlorophenyl ether at 290°); 4′-*chloro-2-methyldiphenylamine*, b. p. 200—205°/20 mm. (from N-4-*chlorophenylbenzimino*-o-*tolyl ether*, m. p. 65°); 2′ : 4′-*dichloro-2-methyldiphenylamine* (III), b. p. 205°/20 mm., m. p. 48° (from N-o-*tolylbenzimino-2 : 4-dichlorophenyl ether*, m. p. 53°). *Benzoyl-2′-chloro-2-methyldiphenylamine*, m. p. 132°, which could not be hydrolysed, is obtained by isomerisation of N-o-*tolylbenzimino-2-chlorophenyl ether*, m. p. 64°, at 290°. All the above diphenylamines except I, II, and III (and 2 : 4-dichlorodiphenylamine) condense with arsenious chloride yielding derivatives of 10-chloro-5 : 10-dihydrophenarsazine. The non-condensation of 2-chlorodiphenylamines supports the view (cf. A., 1930, 1601) that chelation occurs between the 2-chlorine and imino-hydrogen atoms, thus restricting the motion of the latter atom. When only one dihydrophenarsazine derivative is produced from a 3-chlorodiphenylamine, it is probable that this is the 1-chloro-derivative (possibility of chelation); the compound from *m*-chlorodiphenylamine and arsenious chloride is 1 : 10-dichloro-5 : 10-dihydrophenarsazine (cf. A., 1926, 1162). When two condensation products are isolated, the more fusible form is considered to be the 1-substituted isomeride, *i.e.*, the chelated form.

3 : 4-Dichlorodiphenylamine and arsenious chloride give a mixture of 1 : 2 : 10-, m. p. 220° after shrinking at 205°, and 2 : 3 : 10-*trichloro*-5 : 10-*dihydrophenarsazines*, m. p. 265—268°, also formed (with m. p. 230—235° and 273—274°) when 3 : 4-*dichlorodiphenylamine-6′-arsinic acid*, m. p. 150°, prepared by the Ullmann method from 3 : 4-dichloroaniline and *o*-bromophenylarsinic acid, is reduced with sulphur dioxide in presence of hydrochloric acid and a trace of iodine. 3 : 4′-Dichlorodiphenylamine affords a mixture of 1 : 8 : 10-, m. p. 240—242°, and 3 : 8 : 10-*trichloro*-5 : 10-*dihydrophenarsazines*, m. p. 292°. 3 : 5-Dichlorodiphenylamine yields 1 : 3 : 10-*trichloro*-5 : 10-*dihydrophenarsazine*, m. p. 251—252°, oxidised by hydrogen peroxide in acetic acid to 1 : 3-*dichlorophenarsazinic acid*, not melted at 280°. 1 : 2 : 3 : 10-*Tetrachloro*-5 : 10-*dihydrophenarsazine*, m. p. 260°

(from 3 : 4 : 5-trichlorodiphenylamine) is oxidised similarly to 1 : 2 : 3-*trichlorophenarsazinic acid*, not melted at 290°. 1 : 9 : 10- or 1 : 7 : 10- or 3 : 7 : 10-*Trichloro*-5 : 10-*dihydrophenarsazine*, m. p. 298°, is obtained in small yield from 3 : 3′-dichlorodiphenylamine. 4-, 3′-, and 4′-Chloro-2-methyldiphenylamines give 2 : 10-*dichloro-4-methyl-*, m. p. 245° (decomp.), 1(or 3) : 10-*dichloro-6-methyl-*, m. p. 262° (decomp.), and 2 : 10-*dichloro-6-methyl-*, m. p. 199°, -5 : 10-*dihydrophenarsazines*, respectively.

H. Burton.

Derivatives of phenylboric acid, their preparation, and action on bacteria. W. Seaman and J. R. Johnson (J. Amer. Chem. Soc., 1931, **53**, 711—723).—Nitration of phenylboric acid, m. p. 210·6—212·6° (all m. p. are corr.), m. p. (block) 221°, with nitric acid (*d* 1·5, free from nitrous acid) below −9° gives a mixture of approximately 85% of *m*-, m. p. 273° (decomp.), m. p. (block) 319°, and 15% of o-*nitrophenylboric acid*, m. p. 139·2—140·8°, m. p. (block) 147·5° (cf. Ainley and Challenger, A., 1930, 1457). A suspension of the acid in acetic anhydride gives with nitric acid (*d* 1·5) first at −15° to −7° and then at 20°, a mixture (65% yield) of about 95% of o- and 5% of p-*nitrophenylboric acid*, m. p. 305·5° (decomp.), m. p. (block) above 360°. The positions of the nitro-groups are determined by conversion of the acids into bromonitrobenzenes. m-*Aminophenylboric acid*, m. p. 92·8—93·8° resolidifying with m. p. about 200° with darkening, m. p. (block) 176° [*acetyl* derivative, m. p. 274—275°, m. p. (block) about 160° with immediate resolidification; *benzoyl* derivative, m. p. 290°, m. p. (block) about 200° with immediate resolidification], is prepared by a modification of the method of Jacobs, Heidelberger, and Rolf (A., 1919, i, 50) from the *m*-nitro-compound. o-*Benzamidophenylboric acid* (the amino-acid could not be isolated) has m. p. 283—284°, m. p. (block) 319·5° with darkening. The nitrophenylboric acids are more bacteriostatic towards *Staphylococcus aureus* and *B. typhosus* than is phenylboric acid; *m*-aminophenylboric acid and its derivatives are inactive.

H. Burton.

Alkali-organic compounds. IX. Reactions of alkali metal alkyls with mercury and mercuric chloride. K. Ziegler (Ber., 1931, 64, [*B*], 445—448; Ziegler and Colonius, A., 1930, 590).—Mainly a reply to Bergmann (A., 1930, 1568). Sodium diphenylmethyl in ether is converted by mercuric chloride at the ordinary temperature into ααββ-tetraphenylethane; at −80° the change proceeds similarly but more slowly. Lithium benzyl is transformed by mercuric chloride or mercury into mercury dibenzyl, m. p. 110—111°. H. Wren.

Structure of compounds produced by the addition of mercuric salts to olefines. II. E. Griffith and C. S. Marvel (J. Amer. Chem. Soc., 1931, **53**, 789—792; cf. A., 1926, 747).—Treatment of *d*-bornyl cinnamate, b. p. 200—202°/6—7 mm., $[\alpha]_D^{27}$ +32·9° in ethyl acetate, with mercuric acetate in methyl alcohol gives d-*bornyl β-methoxy-α-acetoxymercuri-β-phenylpropionate*, m. p. 90—100°, converted by methyl-alcoholic sodium bromide into two d-*bornyl β-methoxy-α-bromomercuri-β-phenylpropionates*, m. p. 131—132°, $[\alpha]_D^{25}$ +17·3° in ethyl acetate, and m. p. 147—148°, $[\alpha]_D^{25}$ +14·9° in ethyl acetate. Unstable or low-melting mercury derivatives wore obtained from *cinnam*-l-*methylamide*, m. p. 158—159°, $[\alpha]_D^{25}$ −82·9° in methyl alcohol, and d-, b. p. 174—177°/5 mm., $[\alpha]_D^{30}$ +42·4° in ethyl acetate, and l-β-*octyl cinnamates*, b. p. 175—180°/6 mm., $[\alpha]_D^{27}$ −43·3° in ethyl acetate. H. Burton.

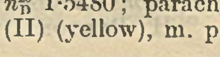
Alkali-organic compounds. X. Ready preparation of lithium benzyl. K. Ziegler and F. Dersch (Ber., 1931, 64, [*B*], 448—452).—Lithium benzyl is conveniently prepared by treating an ethereal solution of magnesium benzyl chloride with lithium phenyl, whereby lithium chloride and, probably, magnesium phenyl benzyl are produced; the last-named compound is converted by further addition of lithium phenyl into lithium benzyl, thus obtained in 0·2—0·4*M* solutions which contain magnesium phenyl. Magnesium *iso*propyl chloride and lithium phenyl afford *lithium* iso*propyl*, converted by *as*-diphenylethylene into the *compound* $CPh_2Li\cdot CH_2Pr^{\beta}$, which with carbon dioxide gives αα-*diphenyl-γ-methylvaleric acid*, m. p. 131—133°. H. Wren.

Magnesium *p*-methoxybenzyl bromide. H. Gilman and E. A. Zoellner (Bull. Soc. chim., 1931, [iv], **49**, 7—9).—Details are given for preparing magnesium *p*-methoxybenzyl bromide, which reacts normally with carbon dioxide. R. Brightman.

Magnesium derivatives of dichlorotriphenylphosphine, and pentaphosphines. V. Grignard and J. Savard (Compt. rend., 1931, **192**, 592—595).—Triphenylphosphine oxide, m. p. 155—157° (details for its improved preparation from phosphorus oxychloride and magnesium phenyl bromide in 65% yield are given), reacts with phosphorus pentachloride in benzene or toluene at 10° to give *triphenylphosphine dichloride*, PPh_3Cl_2, m. p. 176°. This reacts with magnesium methyl or ethyl iodide or bromide thus: $PPh_3Cl_2+2RMgX=2RCl+PPh_3(MgX)_2$, and the magnesium, compounds so formed further react with alcohols to yield pentaphosphines: $PPh_3(MgX)_2+2ROH=2MgX(OH)+PPh_3R_2$, and thus are obtained (15—20% yield) *triphenyl-dimethyl-*, m. p. 163—166°; *-diethyl-*, m. p. 172°, and *-di*-n-*propyl-*, m. p. 179—182°, *-pentaphosphine*. The different type of reaction which occurs with dichlorophenylphosphine and the Grignard reagent, $PPhCl_2+2RMgX=PPhR_2+2MgXCl$, indicates that the chlorine in tervalent phosphorus compounds behaves differently from that which saturates the remaining two valencies in quinquevalent phosphorus derivatives.

J. W. Baker.

ββ′-Dichlorodiethyl ether. II. Heterocyclic compounds containing two members of the oxygen group in the ring. 1 : 4-Selenoxan. C. S. Gibson and J. D. A. Johnson (J.C.S., 1931, 266—272).—ββ′-Dichloro- (m. p. −44°) and di-iodo- (m. p. −19°) -diethyl ether react with aqueous sodium selenide to give 1 : 4-*selenoxan*,



$O\langle\begin{smallmatrix}CH_2\cdot CH_2\\ CH_2\cdot CH_2\end{smallmatrix}\rangle Se$ (I), m. p. −21·5°, b. p. 66°/22 mm., 167·5—168·5°/763 mm., d_4^t 1·597—0·00135*t*, n_D^{20} 1·5480; parachor 245·2, isolated as its *dibromide* (II) (yellow), m. p. 132° (decomp.), which is formed by the action of bromine on I in carbon tetrachloride. The *dichloride*, colourless, m. p. 127—129° (decomp.), and *di-iodide*, deep violet, m. p. 106—107°, are formed similarly. The *mercurichloride*, m. p. 179°, *methiodide*, m. p. 171°, *chloroplatinate* $(C_4H_8OSeCl)_2PtCl_6$, m. p. 149° (decomp.), and *chloroaurate*, decomp. 142—144°, of I are described and their electronic formulæ discussed. Treatment of II with moist silver oxide gives an oily hydroxide, which on treatment with concentrated nitric acid furnishes the *hydroxy-nitrate* $C_4H_8OSe(OH)\cdot NO_3$, decomp. 140—141°, also formed by the action of concentrated nitric acid on I. In benzene solution, II gives with dry ammonia an *ammino*-derivative, $C_4H_8OSeBr_2,2NH_3$, which froths at 93° and turns brownish-yellow at 130°.

J. D. A. Johnson.

Reduction of organic mercury compounds by stannous salts as a method of synthesis of organic tin compounds. K. A. Kotscheschkov and A. N. Nesmejanov (J. Russ. Phys. Chem. Soc., 1930, **62**, 1795—1812).—Reduction takes place giving stannic compounds of the type R_2SnX_2, but deviations from this may occur according to the organic radical, stannous salt, and solvent. *Stannic* compounds of the following were synthesised: di-*p*-tolyl dibromide, m. p. 74°; di-α-naphthyl dichloride, m. p. 137—137·5°; di-β-naphthyl dichloride, m. p. 110—111°; di-β-naphthyl dibromide, m. p. 114—115°; also p-*tolylstannic acid*. E. B. Uvarov.

Chemical individuality of serum-proteins. G. Ettisch and H. Sachsse (Biochem. Z., 1931, **230**, 129—135).—The affinity of proteins for copper, determined by *E.M.F.* methods, has been used to investigate the chemical individuality of the serum-proteins. One third saturation with ammonium sulphate yields the euglobulin obtained by electrodialysis. Paraglobulin prepared by half saturation is an individual intermediate between the euglobulin and the albumin. No direct transformation of albumin into globulin is indicated. F. O. Howitt.

Characterisation of proteins by determination of affinity. G. Ettisch, H. Sachsse, and W. Beck (Biochem. Z., 1931, **230**, 68—92)—*E.M.F.* measurements have been made on protein solutions in presence of the biuret test reagents. Equilibrium between alkali and protein is established in 24 hrs. (shown by *E.M.F.*, depolarisation, viscosity, and light absorption). Globulin from serum-protein (electrodialysis) is distinct from the albumin fraction, especially as regards the electrochemical behaviour at high protein concentrations. The results indicate that the degree of affinity and number of affinity centres for copper are greater in globulin than in albumin.

F. O. Howitt.

Hydrolysis of caseinogen by acids and alkalis. I. S. Yaitschnikov (J. Russ. Phys. Chem. Soc., 1930, **62**, 1871—1878).—Curves are given expressing the yields of protein, peptone, ammonia, amino-, and basic nitrogen produced at various times during the acid or alkaline hydrolysis of caseinogen.

R. Truszkowski.

Denaturation of albumin. W. D. Bancroft and J. E. Rutzler, jun. (J. Physical Chem., 1931, **35**, 144—161).—Heat-coagulated egg-white sols can be peptised by potassium iodide or thiocyanate, carbamide, ammonium thiocyanate and sodium hydrogen carbonate, formaldehyde, and sucrose, whilst sodium hydroxide peptises (some hydrolysis) heat-coagulated albumin. Ether does not denature albumin and egg-white sols can be prevented from coagulating by extraction with ether, which probably removes a coagulant which (cf. crude lecithin from egg-yolk) confers heat stability. The "denaturation" by ether which sometimes occurs is due to removal of adsorbed water. Coagulated egg-white repeptises in boiling water, especially when it contains traces of ether. The sodium nitroprusside test for "denatured" egg-albumin is untrustworthy. Measurements of iso-electric point and immunobiological teats indicate that coagulated and repeptised egg-white sols are identical with the original sol. L. S. Theobald.

Heat-coagulable protein from gelatin. S. E. Sheppard, J. H. Hudson, and R. C. Houck (J. Amer. Chem. Soc., 1931, **53**, 760—765).—Gelatins from calf-skin, bone, hide, etc. contain 0·2—0·6% of a coagulable protein, separable by adjusting the p_H of a gelatin solution to 4·7 and then heating at 80—100°. The isoelectric point of the coagulated protein (N about 14%, S about 0·8%) is (electro-endosmotic method) about p_H 4. The isoelectric point of egg-albumin, denatured by heat, is p_H 4·7. The coagulable protein appears to be identical with the "insoluble gelatin fractions" of Knaggs, Manning, and Schryver (A., 1923, i, 1144) and of Kunitz and Northrop (A., 1929, 458). H. Burton.

Vegetable proteins. II. Typhoidin, the alcohol-soluble protein of *Pennisetum typhoideum*. D. Narayanamurti and C. V. R. Aiyar (J. Indian Chem. Soc., 1930, **7**, 945—952).—The sun-dried grain contains water (7·92%), ash (2·34%), ether-soluble material (6·3%), crude fibre (2·3%), crude protein (9·27%), and carbohydrate (by difference, 71·87%). Details are given for the extraction of a prolamine (termed *typhoidin*) (C 56·8, H 5·56, N 14·3, S 0·605%) from the grain by cold 70% alcohol. The nitrogen distribution in the protein is similar to that in other prolamines. The protein contains relatively high quantities of cystine and tryptophan; the cystine content does not account for the total sulphur. H. Burton.

Iodination of peptone. P. Bruno (Giorn. Farm. Chim., 1930, **79**, 308—309; Chem. Zentr., 1930, ii, 3299).—Peptone (360 g.) is heated with iodine (100 g.) and water (350 g.) below 100°; the product is readily soluble in water to give a clear solution and contains no free iodine.

A. A. Eldridge.

Elimination of sulphur in carbon determinations by direct combustion. W. H. Blatchley (Ind. Eng. Chem. [Anal.], 1931, **3**, 13).—Additions to the usual number of absorption tubes in the train used for carbon determinations are unnecessary if the outlet end of the combustion tube is packed loosely with ignited asbestos; after a few combustions with red lead a sublimate of this substance forms on the asbestos, and oxidises to trioxide and fixes as lead sulphate the whole of the sulphur dioxide evolved.

H. F. Gillbe.

Micro-determination of carboxyl. S. Tsurumi and Y. Sasaki (Sci. Rep. Tôhoku, 1930, 19, 681—688).—A micro-modification of the Fuchs–Hunter–Edwards method for the determination of carboxyl groups (Fuchs, A., 1889, ii, 463; Hunter and Edwards, A., 1913, ii, 535), with an accuracy of 1%, is described. The acid (2—3 mg.) is dropped into a solution of potassium hydrogen sulphide saturated with hydrogen sulphide, and the evolved gas measured. The method fails with excessively weak acids, with those acids the alkali salts of which are insoluble in the sulphide solution, with *p*-nitrophenols, monohalogenodihydric phenols, and with keto-phenols such as methylphloroglucinol. G. Discombe.

Detection of tartaric acid in presence of citric acid by photo-catalysis. T. Pavolini (Giorn. Farm. Chim., 1930, 79, 310—311; Chem. Zentr., 1930, ii, 3319).—The solution is treated with uranyl acetate and exposed for at least 30 min. to sunlight or intense artificial light; tartaric acid alone among the α-hydroxy-aliphatic acids affords glyoxal, which is detected by means of phenylhydrazine or its *p*-sulphonic acid. A A. Eldridge.

Identification of halides as 3 : 5-dinitrobenzoates. I. C. L. Tseng and E. J. H. Chu (Nat. Centr. Univ. Sci. Rep., **A**, 1930, 1, 9—14).—In Mulliken's method, dry benzene is substituted for alcohol. Diphenylmethyl chloride gives diphenylmethyl 3 : 5-dinitrobenzoate, m. p. 142°. Chemical Abstracts.

Modifications of Mulliken's system for the identification of compounds of Order I. C. L. Tseng (Nat. Centr. Univ. Sci. Rep, **A**, 1930, 1, 1—3).—The first four genera are arranged in the order: aldehydes, acids, phenolic compounds, carbohydrates. Additional tests for solubility in water and acidity (Congo-red) are recommended. Chemical Abstracts.

Microchemical identification of cryogenin (*m*-benzamidosemicarbazide). G. Denigès (Bull. Pharm. Soc. Bordeaux, 1930, 68, 49—51; Chem. Zentr., 1930, ii, 2680).—Characteristic hexagonal crystals are obtained from a solution in a mixture of alcohol and chloroform (1 : 2). A solution in 1% potassium chlorate solution becomes orange on addition of hydrochloric acid and violet when made alkaline with sodium hydroxide. A. A. Eldridge.

Colorimetric determination of cryogenin. G. Denigès (Bull. Soc. Pharm. Bordeaux, 1930, 68, 51—52; Chem. Zentr., 1930, ii, 2680; cf. preceding abstract).—The above reaction is employed quantitatively. A. A. Eldridge.

System for microchemical identification of alkaloids. J. F. H. Amelink (Pharm. Weekblad, 1931, 68, 159—185, 211—216, 221—229).—A tabulation is made of the microchemical reactions between platinic chloride and iodide, gold chloride and bromide, mercuric chloride, potassium ferro- and ferri-cyanide, potassium bismuth iodide and periodide, potassium hydroxide, and picrolonic acid, and 78 selected alkaloids. Accounts are given of the preparation of the reagents and the methods of making the tests; a great number of photomicrographs of crystalline products are reproduced. The reactions of percaine (the hydrochloride of the condensation product of α-butylhydroxycinchoninic acid and diethylethylenediamine), diocaine (diallylhydroxyethylenediphenyldiamidine), harmine (banisterine), and harmaline (dihydroharmine) with the selected reagents are described. The crystalline precipitate with gold bromide is characteristic for harmine, and that with platinic chloride for harmaline; the latter gives a blood-red coloration with acetaldehyde and its homologues. S. I. Levy.

Biochemistry.

The oxidation process in red blood-corpuscles. K. Zeile and H. von Euler (Z. physiol. Chem., 1931, **195**, 35—38).—The work of Michaelis and Salomon (A., 1930, 1053) is confirmed. A. Renfrew.

Active iron. VI. Characterisation by benzidine-peroxidase and catalase reactions. A. Simon and T. Reetz.—See this vol., 439.

Influence of the chlorophyll content of fodder on the formation of blood-corpuscles. A. Zih (Pflüger's Archiv, 1930, **225**, 728—736; Chem. Zentr., 1930, ii, 3434).—Seasonal variations in the corpuscle content of the blood of rabbits are due to variations in the amount of chlorophyll ingested. A. A. Eldridge.

Quantity of free water in red blood-corpuscles. E. Schiødt (Biochem. J., 1930, **25**, 8—10; cf. Gough, A., 1924, i, 583; Ege, A., 1927, 892; Krevisky, A., 1930, 942).—The volume values of blood-corpuscles in isotonic, hypotonic, and slightly hypertonic salt solutions when inserted in the equation for the van 't Hoff–Boyle–Mariotte law yield values of about 65% for the quantity of free water. The same blood in highly hypertonic solutions of the same salt gives lower values for the quantity of free water—down to 35%. S. S. Zilva.

Determination of water in blood and serum. M. Dolch and E. Poechmueller (Z. physiol. Chem., 1931, **195**, 28—34).—To 15 c.c. of blood or serum, 100 c.c. of alcohol are added and the mixture is boiled for 10 min. To 20 c.c. of the clear supernatant liquid are added 20 c.c. of xylene and the separation temperature of the xylene–aqueous alcohol mixture is determined. The water content of the blood or serum is then read from a graph. The results are about 2% higher than those obtained by the ordinary method. A. Renfrew.

Glycolysis in blood. II. The pyrophosphate fraction and glycolysis. H. K. Barrenscheen and B. Vásárhelyi (Biochem. Z., 1931, **230**, 330—346).—The pyrophosphate fraction of the bloods of the animals investigated increases in the following order: horse < ox < dog < rabbit < guinea-pig < man < pig.

With the exception of pig's blood, the pyrophosphate fraction of the different bloods increases with increasing glycolytic power. During glycolysis, a small increase of pyrophosphate fraction is accompanied by a decrease in inorganic phosphorus. Acceleration of glycolysis with sulphate causes a decrease of the "pyrophosphate fraction." Attempts to isolate pyrophosphate as such from erythrocytes were unsuccessful, the pyrophosphate being organically combined. Whole blood, corpuscles, and to a smaller extent serum and plasma contain an enzyme which hydrolyses pyrophosphate and is inhibited by fluoride.
P. W. CLUTTERBUCK.

Glycolysis in blood. III. Inhibition of glycolysis. H. K. BARRENSCHEEN and K. BRAUN (Biochem. Z., 1931, **231**, 144—172).—The restriction or inhibition of glycolysis in human erythrocytes (in the experiments with ether rabbit erythrocytes were used) caused by hæmolysis, fluoride, oxalate, ether, chloroform, monochloro-, monobromo-, or monoiodoacetic acid leads always to the conversion of organic into inorganic phosphate in the erythrocytes, the chief source of the inorganic phosphate thus produced being the organic phosphate, which is easily hydrolysed by acid (the pyrophosphate fraction). When hydrolysis is inhibited by fluoride or by the halogenated acetic acids a difficultly hydrolysable hexosediphosphate is produced. Since after glycolysis has been inhibited by hæmolysis the inhibition can be suppressed by the action of phosphate, hydrogen carbonate, or borate, it follows that the glycolytic process is independent of the maintenance of the structure of the cells. From these results and the facts that fermentation with yeast poor in, or free from, co-enzyme is slightly activated by the pyrophosphate fraction from erythrocytes and that when glycolysis has been inhibited by hæmolysis, by fluoride, or by monohalogenoacetic acids, addition of hexosediphosphoric acids leads to accumulation of methylglyoxal, it is concluded that the pyrophosphate fraction contains either the co-enzyme required for glycolysis or the activator of the co-enzyme. W. MCCARTNEY.

Hagedorn–Jensen method for the determination of blood-sugar. H. KRAMER and A. STEINER (Biochem. J., 1931, **25**, 161—165).—The equivalent of 20—30 mg. of sugar per 100 c.c. is derived from reducing substances other than sugar. There is also a retention of 4—22 mg. of fermentable sugar per 100 c.c. in the cotton plugs employed for filtration. Hagedorn and Jensen's table for the calculation of the sugar is criticised. S. S. ZILVA.

Cholesterol metabolism. I. Determination of free and combined cholesterol in small amounts of blood. R. MANCKE (Biochem. Z., 1931, **231**, 103—109).—The author's modification (A., 1927, 275) of the method of Windaus (A., 1909, i, 172) has now been applied to the determination of free and combined cholesterol in 1·0—0·5 c.c. of blood-serum. W. MCCARTNEY.

Influence of lecithin on the stability of serum-proteins. S. WENT and F. FARAGÓ (Biochem. Z., 1931, **230**, 238—244).—The phenomenon of lecithin forming clear solutions in plasma was investigated. In mixtures of aqueous lecithin emulsions and serum there exists a marked reciprocal relationship between the amounts of euglobulin and pseudoglobulin I on the one hand and of pseudoglobulin II and albumin on the other. Each of these pairs of proteins appears to form a complex with lecithin and intermediately situated are serum-protein dispersoids, the stability of which also depends on the amount of lecithin present. F. O. HOWITT.

Globulin and albumin fractions of serum. II. Distribution of lipins, precipitinogens, and bacterial agglutinins amongst the various fractions of cattle-serum. B. LUSTIG and R. KATZ (Biochem. Z., 1931, **231**, 39—44; cf. A., 1930, 1607).—Each of the fractions into which the proteins can be divided by the authors' methods exhibits specificity as regards content of lipins. This content is highest in the albumins and lowest in the euglobulins. Of the eu- and pseudo-globulin fractions those which are soluble in sodium chloride solutions have the highest, those which are soluble in water the lowest, content of total lipins and lecithin. The amount of specific precipitinogens is highest in those eu- and pseudo-globulin fractions which are soluble in sodium chloride solution and lowest in the first and second albumin fractions. Normal agglutinins are found chiefly in the euglobulin fractions and are absent from the albumin fractions. Of the globulin fractions those which are soluble in sodium carbonate solution have the highest, those which are soluble in sodium chloride solution the lowest, content of agglutinins. W. MCCARTNEY.

Refractometric investigation of serum-proteins. III. Specific refraction of the total protein, and the refraction of the non-protein constituents of horse-serum. IV. Specific refraction of the protein fractions of horse-serum. D. VON DESEÖ (Biochem. Z., 1931, **230**, 373—382, 383—394).—III. Values of $n^{17\cdot5}$ and $d^{17\cdot5}$ of normal and immune sera and the protein content are determined. The figures so obtained are used for calculation of the constants which determine the magnitude of the refractive index and the specific gravity (cf. A., 1930, 359).

IV. Tables summarise a large number of results obtained for $n^{17\cdot5}$, $d^{17\cdot5}$, the protein and ammonium sulphate contents (determined gravimetrically) for serum-proteins precipitated by varying degrees of saturation with sulphate and for their filtrates and for solutions of albumin, globulin, and mixtures of these.
P. W. CLUTTERBUCK.

Determination of the $p_{\rm H}$ of blood-serum with the quinhydrone electrode. M. E. HANKE (Proc. Soc. Exp. Biol. Med., 1930, **27**, 972—973).—An apparatus having a total capacity of about 1 c.c., and employing 0·2 c.c. of serum, is described.
CHEMICAL ABSTRACTS.

Antimony and hydrogen electrodes [for determination of $p_{\rm H}$ of blood-serum]. M. VERAIN and TOUSSAINT (Compt. rend. Soc. Biol., 1930, **103**, 611—612; Chem. Zentr., 1930, ii, 2289).—Concordant results were obtained.
A. A. ELDRIDGE.

Determination of urea in small quantities of blood. M. FIORENTINO (Riforma Med., 1929, No.

38, 21 pp.; Chem. Zentr., 1930, ii, 2926).—Blood (0·25 c.c.) is mixed with water (1·5 c.c.) and 50% trichloroacetic acid (0·25 c.c.), kept for 2 min. at 100°, and centrifuged; 1·6 c.c. are then treated with trichloroacetic acid solution (0·2 c.c.) and acetic acid (3 c.c.), 5 c.c. of 5% xanthhydrol solution in acetic acid being added dropwise. After 10 min. the mixture is centrifuged and decanted; 4—5 drops of methyl alcohol are added to the residue and centrifuged after mixing, the procedure being repeated with alcohol and then with ether. The precipitate is then dissolved in 5 c.c. of 0·1*N*-potassium dichromate (containing sulphuric acid) and 5 c.c. of sulphuric acid, the treatment being repeated; after dilution to 45 c.c. with sulphuric acid the liquid is kept for 15 min. with intermittent mixing. After dilution with water (200 c.c.) and cooling, potassium iodide is added and the iodine titrated with *N*/40-thiosulphate.

A. A. ELDRIDGE.

Fate of choline in the blood. F. WREDE and E. BRUCH (Z. physiol. Chem., 1931, **195**, 255—259).—About 80% of the choline added to defibrinated ox-blood or to sheep's serum can be recovered after 7 hrs. at 37° by the method previously described (A., 1929, 1191). This is contrary to the findings of Page and Schmidt (A., 1930, 1614). H. BURTON.

Action of blood on uric acid. A. ROWIŃSKA (Acta Biol. Exp., Warsaw, 1930, **6**, 37—44).—Hæmolysed human or avian blood destroys uric acid. The velocity of decomposition is retarded by diminution of oxygen supply. Unhæmolysed blood does not catalyse the oxidation of uric acid.

R. TRUSZKOWSKI.

Changes, caused by ultra-violet irradiation, in the distribution of chlorine in blood. J. GLASS (Biochem. Z., 1931, **231**, 45—53).—In the blood of rabbits which are exposed for 2—4 hrs. to powerful ultra-violet radiation the ratio of the chlorine content of the corpuscles to that of the plasma is increased. A similar increase is found after 24 hrs. in the blood of men who have been exposed to the radiation for 3—8 min. It follows that such irradiation alters the acid–base equilibrium of the blood, producing acidosis. W. MCCARTNEY.

Reciprocal influence of the inorganic constituents of blood-serum on their physical condition. H. G. SCHOLTZ (Biochem. Z., 1931, **231**, 135—143).—Experiments with horse- and ox-serum to which approximately isotonic potassium, sodium, calcium, or magnesium salts were added, the mixtures being subsequently subjected to ultrafiltration, and on cats to which some of the salts were administered, show that calcium–phosphate and magnesium–phosphate complexes can be produced in the serum. The formation of the complexes is more pronounced *in vitro* than *in vivo*. Addition of calcium chloride to serum increases the amount of potassium which can be separated by ultrafiltration. Similarly, addition of magnesium chloride increases both *in vitro* and *in vivo* the amount of calcium which can be separated by ultrafiltration. The results support the view that serum contains colloidal potassium compounds and point to analogy with the permutit reaction.

W. MCCARTNEY.

Determination of the physical state of the mineral constituents of serum by electro-ultrafiltration. R. SPIEGLER (Biochem. Z., 1931, **230**, 253—258).—Methods are described whereby serum is subjected to ultrafiltration and the residue to electro-ultrafiltration for varying lengths of time, and it is claimed that quantitative fractional separation of the mineral constituents is attained.

P. W. CLUTTERBUCK.

Serum-electrolyte in normal and pathological conditions. D. W. ATCHLEY and E. M. BENEDICT (J. Clin. Invest., 1930, **9**, 265—294).—Serum-electrolyte partitions were made in normal and pathological conditions. If hydrogen carbonate, chloride, protein, phosphate, sulphate, and ketones were measured, the so-called "undetermined acids" were negligible. The normal mean total base was 151·9 and the total acid 151·7 mille-equiv. per litre. Variations in pathological conditions are recorded.

CHEMICAL ABSTRACTS.

Hydrotropic solution of calcium, in relation to the solution of calcium in serum. A. VON KÚTHY and H. BANGA (Biochem. Z., 1931, **230**, 458—465).—The similarity of the hydrotropic solution of calcium in sodium salicylate solutions and the state of solution of calcium in serum is emphasised, the calcium in both cases being present partly in the ionised condition and partly as a negatively-charged non-diffusible complex. P. W. CLUTTERBUCK.

Micro-determination of calcium and phosphorus in blood and tissues. G. WIDMARK and B. VAHLQUIST (Biochem. Z., 1931, **230**, 245—252).—The use of a new filter enables the usual methods to be somewhat simplified. The calcium in 2 c.c. of plasma can be determined with an accuracy of 2—3% and the phosphatide-phosphorus in 1 c.c. of plasma and the acid-soluble phosphorus in 2 c.c. of plasma with an accuracy of 1%. The same accuracy is obtained in determinations in tissues when the calcium content is of the order of 0·2—0·3 mg. and the phosphorus content 0·05—0·1 mg.

P. W. CLUTTERBUCK.

Phosphorus distribution, sugar, and hæmoglobin in the blood of fish, eels, and turtles. C. M. MCCAY (J. Biol. Chem., 1931, **90**, 497—505).—The blood of pike and carp contains about four times as much phosphorus as cow's blood, eel blood being intermediate. The plasma-phosphorus and blood-sugar of the pike are higher than the corresponding values for the carp. Turtle blood has low values for plasma constituents. Between spawning and death, the blood changes of the lamprey-eel consist mainly of losses of hæmoglobin and dextrose.

A. COHEN.

Physico-chemical properties of crocodile blood (*Crocodilus acutus*, Cuvier). D. B. DILL and H. T. EDWARDS (J. Biol. Chem., 1931, **90**, 515—530).—The serum-protein, hæmoglobin content, and buffer value of crocodile blood are lower, and the effect of acid in reducing the affinity of hæmoglobin for oxygen is greater, than in man. A. COHEN.

Relation between blood-sugar and -coagulation time. A. PARTOS (Pflüger's Archiv, 1930, **224**, 448—450; Chem. Zentr., 1930, ii, 3308).—In normal or depancreatised cats rise of blood-sugar is accompanied by a rise in the coagulability of the blood, and conversely. Hyperglycæmic substances (morphine, adrenaline) increase the blood-coagulability proportionally to the rise in blood-sugar; similarly, retardation of coagulation by novirudin is accompanied by low blood-sugar values. A. A. Eldridge.

Effect of reduction of atmospheric pressure on the resistance of red blood-corpuscles to the action of hypotonic sodium chloride solutions. C. Naegeli (Biochem. Z., 1931, **231**, 95—102).—The resistance to the action of hypotonic sodium chloride solutions of the erythrocytes of the blood of rabbits is greatly influenced by the pressure of the air in which they live. After periods from 144 to 192 hrs. at pressures of 260—340 mm. the concentration of the salt solution which just fails to produce hæmolysis is much lower and that of the salt solution which is just sufficient to produce complete hæmolysis is much higher than in the case of erythrocytes from the blood of rabbits living in air at ordinary pressures. W. McCartney.

Hæmolytic action of potassium cyanide and its neutralisation by certain carbohydrates. P. Moretti and G. Muscolino (Arch. Farm. sperim., 1931, **51**, 167—171).—In certain concentrations and at temperatures above 37°, potassium cyanide exerts *in vitro* a hæmolytic action on the red corpuscles of ox-blood. This effect is weakened when the salt combines with carbohydrates capable of neutralising its toxic action. Strict parallelism is observed between the antitoxic and antihæmolytic actions of the different carbohydrates (cf. A., 1930, 1618). T. H. Pope.

Anti-ricin. F. Reuter (Biochem. Z., 1931, **231**, 175—232).—By means of experiments with blood-serum containing anti-ricin the conditions under which the latter can best be purified by adsorption on purified kaolin or on aluminium hydroxide and subsequent elution with phosphate buffer solutions have been investigated. Provided that sera which do not contain too much anti-ricin are used the degree of purification of the latter is increased if the adsorption is preceded by fractional salting out and electrodialysis. The anti-ricin content of the dried sera and of the electrodialysates increases when these materials are preserved. Anti-ricin is not attacked by either activated trypsin or activated pepsin. W. McCartney.

Chemical and immunological study of egg-protein obtained under restricted diets. L. Gerber and R. H. Carr (J. Nutrition, 1930, **3**, 245—256).—Ammonia-nitrogen (4·75 and 8·40% of total nitrogen, respectively, for eggs of pigeons fed on rye and barley) showed the largest deviations; the total nitrogen content was fairly constant. Feeding with hemp, soya beans, and wheat increased the monoamino-nitrogen, with kafir the diamino-nitrogen, or with maize and kafir the non-amino-nitrogen. Immunological relationships were investigated. Embryo development was assisted by egg-proteins from hemp, soya-bean, and wheat diets more than that from maize or oats. Chemical Abstracts.

Cholesterol of protoplasm. V. Investigation of the suprarenal glands of the ox. G. Pfeiffer (Biochem. Z., 1931, **230**, 439—445).—A method is outlined for the hydrolysis of suprarenal gland substance with 2% sodium hydroxide and for the isolation of the cholesterol fractions. The large cholesterol content obtained is regarded as due to the accumulation of cholesterol during the breakdown of erythrocytes in the formation of the gland hormone (cf. A., 1930, 945, 1204). P. W. Clutterbuck.

Cholesterol compounds in protoplasm. VI. Cholesterol compounds of the spleen in cattle. G. Pfeiffer (Biochem. Z., 1931, **231**, 239—243).—The amount of cholesterol and its derivatives in the spleens of cattle is similar to that in their livers (calculated, in both cases, on the dry weight), the similarity being particularly pronounced in the case of the material which can be precipitated by digitonin. There is practically no difference between the amount of oxycholesterol in the spleen and that in the erythrocytes. It is concluded that the accumulation of cholesterol in the spleen is, in part, a consequence of the decomposition of red blood-corpuscles which takes place there. W. McCartney.

Presence and rôle of cholesterol in the shells of Lamellibranchs. A. de Waele (Natuurwetensch. Tijds., 1931, **13**, 51—56).—The shell of *Anodonta cygnea* contains 0·1047 g. of cholesterol per kg., which by its affinity for water enables the impervious shell to retain enough moisture to allow elimination of carbon dioxide. Owing to the presence of the sterol, the shell cannot be dried by heating to 105°, but must be first extracted with ether, the residue after evaporation of which must be allowed for in the analysis. S. I. Levy.

Decomposition of cholesterol by *X*-rays. A. H. Roffo and L. M. Correa.—See this vol., 443.

Effect of *X*-irradiation on cholesterol and its fatty acid esters *in vitro* and *in vivo*. R. Hummel.—See this vol., 443.

Variations in sign of double refraction in myelinic and similar figures. J. Nageotte (Compt. rend., 1931, **192**, 584—586).—The positive double refraction of a fresh ethereal extract of brain or pure lecithin immersed in water becomes negative when oxidation occurs. This is due to the formation of hydrates favoured by oxidation. In the absence of water, glass-mounted specimens of fresh or oxidised material show no change of sign. A. Cohen.

Biological significance and distribution of fat in the pregnant uterus of the bat. M. Kadimura (Keijo J. Med., 1930, **1**, 475—494; cf. A., 1930, 1609).—The distribution of fat in different uterine tissues of the pregnant bat has been studied microscopically. Fat is stored in the placenta during the early stages of pregnancy and functions in a similar manner to glycogen (*loc. cit.*), serving later as a nutrient for the fœtus during its development. A. Cohen.

Fatty acids of the cat's kidney. I. K. Turner (Biochem. J., 1931, **25**, 49—56).—The fatty acids consist of palmitic, stearic, oleic, and linoleic acids together with at least two new liquid saturated acids.

A comparison is made between the simple glyceride and phospholipin fraction from cat and ox kidneys.
S. S. Zilva.

Specificity of lens-protein with special reference to the precipitin content. J. Kunifusa (Keijo J. Med., 1930, 1, 409—427).—Lens-protein possesses not only organ- but also species-specificity. The precipitin content, rather than the titre, is of especial significance with regard to specificity; on it depends the difference between the chief and the subsidiary reactions. Urea and dextrose appear to prevent the combination of precipitinogens with precipitins; under the influence of these substances the species-specificity is emphasised. A. Cohen.

Micro-determination of reduced and total glutathione in the liver. J. Kühnau (Biochem. Z., 1931, 230, 353—372).—An iodide titration method is described for determination of reduced glutathione and used also for total glutathione, the oxidised form being first converted into the reduced by means of cyanide. The determination is carried out on 0·5 g. of liver with an accuracy of ±4%. The influence of dilution factors, acidity, and temperature on the iodine-combining power of glutathione is investigated and the reducing action of sodium cyanide on oxidised glutathione is measured. P. W. Clutterbuck.

Relation between cystine yield and total sulphur in kemp and outer-coat animal fibres. C. Rimington (Biochem. J., 1931, 25, 71—73).—The entire sulphur in Scotch blackface kemp, Welsh mountain wool kemp, and lamb's birth-coat can be accounted for as cystine. In the case of two separate samples of camel hair, both true hair (inner coat) and coarse outer-coat fibres contained more sulphur than could be accounted for as cystine. The brownish-red pigment present in these samples may account, in part at any rate, for the discrepancy.
S. S. Zilva.

Iodine content of the bile and thyroid gland of the ox under the influence of seasonal variations in fodder. G. Pfeiffer (Biochem. Z., 1931, 230, 290—298).—An increase in weight of the thyroid gland is obtained from winter to summer in oxen of all ages. The relative and absolute iodine contents of the thyroid increase with increasing age and gland weight and reach maximal values in the fifth to sixth year. Change from the naturally iodine-deficient winter fodder to the iodine-rich fodder of the summer months does not affect the thyroid iodine content. Secretion of bile increases with increasing age. The iodine content of the bile is increased in the summer months by 120% over the winter months.
P. W. Clutterbuck.

Iodine content of normal and pathological thyroid glands. N. von Hedry (Arch. klin. Chir., 1929, 154, 611—622; Chem. Zentr., 1930, ii, 3050).—Normal thyroid glands contain 0·014% of iodine (average); goitres after removal contained 0·00087% of iodine, the total iodine content being approximately normal. The condition of thyroid gland function was independent of the iodine content.
A. A. Eldridge.

***X*-Ray analysis of bone and teeth.** H. H. Roseberry, A. B. Hastings, and J. K. Morse (J. Biol. Chem., 1931, 90, 395—407).—*X*-Ray spectrograms of powdered bone and tooth enamel indicate that they possess a crystal structure similar to that of dahlite and other members of the apatite series, and that the calcium salts present in bone and enamel are represented by the formula $CaCO_3,nCa_3(PO_4)_2$, n being 2 or 3. From Laue photographs it is concluded that enamel has a close-packed hexagonal lattice, a_0 20·8, b_0 12, c_0 8·82 Å., referred to orthorhombic axes. A. Cohen.

Equilibrium between cerebrospinal fluid and blood-plasma. III. Distribution of calcium and phosphorus between cerebrospinal fluid and blood-serum. IV. The calcium content of serum, cerebrospinal fluid, and aqueous humour at different levels of parathyroid activity. H. H. Merritt and W. Bauer (J. Biol. Chem., 1931, 90, 215—232, 233—246).—III. In normal individuals the average calcium content of the serum is 10 mg. per 100 c.c., varying from 9·35 to 10·6 mg., and of the cerebrospinal fluid, 5 mg. per 100 c.c., varying from 4·5 to 5·23 mg. The ratio of the cerebrospinal fluid-calcium to the serum-calcium varies from 45 to 53% with an average of 50%. There is no significant change in this ratio with changes in the serum-protein content, although both serum-calcium and cerebrospinal fluid-calcium tend to vary directly with the serum-protein content. In various non-suppurative diseases of the central nervous system there is no change in the serum- and cerebrospinal fluid-calcium, but in cases of meningitis a slight diminution of serum-calcium and an increase of cerebrospinal fluid-calcium occurs. In pulmonary tuberculosis there is a slight decrease in the serum- and cerebrospinal fluid-calcium content. Water-drinking during the antidiuretic action of vasopressin causes a decrease in the serum- and cerebrospinal fluid-calcium. Towards the end of pregnancy reduction of the cerebrospinal fluid-calcium occurs. The amniotic fluid-calcium content varies between 5·4 and 8·8 mg. per 100 c.c. with an average of 6·59 mg. per 100 c.c. In cats the content of the cerebrospinal fluid and aqueous humour of the eye averages 54 and 60%, respectively, of the serum-calcium content. In non-suppurative diseases of the central nervous system, the cerebrospinal fluid-phosphorus content varies between 31 and 45% of the serum-phosphorus with an average of 38%. In suppurative diseases of the nervous system, the ratio of cerebrospinal fluid-phosphorus to serum-phosphorus varies between 0·35 and 1·23 with an average of 0·40.

IV. When the serum-calcium of man or of animals is raised by the administration of parathyroid extract, very little change occurs in cerebrospinal fluid-calcium. This is likewise little altered during parathyroid tetany. W. O. Kermack.

Determination of total sterol and ergosterol in cow's milk. H. Hentschel and O. Bachmann. **Comparative values for milk of different origin.** O. Bachmann (Z. ges. exp. Med., 1930, 71, 744—754; Chem. Zentr., 1930, ii, 2322).—Potassium hydroxide is added to the milk, and the fat extracted with ether; after saponification, the unsaponifiable fraction is extracted with ether and treated with digitonin solution. The factor is 0·2431. The following sterol contents of milk (mg. per litre) are recorded: Rosenheim 77, Allgäu 57, Berlin 60, Central Germany 101. Corresponding values for inactive ergosterol were: 0·19, 0·13, 0·10, —. The spectrum of the fourth sample suggested the presence of activated ergosterol. A. A. ELDRIDGE.

Influence of fodder containing vitamin-*D* on milk. ROEMELE and STÖHR (Milchwirt. Forsch., 1930, 10, 413—423; Chem. Zentr., 1930, ii, 3433).—Admixture of a vitamin-*D* preparation with maize meal did not affect the vitamin-*D*, fat, or calcium content of the milk, its quantity, or the f. p. of the fat. A. A. ELDRIDGE.

Human milk. VI. Vitamin potency as influenced by supplementing the maternal diet with yeast. S. S. MCCOSH, I. G. MACY, and H. A. HUNSCHER (J. Biol. Chem., 1931, **90**, 1—13).—The vitamin-*B* contents of the milks of three women were inversely proportional to the quantity of milk secreted daily. The addition of 10 g. of yeast daily to the diet resulted in the secretion in the milk of some factor which whilst not increasing the appetite favoured more economic utilisation of the food consumed by the experimental animals.
W. O. KERMACK.

Milk peroxidase. W. GRIMMER and H. ENGEL (Milchwirt. Forsch., 1930, **10**, 273—296; Chem. Zentr., 1930, ii, 3585).—Precipitation with various reagents does not separate the peroxidase from the milk-albumin. In pancreatin digestion the residual albumin exhibits a marked increase in peroxidase activity. The peroxidase is not identical with the albumin; it may exhibit similar precipitation reactions, or be attached to the albumin molecule complex.
A. A. ELDRIDGE.

Action of peptone on the gastric secretion. I. TESSIERI (Sémana med., 1930, II, 1579—1586).—The quantity, acidity, and duration of gastric secretion are increased. CHEMICAL ABSTRACTS.

Excretion of sodium salicylate in the bile. B. HALPERT, M. T. HANKE, and G. M. CURTIS (J. Clin. Invest., 1930, 9, 359—362).—Oral ingestion of a medicinal dose of sodium salicylate in biliary disease is not followed by its appearance in the bile.
CHEMICAL ABSTRACTS.

Composition of bile following the relief of biliary obstruction. C. H. GREENE, W. WALTERS, and C. H. FREDRICKSON (J. Clin. Invest., 1930, 9, 295—310).—The output of bilirubin was constant. The formation of bile acids is inhibited by biliary obstruction, with rapid return to normal in absence of liver injury. Bile-chloride is higher than blood-serum-chloride; bile-urea varies directly with blood-urea. CHEMICAL ABSTRACTS.

Polarimetric determination of bile acids in body-fluids and organs. M. JENKE (Arch. exp. Path. Pharm., 1931, **159**, 180—182; cf. Rosenthal, this vol., 251).—Rosenthal's modification of the polarimetric method of the author for the determination of bile acids is likely to introduce considerable error. The polarimetric determination of bile acids is essentially inapplicable to blood, organs, and urine which contain only very small amounts.
W. O. KERMACK.

Determination of urobilin in urine. E. LEIKOLA (Acta Soc. Med. Fenn. Duodecim, 1929, **11**, 9 pp.; Chem. Zentr., 1930, ii, 3446).—The light absorption of the urine is measured at 530, 490, and 450 mμ, whence the quantity of urobilin may be calculated, since the extinction-coefficient curve of urine is regular in the absence of foreign colouring matters. For the determination of urobilinogen the urine is treated with hydrogen peroxide, and the urobilin content is again determined. A. A. ELDRIDGE.

Solubility, dissociation, and tension of carbonic acid in urine. F. MAINZER and M. BRUHN (Biochem. Z., 1931, **230**, 395—410).—A method for determination of the carbon dioxide tension of urine depends on the use of the Henderson–Hasselbalch equation and requires, therefore, the determination of the solubility coefficient ($\alpha_{38°}$) and the apparent dissociation constant (or its negative logarithm, $p_{K'}$) of carbonic acid. The values for 20 urines are for $\alpha_{(CO_2,\ 38°)}$ between 0·441 and 0·514, for $p_{K'}$ between 5·81 and 6·30, and for the tension $p_{(CO_2,\ 38°)}$ between 13·3 and 242·4 mm. mercury. P. W. CLUTTERBUCK.

Determination of purine bases in urine. FISCHER and HUPPMANN (Süddeut. Apoth.-Ztg., 1930, **70**, 465—466; Chem. Zentr., 1930, ii, 2680).—Precipitation by Krüger and Schmid's method is preferred. A. A. ELDRIDGE.

Statistical analysis of the laws governing urea excretion in man. E. J. CONWAY (Proc. Roy. Irish Acad., 1931, **35 B**, 574—594).—A large quantity of data relating to urea excretion in man has been analysed statistically with reference to the diffusion secretion formula of the author (cf. Amer. J. Physiol., 1929, 88, 1). W. O. KERMACK.

Fading of tropeolin-OO in the titration of organic acids in urine. K. L. MCCLUSKEY (J. Biol. Chem., 1931, **90**, 197—201).—The fading of the indicator occasionally observed when pathological urine is titrated for organic acids by the method of Van Slyke and Palmer (A., 1920, i, 459; ii, 131) is due to the presence of an unidentified substance (which presumably converts the azo- into the hydrazo-compound) which is readily oxidised in acid solution. Its effect may be eliminated by aëration of the urine in presence of hydrochloric acid. Urine as the result of aëration may give results up to 5% lower than the untreated urine. This difference is not due to loss of volatile acids, to incomplete removal of the carbonates, to changes in the uric acid, creatinine, and creatine, or to the salt effect on the indicator, but may be due to pigment content.
W. O. KERMACK.

Electrolyte equilibrium in blood in experimental acidosis. H. N. HARKINS and A. B. HASTINGS (J. Biol. Chem., 1931, **90**, 565—595).—The effects of hydrochloric acid injection into anæsthetised dogs on the concentrations of blood-constituents are described and discussed. Injection is followed by an immediate and temporary low p_H, anuria, and increased rate of respiration. Since the p_H remains low after the respiration returns to normal, the p_H does not control respiration. The distribution of diffusible ions between cells and serum in experimental acidosis *in vivo* may be accounted for by the same laws as operate *in vitro*. A. Cohen.

Hæmoglobin production. II. Relief of anæmia due to milk diet by feeding amino-acids. D. L. Drabkin and H. K. Miller (J. Biol. Chem., 1931, **90**, 531—543; cf. Drabkin and Waggoner, this vol., 247).—Rats suffering from anæmia on a milk diet containing iron recovered when the diet was supplemented by arginine, glutamic acid, and their salts. Partial recovery was observed with tryptophan, pyrrolidonecarboxylic acid, and proline (72% purity), and sodium aspartate caused temporary relief followed by relapse. Alanine, alanine hydrochloride, histidine dihydrochloride, and hydrochloric acid failed to effect hæmoglobin regeneration. All materials were free from copper and contained insignificant traces of iron. The active substances are regarded as possible sources of pyrrole radicals which may be utilised in the synthesis of hæmoglobin. A. Cohen.

Ineffectiveness of manganese in nutritional anæmia. W. E. Krauss (J. Biol. Chem., 1931, **90**, 267—277).—Rats suffering from nutritional anæmia as the result of feeding on a milk diet were not cured by the addition to the diet either of manganese (0·1 mg. per day) alone or along with iron (0·5 mg. per day), whilst the addition of copper brought about recovery. The conclusions of Titus, Cave, and Hughes (A., 1929, 206) that manganese has a curative action in nutritional anæmia are therefore erroneous. W. O. Kermack.

Nitrogen and sulphur metabolism in Bright's disease. I. Retention in nephrosis. G. P. Grabfield (J. Clin. Invest., 1930, **9**, 311—318).—Considerable retention of nitrogen and sulphur, a high urinary nitrogen : sulphur ratio, and a low ratio in the retained protein were observed. Chemical Abstracts.

Lactic acid in the blood of cancer patients treated with X-rays and with radium. E. Liverani (Arch. Farm. sperim., 1931, **51**, 177—188).—Radium or X-ray treatment of 15 individuals suffering from neoplasms resulted, in most cases, in a diminution of the lactic acid content of the blood; such diminution was not observed in 8 non-neoplastic cases. T. H. Pope.

Effect of fermentation poisons on experimental tumours. I—III. L. Karczag (Biochem. Z., 1931, **230**, 411—419, 420—434, 435—438).—I. By means of a yeast-zymin test, a large number of substances, chiefly dyes, are divided into enzyme poisons (inhibition of zymin but not of yeast), protoplasm poisons (inhibition of yeast only), and those substances which are both protoplasm and enzyme poisons or have no action at all. With substances acting as enzyme poisons, the nitrogen of the molecule appears to play a decisive rôle, especially the position of nitro- and cyano-groups in the side-chain. None of the investigated enzyme and protoplasm poisons has any beneficial influence on tumours in mice.

II. [With C. Sellei.] The inhibitory effect on the glycolysis of tumour cells *in vitro* and on respiration of the following fermentation poisons decreases in the order given; ethyl-red, chrysoidin, Magdala-red, *iso*quinoline-red, Martius-yellow. The substances acting as protoplasm poisons to the yeast cell are not protoplasm poisons to the tumour cell and the effect is due to enzymic inhibition only. Whereas the action of cyanide on glycolysis is reversible, that of these poisons is irreversible. The fermentation poisons of yeast cells are also poisons of *B. coli* fermentations.

III. Rous sarcoma powder is able to ferment sugar slowly with formation of gas. P. W. Clutterbuck.

Fat-soluble vitamins in tumour tissues. M. Sumi and W. Nakahara (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1931, **15**, 69—74).—The oils obtained by extraction with ether of the dried tissue of transplantable tumours of four types are described; 12—16% of cholesterol is present, and the presence of admixed ergosterol may be demonstrated spectrographically. The presence of vitamin-*D* in the oils is shown by the cure of rickets in rats by doses of 1—2 drops daily. Colour reactions for vitamin-*A* were negative. R. K. Callow.

Chinese antidiabetics. N. Sugihara. **I, II. Effect on blood-sugar of rabbits.** P. Min (Folia Pharmacol. Japon., 1930, **11**, No. 1, 11—21, 21—33).—Of all the drugs examined, aqueous extracts of *Rehmannia lutea* only reduced the blood-sugar without preliminary hyperglycæmia. Chemical Abstracts.

Blood-volume and plasma-electrolyte changes in the dehydration of infants. R. McIntosh, L. Kajdi, and D. Meeker (J. Clin. Invest., 1930, **9**, 333—357).—Determinations with infants suffering from diarrhœa-dehydration are recorded. The serum-chloride, -hydrogen carbonate, and -total fixed base were usually decreased. Chemical Abstracts.

Metabolism in experimental yellow fever in *Macacus rhesus*. A. M. Wakeman and C. A. Morrell (Arch. Int. Med., 1931, **47**, 104—115).—Intravenous injection of dextrose in monkeys with yellow fever does not alleviate the hypoglycæmia which is manifested as early as 24 hrs. before death. Disturbance of carbohydrate metabolism precedes that of deamination and urea formation. With a blood-sugar content of less than 45 mg. per 100 c.c. little glycogen is found in the liver of infected monkeys, although symptoms of hypoglycæmic shock are not readily produced. P. G. Marshall.

Distribution of nitrogen and sulphur in the urine during conditions of increased catabolism. D. P. Cuthbertson (Biochem. J., 1931, **25**, 236—244; cf. A., 1930, 1310).—The catabolic loss of nitrogen and sulphur which results from tissue injury (bone fractures, minor operations) reached a maximum about the third to eighth day following the injury. The maximum daily loss of nitrogen might even exceed 20 g. The increase in nitrogen was due to a practically proportionate increase in urea excreted and the increase in sulphur to a slightly greater proportionate increase in the excretion of inorganic sulphates. The excretion of ammonia fluctuated;

that of amino-acids and uric acid generally rose. Ethereal sulphate tended to diminish slightly. Creatinine and neutral sulphur remained practically constant, any increase not being proportional to the total increase of nitrogen or sulphur, respectively. Traces of creatine were observed particularly during phases of increased catabolism. Traces of heat-coagulable protein were occasionally found, particularly during the time of the maximum excretion of the nitrogenous catabolites. S. S. Zilva.

Blood-calcium during the healing of fractures. C. Loreto (Arch. Farm. sperim., 1931, **51**, 145—164, 189—192, 217—227).—The blood-calcium does not vary appreciably as the result of a fracture, but during the healing of the fracture, from the twentieth to the ninetieth day, the calcium content of the fractured bone is greater than that of the other normal homonymous bone. T. H. Pope.

Iodine theory of goitre. C. A. Hellwig (Klin. Woch., 1930, **9**, 1913—1916; Chem. Zentr., 1930, ii, 2911).—Rats kept for a long period on a diet poor in iodine (barley and distilled water) did not develop a goitrous thyroid; in fact the thyroid became markedly atrophied. A diet rich in calcium (the drinking water contained 2% of calcium chloride), however, caused true epithelial hyperplasia. A. A. Eldridge.

Extent of goitre in Hungary and its connexion with the iodine content of drinking water. J. Straub (Z. Hyg., 1930, **111**, 472—479).—No relation has been found. Chemical Abstracts.

Brown pigment in hæmatochromatosis. M. Jacoby (Biochem. Z., 1931, **230**, 225—227).—The pigment was insoluble in alcohol, ether, acetone, chloroform, benzene, phenol, toluene, and carbon tetrachloride. Extraction by 0·85% sodium chloride and then water gave a solution which contained only traces of hæmoglobin and methæmoglobin. The pigment was isolated by precipitation by saturated ammonium sulphate. Analysis indicated a ratio 4N : Fe. F. O. Howitt.

Terminal hypoglycæmia. E. G. Schmidt [with T. N. Carey] (Arch. Int. Med., 1931, **47**, 128—134).—From 33 non-diabetic cases only 6 showed a pronounced terminal hypoglycæmia which was not manifested prior to death, whilst at least an equal number of cases actually showed a rise in blood-sugar. Little change occurs in the blood-sugar, -chlorides, or -urea within 1 hr. of death, although the carbon dioxide-combining power decreases somewhat. P. G. Marshall.

Effect of experimental obstructive icterus in the dog on blood-bile salts, -bilirubin, and -cholesterol. B. V. Fuentes, E. Apolo, and J. Esculies (Z. ges. exp. Med., 1930, **73**, 412—421; Chem. Zentr., 1930, ii, 2796).—Values for cholesterol diminished; for bile salts they were after 7 days 4—5 times the normal which they later approached, whilst for bilirubin a maximal value was attained after 3—7 days and afterwards maintained. A. A. Eldridge.

Cholesterol partition of the blood-plasma in parenchymatous diseases of the liver. E. Z. Epstein (Arch. Int. Med., 1931, **47**, 82—93).—In acute parenchymatous diseases of the liver the level of cholesteryl esters, which is low or even absent in the early stages, rises to normal during recovery, which is facilitated by a diet high in carbohydrates and low in fat. The cholesterol balance is not disturbed during atrophic cirrhosis brought on by alcoholism. P. G. Marshall.

Lipuria; lipæmia. H. Pecker (J. Pharm. Chim., 1931, [viii], **13**, 197—199).—In a case of lipoid nephritis a mild lipuria (0·52 g. per litre) and a marked lipæmia (blood-lipins 1·81%) were observed. The latter also occurred in the case of a diabetic (blood-lipins 2·64%). F. O. Howitt.

Blood-lipins in nephrosis and chronic nephritis with œdema. L. Lichtenstein and E. Z. Epstein (Arch. Int. Med., 1931, **47**, 122—127).—In varying types of nephrosis and in seven cases of chronic glomerulo-nephritis with œdema a marked increase in cholesterol, cholesteryl esters, and phosphatides was found. The ester fraction may be 80—90% of the total cholesterol. There is no correlation between lipinæmia and decrease in serum-protein content, which occurs chiefly at the expense of the albumin fraction. P. G. Marshall.

Potassium content of the heart in œdematous and non-œdematous conditions. L. C. Scott (Arch. Int. Med., 1931, **47**, 116—121).—The water content of the heart is remarkably constant whatever the cause of death, whilst both the sodium and potassium contents may vary widely without relation to the presence or absence of œdema, and either of these elements may predominate. P. G. Marshall.

Rickets. I. Protracted observation of calcium and phosphorus metabolism in infants. E. Rominger, H. Meyer, and C. Bomskov (Z. ges. exp. Med., 1930, **73**, 343—381; Chem. Zentr., 1930, ii, 2798—2799).—In the first stage of rickets a small or negative phosphate balance and a good calcium balance are observed; in the second stage both balances are slightly positive or negative, whilst in the third stage there is a high phosphate balance, the calcium balance also becoming abnormally high in the fourth stage. Administration of "vigantol" improves at first the retention of phosphate and then that of calcium. Therapeutic doses do not appear to affect the metabolism of normal children. A. A. Eldridge.

Acid-base equilibrium of blood in pathological conditions. I. Toxæmias of pregnancy. E. Muntwyler, N. Limbach, A. H. Bill, and V. C. Myers (J. Biol. Chem., 1931, **90**, 607—617).—A decreased plasma-hydrogen carbonate was observed in cases of toxæmia of pregnancy. The average ante-partum blood-p_H was 7·47 and the total base concentration was lower than normal. Considerable post-partum increases in the hydrogen carbonate and total base were found, with smaller increases in total acid, protein, and p_H of the blood. The lowered plasma-hydrogen carbonate is not due to abnormal acids, but to hyperventilation. A. Cohen.

Lactic acid in the blood in acute infections. E. Liverani (Arch. Farm. sperim., 1931, **51**, 245—

265).—An increase of the lactic acid content of the blood is observed in the acute stages of a number of infections, particularly when toxæmia is marked. This is due to several causes—increase of general metabolism, functional insufficiency of the liver, deficient oxygenation of the tissues, and increased absorption from the intestine as a result of increased fermentation. R. K. Callow.

Alcohol utilisation by man at high altitudes. A. Bornstein and A. Loewy (Biochem. Z., 1931, **230**, 51—67; cf. A., 1928, 197).—Following the administration of alcohol the blood-alcohol rises more rapidly at high than at low altitudes, whilst the rate of recovery is the same in both cases. The *R.Q.*, normally higher in elevated regions, is lowered to a greater extent, frequently to the level of pure alcohol combustion, but its return to the normal is more rapid. No specific dynamic action is found on administration of alcohol alone, but simultaneous carbohydrate ingestion results in an action markedly stronger than in the corresponding experiments at low levels. F. O. Howitt.

Fate of lævulose in the animal. II. Do digestive juices convert lævulose into dextrose? W. W. Oppel (Biochem. Z., 1931, **230**, 269—284; cf. A., 1929, 462).—Incubation of lævulose for a short time (1—5 hrs.) with digestive juices (gastric, intestinal, and pancreatic) in the absence of toluene and for a longer time (20 hrs.) in presence of toluene at varying physiological $p_{\rm H}$ did not bring about any conversion of the sugar into dextrose.

P. W. Clutterbuck.

Intermediary carbohydrate metabolism. VI. Sugar assimilation, phosphorus and water metabolism on continuous intravenous injection of dextrose, lævulose, and galactose. M. Wierzuchowski, W. Pieskow, and E. Owsiany. **VII. Production of lactic acid on continuous intravenous injection of dextrose, lævulose, and galactose.** M. Wierzuchowski and M. Łaniewski. **VIII. Respiratory metabolism on intravenous injection of dextrose, lævulose, and galactose.** M. Wierzuchowski (Biochem. Z., 1931, **230**, 146—172, 173—186, 187—224; cf. A., 1928, 197).—VI. In dogs having normal fasting blood-sugar averaging 0·091—0·104% (of which 0·054—0·067% was due to dextrose), during the first hour of dextrose (2 g. per kg. per hr.) injection the blood-dextrose increases, and then sinks in the course of the next 2 hrs., indicating a diphasic action. Such an action does not occur with lævulose or galactose. The final dextrose level is below that of the original. Lævulose follows a somewhat parallel course, but with galactose the assimilation is much slower, as shown by the blood and urine values. With simultaneous insulin administration the diphasic action of dextrose disappears, whilst the assimilation of dextrose and galactose, but not of lævulose, is increased, the influence of the hormone being greatest on the galactose assimilation. Injection of lævulose or galactose does not increase the blood-dextrose, and with insulin administration actually decreases it. Dextrose or lævulose injection fails to increase the non-dextrose reducing substances of the blood. No relation exists between the blood- or urine-phosphate values and any phase of the sugar metabolism investigated. The blood dilution is greatest for continuous injection of galactose and least with lævulose. Where insulin increases assimilation there is a concurrent state of anhydræmia. The amount of urine excreted is related to the sugar excretion.

VII. The lactic acid production following injection of the sugars at the rate of 2 g. per kg. per hr. was investigated in fasting dogs, the blood concentration and hourly excretion of lactic acid of which were 0·007—0·025% and 1·4—5·1 mg., respectively. For each sugar the increase in blood-lactic acid and the simultaneous excretion of the acid are characteristic and follow parallel courses. Lævulose gives rise to greater amounts of lactic acid than dextrose, whilst the production from galactose varies between the two values. The blood-lactic acid during injection of the sugars reaches a level equal to that produced by muscular work. Simultaneous administration of insulin leads to increased lactic acid formation by all three hexoses. Parallel with but not stoicheiometrically related to the lactic acid increase is the resulting condition of acidosis.

VIII. Injection into dogs at the rate of 2 g. per kg. per hr. results in values of *R.Q.* of 0·23 (dextrose), 0·24 (lævulose), and 0·13 (galactose), these values being increased to 0·26, 0·30, and 0·18 on simultaneous administration of insulin. The specific dynamic action is greatest for galactose and least for dextrose, the greatest increase in heat production being during the second and third hour of injection. The extent of the increase in heat production due to simultaneous administration of insulin depends on the glycæmic level. The maximum sugar oxidation is 0·5 g. per kg. per hr. With a condition of hyperglycæmia insulin increases the oxidation of injected dextrose by 15%, that of lævulose by 24%, and that of galactose by 87%. A quantitative relationship exists between the specific dynamic action of the hexoses and their oxidation, the quotients of which are 3·04 for dextrose, 2·48 for lævulose, and 1·82 for galactose. The heat production and increase in *R.Q.* during the maximum rate of oxidation indicate that the utilisation of all three sugars is inversely proportional to the concentration of the injected hexose in the blood. The blood-lactic acid does not run parallel to the heat production, but for a definite amount of assimilated sugar the specific dynamic action and the oxidation of the introduced sugar are the greater the more lactic acid the organism produces from the sugar assimilated.

F. O. Howitt.

Carbohydrate metabolism. II. Dextrose-lactic acid cycle in diabetes. H. E. Himwich, W. H. Chambers, Y. D. Koskoff, and L. H. Nahum (J. Biol. Chem., 1931, **90**, 417—426).—In depancreatised and phloridzinised dogs the lactic acid content of the blood of the femoral and portal veins is significantly higher than that of the blood of the femoral artery and hepatic vein, respectively. The dextrose content shows the reverse relationships. In the diabetic animal, therefore, the same cycle exists as in the normal animal (A., 1930, 368), whereby lactic acid formed by muscle is removed by the liver which liberates dextrose into the blood. A. Cohen.

Various methods of sugar degradation in the animal organism. II. E. Bumm and K. Fehrenbach (Z. physiol. Chem., 1931, **195**, 101—112).—The work of Ashford and Holmes (A., 1929, 1194) on the rôle of phosphate in the glycolysis of brain substance is amplified. Neither co-zymase nor hexokinase accelerates the production of lactic acid during this glycolysis. Co-enzyme-*T* (A., 1928, 1274) increases the formation of lactic acid by 40—90%. Arsenate has no effect. Glycolysis in retina substance appears to be independent of phosphate.

A. Renfrew.

Equilibrium between glycogen and lactic acid. W. D. Bancroft and G. Bancroft (J. Physical Chem., 1931, **35**, 194—214).—The theories concerning the chemical changes which occur in muscle during fatigue and recovery are discussed.

L. S. Theobald.

Glycogen formation in rats. II. E. M. Greisheimer and O. H. Johnson (J. Nutrition, 1930, **3**, 297—302).—Liver-glycogen was significantly higher with a high-sucrose diet, and lower when 87% of the calories was given as lard or caseinogen. Comparative diet values are: McCollom No. 1, 1; sucrose 1·85; caseinogen 0·61; fat 0·44.

Chemical Abstracts.

Significance of raw egg-yolk for glycogen deposition in the liver. I. Abelin (Klin. Woch., 1930, **9**, 1759—1761; Chem. Zentr., 1930, ii, 3310).—A favourable effect was observed.

A. A. Eldridge.

Glycogen content of the liver after administration of mineral (sodium sulphate) water. W. Arnoldi (Z. ges. exp. Med., 1930, **73**, 452—457; Chem. Zentr., 1930, ii, 2797).—Experiments with rabbits and rats led to an increase in the glycogen content of the liver. On administration of Franzensbad water with a diet high in carbohydrate the diminution in glycogen is less marked than normally; with a diet rich in protein and fat the liver-glycogen decreases. A. A. Eldridge.

Conversion of fat into carbohydrate in the organism. M. Henze (Z. physiol. Chem., 1931, **195**, 248—254).—Hexan-γ-ol-βε-dione (I) (A., 1930, 1022; this vol., 69), prepared from acetoacetic acid and methylglyoxal, is oxidised by cold alkaline potassium permanganate solution to pyruvic acid. It is, therefore, possible to convert a C_4 into a C_3 chain (and thence into sugar). When I is fed to rabbits about 2 g. are decomposed, the remainder being excreted in the urine. Treatment of I with liver-pulp causes complete decomposition. H. Burton.

Significance of conjugated bile-acids for fat resorption. IV. F. Verzár and A. von Kúthy (Biochem. Z., 1931, **230**, 451—457).—A much larger amount of fat is resorbed from a washed tied-off loop of intestine in the living animal in presence of a known amount of bile-acid than can be made diffusible in experiments *in vitro*. It is suggested that the bile-acids are adsorbed by the epithelial cells of the intestinal mucous membrane and are there used repeatedly in the formation of the water-soluble fat complex (A., 1929, 466, 1194).

P. W. Clutterbuck.

Biochemistry of muscle. A. Palladin (Bull. Soc. Chim. biol., 1931, **13**, 13—28).—A lecture.

Significance of arginine-phosphoric acid in the metabolism of active crustacean muscle. E. Lundsgaard (Biochem. Z., 1931, **230**, 10—18).—Crab (*Maia squinado*) muscle is much less sensitive to iodoacetic acid than frog-muscle. Following inhibition of lactic acid formation, the total activity of the muscle changes in a manner similar to that of frog muscle. Arginine-phosphoric acid plays the same rôle in the metabolism of the former as creatinine-phosphoric acid does in the latter (cf. Meyerhof and Lohmann, A., 1928, 1277), and hence the degradation of arginine-phosphoric acid in crustacean muscle is an energy-providing reaction similar to that of creatinine-phosphoric acid in vertebrate muscle.

F. O. Howitt.

Amino-nitrogen of blood, muscle, and proteins and its rôle in chemical processes of the working muscle. T. Mann (Acta Biol. Exp., Warsaw, 1930, **6**, 45—52).—The amino-group content of the blood-proteins of three persons was the same before and after exertion and, similarly, no difference was found in isolated symmetrical frog-muscles, one resting and the other stimulated to exhaustion. The amino-groups of blood and muscle proteins are not involved in the chemical processes of muscular exertion.

R. Truszkowski.

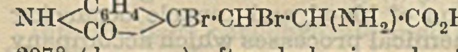
Production of ammonia in and ammonia content of muscle and their connexion with function and change of condition. VIII. Supposed changes in the amino-nitrogen content of the proteins of blood and muscle occurring during the chemical processes which accompany muscular work. T. Mann (Biochem. Z., 1931, **231**, 33—38).—Neither in human blood nor in isolated frog-muscle do changes in the amount of amino-nitrogen accompany the metabolic processes which occur during muscular work. It follows that the theory of Bliss (A., 1929, 339) must be rejected.

W. McCartney.

Intermediary metabolism of histidine. III. S. Edlbacher and J. Kraus (Z. physiol. Chem., 1931, **195**, 267—272; cf. A., 1926, 1171; 1930, 1619).—The low value for the amount of ammonia formed during the enzymic decomposition of histidine found by Kauffmann and Mislowitzer (A., 1930, 1619) is due to their use of sodium carbonate for its liberation. During the hydrolysis of histidine an intermediate is produced which is not hydrolysed by acid or carbonate. Formamide and glutamine are not hydrolysed by sodium carbonate but are hydrolysed by acid. H. Burton.

Intermediary metabolism of tryptophan. Y. Kotake. **I. Kynurenine, an intermediate metabolic product.** Y. Kotake and J. Iwao. **II. Fission of kynurenine with barium hydroxide solution.** Y. Kotake and M. Kiyokawa. **III. Fission of kynurenine with sodium hydrogen carbonate solution.** Y. Kotake and G. Schichiri. **IV. Mechanism of formation of kynurenic acid in the organism.** Y. Kotake. **V. Formation of kynurenic acid from kynurenine by micro-organisms.** G. Schichiri and M. Kiyokawa. **VI.**

Excretion of kynurenic acid in bile and its stability in the organism. Y. Kotake and K. Ichihara. **VII. Site of formation of kynurenic acid in the organism.** K. Ichihara, S. Otani, and J. Tsujimoto [with Y. Okagawa and T. Kiyomatsu]. **VIII. Origin of urochrome.** Y. Kotake and H. Sakata [with Y. Shirabe and S. Otani]. **IX. Action of trytophan in experimental anæmia and its relation to the spleen.** Y. Okagawa and M. Tatsui. **X. *dl*-Indolyl-lactic acid and its use in nutrition.** K. Ichihara and N. Iwakura. **XI. Action of methyltryptophan in experimental anæmia and in nutrition.** Z. Matsuoka and T. Nakao (Z. physiol. Chem., 1931, **195**, 139—147, 147—152, 152—158, 158—166, 166—171, 171—179, 179—184, 184—191, 192—202, 202—207, 208—214).—I. After subcutaneous injection of tryptophan into rabbits fed on polished rice, the urine contains kynurenic acid and a *substance* (termed *kynurenine*), probably $(o)\text{-}NH_2\cdot C_6H_4\cdot C(CO_2H)\vdots CH\cdot CH(NH_2)\cdot CO_2H$, m. p. 190° (decomp.) after colouring at 170° and sintering at 180°, $[\alpha]_D^{17}$ $-28{\cdot}5°$ in water, which is isolated as the *sulphate*, darkens at 165° and becomes black at 180°, $[\alpha]_D^{16}$ $+10{\cdot}7°$ in water, by the following process. The urine is acidified with sulphuric acid, the kynurenic acid filtered off, the filtrate evaporated to small bulk, and then mixed with alcohol, whereby kynurenine sulphate and inorganic salts separate; the sulphate is then extracted with 60% alcohol. Kynurenine gives the ninhydrin reaction, affords a (?) *diethyl ester* (*dihydrochloride*), and treatment of the sulphate with bromine water furnishes the *lactam dibromide*,



$NH<{C_6H_4 \atop CO\text{—}}>CBr\cdot CHBr\cdot CH(NH_2)\cdot CO_2H$, m. p. 206—207° (decomp.) after darkening about 200°. When kynurenine is fed to a rabbit, 20—40% is excreted in the urine as kynurenic acid.

II. Kynurenine is stable towards boiling 25% sulphuric acid, but is readily decomposed by boiling 1% barium hydroxide solution to ammonia, carbon dioxide, *o*-aminoacetophenone [*hydrochloride*, m. p. 264—265° after becoming red at 160°; acetyl derivative, m. p. 75—76° (*bromo*-derivative, m. p. 157—158°)], kynurenic acid, and a small amount of an amorphous yellow substance.

III. Kynurenine is decomposed by boiling with 2% sodium hydrogen carbonate solution to ammonia, a small amount of *o*-aminoacetophenone, about 20% of kynurenic acid, and an unstable orange-yellow substance (*A*), m. p. 80—160° (according to the time of the boiling). Further treatment of *A* with sodium hydrogen carbonate or barium hydroxide solution gives some *o*-aminoacetophenone. *A* dissolves partly in warm water; extraction of the resulting solution with ether in presence of charcoal affords "*kynurenine-yellow*," m. p. 182°, which gives Ehrlich's diazo-reaction and Jaffé's kynurenic acid reaction. When an ethereal solution of "kynurenine-yellow" is kept in air, kynurenic acid is slowly deposited. The results of the alkaline fission of kynurenine support the formula assigned.

When a mixture of kynurenine and aqueous phenylhydrazine hydrochloride is made alkaline with sodium hydrogen carbonate solution, the mixture boiled for several min., and then treated with sulphuric acid, a blue coloration is produced. This test can be used for the detection of kynurenine; the blue colour is ascribed to the formation of a pyrazole.

IV. Kynurenic acid is probably formed from tryptophan as follows: tryptophan⟶α-amino-β-2-hydroxy-3-indolylpropionic acid⟶α-amino-α′-*o*-aminophenylglutaric acid⟶kynurenine⟶β-*o*-aminobenzoylpyruvic acid⟶kynurenic acid.

V. Kynurenic acid is produced when *Oidium lactis* and *Willia anomala* are grown on media containing sucrose, inorganic salts, and kynurenine. Secondary products are a substance, m. p. 122°, and a water-soluble green compound, respectively. The green compound has properties similar to those of the urochromogen of Weiss (A., 1923, i, 417).

VI. Kynurenic acid is isolated in considerable amount from fistula bile of dogs after subcutaneous injection of an aqueous suspension of tryptophan. Bile obtained similarly from rabbits contains no kynurenic acid; the acid is present in the urine. Subcutaneous injection of kynurenic acid (as the sodium salt) into dogs with gall-bladder fistulas is followed by the excretion of the total amount in the bile and urine; the major part is in the urine. Similar experiments with rabbits show that excretion is slower, but the whole of the acid can be isolated from the urine (a small amount may be excreted in the bile). The results show that kynurenic acid is not an intermediate, but is an end-product, in the metabolism of tryptophan.

VII. Little or no kynurenic acid is found in the blood or urine of dogs from which the liver has been extirpated when injected (subcutaneously or intravenously) with tryptophan. Perfusion of the surviving liver with blood (diluted with Ringer's solution) containing kynurenine gives kynurenic acid. These results and those of Matsuoka and Takemura (A., 1923, i, 72) show that kynurenic acid is formed mainly in the liver. Excretion of kynurenic acid in fistula bile of dogs increases after splenectomy.

VIII. Ingestion of tryptophan results in an increase in the urochrome fraction of the urine; the results of Tani (Med. Ges. Osaka, 1925, **24**, 1457) are thereby confirmed. Kynurenine has a similar action.

IX. Injection of tryptophan into dogs with experimental anæmia (phenylhydrazine hydrochloride) accelerates their recovery, particularly with regard to the hæmoglobin content. This action of tryptophan cannot be noticed for a time if the animals have previously undergone splenectomy. The tryptophan contents of the liver and kidney of the dog do not alter during 40 days after splenectomy; the amount in the liver does increase, however, after 80—120 days.

X. *dl*-α-Hydroxy-β-indolylpropionic acid, m. p. 145—146° [*barium* salt ($+3H_2O$)], prepared from the *l*-acid and barium hydroxide solution at 150—160°, when subcutaneously injected into the rabbit results in the excretion in the urine of some unchanged material, *l*-α-hydroxy-β-indolylpropionic acid, and a small amount of kynurenic acid. Rats fed on a tryptophan-free diet undergo normal growth when the diet is supplemented by *dl*-α-hydroxy-β-indolylpropionic acid; the *l*-acid and α-keto-β-indolylpropionic acid are not able to replace tryptophan.

XI. 2-Methyltryptophan has the same action as tryptophan in experimental anæmia, but it cannot replace tryptophan in the diet. H. Burton.

Formation of uric acid in birds. Intermediary reserve material in the liver of birds. G. Pupilli (Arch. Fisiol., 1928, **26**, 27 pp.; Chem. Zentr., 1930, ii, 3596).—Uric acid is synthesised from lactic acid and urea under aërobic conditions in presence of birds' liver extract. Fresh hen's or goose's liver affords a crystalline compound resembling hydroxypyruvic or formylglyoxylic acid; it is an oxidation product of lactic acid and a link in the synthesis of uric acid.

A. A. Eldridge.

Meat in nutrition. I. Beef-muscle. P. M. Nelson, M. H. Irwin, and L. J. Peet. **II. Dietary factors influencing lactation. III. Hæmoglobin formation.** L. J. Peet, P. M. Nelson, and E. A. Smith (J. Nutrition, 1930, **3**, 303—311, 313—323, 325—330).—I. Growth and reproduction, but not lactation, of rats were adequately maintained on a meat diet; addition of yeast, salt mixture, or protein was ineffective.

II. Diet modifications supporting lactation are described.

III. Hæmoglobin formation was favoured by addition to a meat diet of autoclaved yeast, yeast, tikitiki, lemon juice, or wheat-germ oil.

Chemical Abstracts.

Food requirements for the growth of the rat. VI. Influence of food consumption and efficiency quotient of the animal. L. S. Palmer and C. Kennedy (J. Biol. Chem., 1931, **90**, 545—564).—Yeast and wheat embryo extract have the same influence as vitamin-B_1 and -B_2 on the growth of rats having equal food intake and efficiency of food utilisation. The stimulant effect on growth exerted by fresh lettuce, liver, and carrots combined with yeast appears to be due to their effects on food consumption. The differences in growth rate of the two sexes, and between individuals on the same diet, are largely determined by differences in the efficiency index deduced from the efficiency of food utilisation.

A. Cohen.

Effects of vitamin deficiency on the coefficients of digestibility of protein, fat, and carbohydrate. R. R. St. Julian and V. G. Heller (J. Biol. Chem., 1931, **90**, 99—110).—The coefficient of digestibility ([amount ingested—amount in fæces]/amount ingested) of fats, carbohydrates, and proteins has been determined in rats fed on a complete diet and on one lacking vitamin-A, -B_1, -B_2, or -D and in guinea-pigs on a complete diet and on one lacking vitamin-C. The vitamin deficiency did not in any instance significantly affect the coefficients of digestibility.

W. O. Kermack.

Physiological effects of diets rich in egg-white. H. T. Parsons (J. Biol. Chem., 1931, **90**, 351—367).—Rats fed on a diet of high protein content and containing all the known accessory factors developed in a few days a general disturbance in health characterised by digestive disturbances and hæmaturia and usually soon ending fatally provided that the protein consisted of egg-white, raw or cooked, commercial dried or fresh, but not when other types of protein such as caseinogen or beef powder were used. Dried liver protects the animals, the addition of 1% to the egg-white for 1 week being apparently about the minimum dose. 5% of dried liver fed for 3 days before the egg-white diet also protects. When the animals which have been partly protected so as to survive the first few weeks of feeding on a diet rich in egg-white are allowed to continue on this diet a second type of disease sets in characterised by dermal and neural symptoms. The addition of 20% of dried liver completely protects against this late manifestation, but 10% or less is usually insufficient. The early symptoms brought about by egg-white markedly resemble the effects of overdosage with cystine, whilst the later symptoms are not dissimilar to those of pellagra.

W. O. Kermack.

Nutrient requirements of poultry. G. Scott-Robertson, J. B. Orr, J. H. Prentice, and A. J. Macdonald (Scot. J. Agric., 1930, **13**, 410—415).—A supplement of sodium chloride (up to 1% of the ration) to a grain–soya bean meal ration increased the rate of growth of poultry and the number of eggs laid; transference of the birds to fresh pasture corrected the salt-deficiency of the ration. Under the conditions of the experiment, sulphur, iron, and potassium iodide were omitted from the mineral supplement without effect. A. G. Pollard.

Effect of a diet of sweet clover on the serum-calcium. C. Y. Cannon and D. Greenwood (J. Dairy Sci., 1930, **13**, 424—431).—The serum-calcium of young rabbits was decreased, becoming again normal, on a lucerne diet. The diminution is associated with failure of blood to clot; the surface tension of the blood may be raised so that the platelets fail to rupture, thus interfering with the formation of thrombin. Chemical Abstracts.

Calcium and phosphorus metabolism of heavily milking cows. C. F. Huffman, C. S. Robinson, and O. B. Winter (J. Dairy Sci., 1930, **13**, 432—448).—Positive calcium and phosphorus balances of heavily milking cows can be maintained on a diet of lucerne, silage, and grain, or of timothy hay, silage, and grain supplemented by bone flour. Calcium and phosphorus are somewhat more efficiently utilised during high than during low milk production. The total intake is more significant than the ratio in food. Chemical Abstracts.

Resorption and effect of calcium gluconate. E. Rothlin (Z. ges. exp. Med., 1930, **70**, 634—657; Chem. Zentr., 1930, ii, 2154).—Oral administration of calcium gluconate or chloride leads to a longer continued increase in blood-calcium than intravenous administration; the effects of subcutaneous and intravenous administration are intermediate.

A. A. Eldridge.

Biochemistry of aluminium. II. Excretion and absorption of aluminium in the rat. K. MacKenzie (Biochem. J., 1931, **25**, 287—291).—Rats receiving aluminium in their diet do not absorb it. The metal is excreted entirely by the alimentary canal.

S. S. Zilva.

Magnesium absorption in dogs. J. E. Winter and C. H. Richey (J. Pharm. Exp. Ther., 1931, **41**,

245—254).—The absorption of magnesium chloride and oxide given by the mouth was investigated in fasting dogs the normal serum-magnesium of which ranged from 0·00065 to 0·00223%. The stomach appears to be the main site of absorption.
F. O. Howitt.

Manganese metabolism of the rat. J. T. Skinner, W. H. Peterson, and H. Steenbock (J. Biol. Chem., 1931, 90, 65—80).—The average concentration of manganese in rats fed on the Steenbock ration was highest at birth, decreased during the first 12 days, rose to a second maximum at 21 days, and then decreased. The average total quantity of manganese in the rats was 0·0015 mg. at birth and 0·0676 mg. at 180 days of age. The manganese content of the newly born rat was increased 40% by adding extra manganese (as manganese sulphate) to the diet of the mother during gestation. During the first 12 days while the rats were receiving only mother's milk the storage of manganese was slow and could not be increased by adding manganese to the mother's ration. Addition of manganese to the rations of the young rats increased the rate of storage. The element is stored chiefly in the liver, muscle, bone, and hide, and by the addition of manganese to the ration, the amounts in bone, hide, liver, and kidney were increased by 191, 79, 29, and 29%, respectively. On a stock ration, adult rats excreted 80% of the manganese in the fæces, but with addition of manganese to the diet this increased to 99%. Addition of copper and iron, either singly or together, decreased the retention of manganese. W. O. Kermack.

Iron requirement in early childhood. M. S. Rose, E. McC. Vahlteich, E. Robb, and E. M. Bloomfield (J. Nutrition, 1930, 3, 229—235).—A normal diet, uncontaminated with iron, afforded insufficient iron for the needs of a girl aged 31 months. The intake of copper, about 0·2 of that of iron, was sufficient. Chemical Abstracts.

Metabolic changes associated with pigmentary effector activity and pituitary removal in *Xenopus lævis*. I. Respiratory exchange. II. Calcium and magnesium content of the serum. E. Charles (Proc. Roy. Soc., 1931, B, 107, 486—503, 504—510).—I. The factors controlling the metabolic rate of *X. lævis* have been investigated. Removal of the whole pituitary gland, or of the anterior lobe only, significantly decreases the rate of respiratory exchange, the pulmonary rate being depressed more than the dermal rate. Hypophysectomised animals have a significantly higher respiratory quotient than normal animals. The rate at which oxygen is absorbed through the lungs by *X. lævis* is 2—3 times as great as that at which it is absorbed through the skin.

II. The average calcium content of the serum of *X. lævis* was 7·61±0·25 mg. and 9·82±0·13 mg. for males and females, respectively. The corresponding values for the average magnesium content were 1·60±0·09 mg. and 2·35±0·10 mg. Excision of the whole pituitary or of the anterior lobe alone caused a fall in these values. No certain correlation could be detected between calcium and magnesium content and pigmentary effector activity. W. O. Kermack.

Fate in the organism of sulphur parenterally administered. R. Meyer-Bisch and F. Techner (Biochem. Z., 1931, 231, 110—112).—Intramuscular administration of sulphur emulsions to dogs and rabbits has no effect either on the total sulphur content of their livers or on the amount of sulphuric acid which can be liberated from the livers by hydrolysis. The liver probably does not play an important part in the changes in sulphur metabolism which follow parenteral administration of sulphur.
W. McCartney.

Permeability of the heart to sodium and potassium ions. H. P. Kryńska and W. R. Witanowski (Acta Biol. Exp., Warsaw, 1930, 6, 53—57).—The dried frog's ventricle contains 0·28% Na and 1·25 K; similar values are found for human and rabbit heart muscle. A surviving frog's heart gives up potassium ions to, and takes up sodium ions from, Ringer's solution; the amount of sodium removed from the fluid is, however, less than equivalent to the amount of potassium lost by the heart.
R. Truszkowski.

Action of trypaflavin on metabolism. G. Monasterio (Arch. exp. Path. Pharm., 1931, 159, 172—179).—The administration of small doses of trypaflavin to various animals (rabbits, dogs, mice, and rats) results in a hyperglycæmia which is caused by an increased production of adrenaline and is accompanied by a decrease in liver-glycogen and disturbances in the gaseous metabolism. Administration of larger doses of trypaflavin brings about a hypoglycæmia which may result in convulsions and death. In the depancreatised dog the effect is still exerted but to an inconstant degree. The hypoglycæmic action does not occur as a result of an increase in the rate of polymerisation or of oxidation of dextrose.
W. O. Kermack.

Experimental hyperglycæmia and the reticulo-endothelial system. R. Messina (Arch. Farm. sperim., 1931, 51, 229—240, 267—292).—The blood-sugar level of rabbits is raised by continued intravenous injection of trypan-blue, but not of basic iron saccharate. Death ultimately results in each case. In rabbits treated with either substance the hyperglycæmia which follows injection of dextrose becomes progressively more intense and more prolonged. This is attributable to the blocking of the reticulo-endothelial system. The hyperglycæmic effect of the injection of adrenaline becomes progressively less, owing to the exhaustion of glycogen reserves. The part played by endocrine disturbances is uncertain. The mechanism of the participation of the reticulo-endothelial system in carbohydrate metabolism is discussed. R. K. Callow.

Guanidine structure and hypoglycæmia. II. F. Bischoff and M. L. Long (J. Pharm. Exp. Ther., 1931, 41, 127—137; cf. A., 1929, 468).—Diphenetyl- and dianisyl-guanidines administered enterally are more toxic (as measured by changes in the carbamide- and amino-acid-nitrogen of the blood) than ditolylguanidine. Their action is accompanied by albuminuria and transient hyperglycæmia. Administration of benzthiazole-, benziminazole-, and benzoxazole-guanidines results in varying degrees of kidney damage, but not in a rise of the amino-acid-nitrogen of the blood. The oxazole derivative alone effects a mild hypoglycæmia, whilst the thiazole and iminazole derivatives produce no effect and an increase in the blood-sugar, respectively.

F. O. Howitt.

Action *in vivo* of synthalin on cell oxidation. O. Kauffmann-Cosla and O. Vasilco (Arch. exp. Path. Pharm., 1931, **159**, 154—162).—The administration of synthalin in mild diabetes may result in the disappearance of dextrose from the urine, but the place of the reducing sugar is taken by other carbon-containing compounds such as lactic acid and acetaldehyde. Synthalin therefore does not possess the same property as insulin of stimulating cell oxidation.

W. O. Kermack.

Influence of colloids on the action of histamine. B. Behrens (Biochem. Z., 1931, **231**, 92—94).—Since histamine is only very slightly adsorbed by kaolin or talc and since the action of the base on the surviving intestine or uterus is scarcely if at all influenced by the presence of these substances the results and explanation of Bernfeld (A., 1930, 1472) cannot be accepted. W. McCartney.

Comparative changes in gastric acidity and urinary reaction after injection of histamine. M. J. Matzner and I. Gray (Arch. Int. Med., 1931, 47, 202—205).—Following subcutaneous injection of histamine into patients as a gastric stimulant, free hydrogen chloride was found in the gastric secretion in about 50% of cases, and in not more than 50% of these did the urine show an alkaline tide.

A. Cohen.

Pharmacological effect of the substitution of methyl in the β-carbon group of methylamino-*p*-hydroxyphenylcarbinol. Raymond-Hamet (Compt. rend., 1931, **192**, 450—452).—The substitution causes the manifestation of properties resembling those of adrenaline, which the parent substance itself does not possess. P. G. Marshall.

3 : 4-Dihydroxy-ephedrine and -*nor*ephedrine. Raymond-Hamet (Compt. rend., 1931, **192**, 300—302; cf. this vol., 120).—The physiological action of 3 : 4-dihydroxy-ephedrine and -*nor*ephedrine resembles that of adrenaline rather than that of ephedrine. Thus, as with adrenaline, but not with ephedrine, their hypertensive action is sensitised by cocaine, they do not become hypotensive in large doses, and they have a strong and lasting inhibitive effect on the intestinal functions. It is concluded, therefore, that the physiological action is not modified by the introduction of a methyl group on the β-carbon atom of the side-chain, but is profoundly affected by the substitution of two phenolic hydroxyl groups in the 3 : 4-positions. J. W. Baker.

Influence of nicotine on the blood-sugar. R. Töppner (Arch. exp. Path. Pharm., 1931, **159**, 223—232).—Subcutaneous injection of nicotine (3 mg. of nicotine tartrate per kg. body-weight) into rabbits or the inhalation of tobacco smoke by healthy men results in a rise of blood-sugar during the first ½—1 hr. followed by a fall to somewhat below the normal level after about 3 hrs. When hyperglycæmia resulting from administration of dextrose or from pancreatic disease is present, the hyperglycæmic action of nicotine is less marked but the hypoglycæmic effect is rather more pronounced. W. O. Kermack.

Pharmacological properties of the alkaloids of *Helleborus*. G. Franzen (Arch. exp. Path. Pharm., 1931, **159**, 183—201).—The properties of the alkaloids of *H. viridis*, celliamine, sprintillamine, and sprintilline, resemble those of cevadine, aconitine, and delphinine, but, unlike the latter group, they exert a stimulating action on the respiratory centre of warm-blooded animals. W. O. Kermack.

***Panax ginseng*. V. Toxicity of nerve poisons in rats fed on *P. ginseng*. VI. Comparison of composition and action of *P. ginseng* and *P. quinquefolius*.** N. Sugihara and P. Min. **VII. and VIII. Pharmacological actions of "panaxic acid" and "panacene."** N. Sugihara and K. Kin (Keijo J. Med., 1930, 1, 685—710, 711—772; cf. A., 1930, 1617).—V. The effect of feeding *Panax* extract to rats is antagonistic to that of adrenaline and atropine, but hastens the appearance of convulsions and death caused by physostigmine and pilocarpine.

VI. *P. ginseng*, which is richer in active constituents, is more effective than *P. quinquefolius* in causing curvature of the tail and convulsions in mice.

VII. An account of the pharmacology of "panaxic acid," a mixture of saturated and unsaturated fatty acids obtained by alkaline hydrolysis of the ethereal *Panax* extract.

VIII. A parallel study of "panacene," the oil obtained by steam-distillation of the ethereal *Panax* extract. A. Cohen.

Santonin. I. Excretion of santonin. H. W. Knipping and H. Seel (Arch. exp. Path. Pharm., 1931, **159**, 202—212).—The administration of santonin to normal animals and men accelerates urinary flow. In rabbits, the liver or kidneys of which were damaged by administration of phosphorus or excess of ergosterol, santonin exerted a slightly favourable action on the urinary output, being itself excreted at approximately the normal rate. In patients suffering from diseases of the liver, kidneys, or circulation a slight increase was observed in the time taken for the completion of the urinary excretion of santonin (normally 24 hrs.), but the differences were not sufficiently well marked to be of use for diagnostic purposes.

W. O. Kermack.

Hydroxypyruvaldehyde: its preparation and physiological behaviour. A. Hynd (Biochem. J., 1931, 25, 11—19).—The effect produced by monomeric and polymeric hydroxypyruvaldehyde when injected subcutaneously into mice is the same and is similar to that produced by glyoxal. It is quite distinct from that produced by glucosone. When hydrogen sulphide is used in the preparation of hydroxypyruvaldehyde (cf. Evans and Waring, A., 1926, 1227) the resulting product is contaminated with sulphur-containing by-products. Some of these are thermostable, others thermolabile. The latter produce toxic effects similar to those following the administration of cyanides. Similar toxic compounds are obtained when dihydroxyacetone or glyoxal, but not the sugars or glucosone, are treated with hydrogen sulphide. The reported greater toxicity of "dimeric" hydroxypyruvaldehyde (cf. Kermack, Lambie, and Slater, A., 1929, 844) is due to the presence of an unstable toxic product. S. S. Zilva.

Chemistry of anæsthesia. W. D. Bancroft and G. H. Richter (J. Physical Chem., 1931, **35**, 215—268).—A review of the theories concerning anæsthesia. Bernard's theory that reversible coagulation of the colloids of the sensory nerves produces or accompanies anæsthesia is supported. L. S. Theobald.

Gaseous higher hydrocarbon narcotics. H. Killian (Schmerz, Nark., Anæsth., 1930, **3**, 121—159; Chem. Zentr., 1930, ii, 2155).—In the series of unsaturated hydrocarbons the solubility increases; that of compounds possessing double and triple linkings is greater than that of homologous unsaturated simple substances, whilst branching of the chain has the opposite effect. For ethylene and narcylene the solubility in blood is greater than that in water. In the olefine series the narcotic power markedly rises, but the toxicity limit falls, with increase in the number of carbon atoms. The rise in narcotic power increases with the presence of double linkings and decreases with that of side chains, parallel with the changes in solubility in water, blood, and oil. Spectroscopic investigations did not indicate the formation of true compounds with hæmoglobin. A. A. Eldridge.

Comparison of narcotic action on the intestine and on the whole animal. E. Frey (Arch. exp. Path. Pharm., 1931, **159**, 163—171).—The activities of various narcotics applied to the whole animal are not proportional to their activities on the isolated intestine, barbituric acid derivatives being relatively inactive on the intestine. The activities of barbituric acid derivatives on the isolated intestine is facilitated by an acid reaction and similarly luminal has greater activity on an animal receiving an acid diet than on one receiving an alkaline diet. W. O. Kermack.

Toxicological investigation of chloral hydrate. L. W. Rising and E. V. Lynn (J. Amer. Pharm. Assoc., 1931, **20**, 9—11).—Periodic determinations of chloral hydrate which had been mixed with minced, fresh sheep's stomach with and without various preservatives and kept in sealed bottles showed that mercuric chloride was the best preservative, the maximum loss of poison in the treated sample being less than 9% after 7 months. Even in the unpreserved samples probably 18 months would elapse before the aldehyde was completely dissociated. Loss of chloral in the specimen treated with alcohol was very rapid and after 3 months was greater than in that unpreserved and subjected to the ordinary putrefactive changes. Arsenious acid, embalmer's fluid, and formaldehyde in that order were most efficient after mercuric chloride. E. H. Sharples.

Effect of lithium on the sea-urchin egg. J. Runnström (Acta Zool., 1928, **9**, 365—424; Chem. Zentr., 1930, ii, 3424).—Comparative plasmolysis experiments are described. A. A. Eldridge.

Action of various salts on the first stage of the surface precipitation reaction in *Arbacia* egg protoplasm. L. V. Heilbrunn (Protoplasma, 1930, **11**, 558—573).—The film formation on the extruded protoplasm of *Arbacia* eggs is examined. Salt solutions retard or inhibit the first stage of the reaction in the order $Mg > NH_4 > Na > K > Li$. Although calcium is essential to the reaction, high concentrations of calcium salts have a similar retarding effect to other cations. The thiocyanate ion has a greater effect on the reaction than the chloride ion. The presence of a lipase as the active catalyst of the reaction is suggested. A. G. Pollard.

Action of tincture of iodine and mustard oil on the gaseous metabolism and blood circulation in the skin. E. Sametinger (Arch. exp. Path. Pharm., 1931, **159**, 1—11).—Tincture of iodine applied to the ear of the dog increases the oxygen uptake and carbon dioxide production, but there is practically no change in the quantity of blood circulating through the ear. Mustard oil increases the rate of circulation and accelerates the carbon dioxide production, but inhibits the oxygen uptake during the first hour. During the next 2—5 hrs. the carbon dioxide production decreases, whilst the oxygen uptake increases above normal, the rate of circulation decreases, and œdema develops. W. O. Kermack.

Determination of lead in fæces and urine and its significance in the diagnosis of lead poisoning. F. Fretwurst and A. Hertz (Arch. Hyg., 1930, **104**, 215—225; Chem. Zentr., 1930, ii, 3446).—The fæces and urine of persons whose work did not bring them into contact with lead contained, respectively, 0—0·14 (in one case 0·6) mg. per 100 g. and 0·01—0·07 mg. per litre; values for persons working with lead but showing no toxic symptoms were 0—0·2 and 0—0·05, whilst for workers with lead who exhibited symptoms of poisoning they were 0·02—0·9 and 0—0·13. A tap-water after 12 hrs. in the pipes contained 0·03 mg., and another (Hamburg) contained 0·07 mg. of lead per litre. A. A. Eldridge.

Absorption of finely-divided mercury. G. Vitte (Bull. Soc. Pharm. Bordeaux, 1930, **68**, 80—93; Chem. Zentr., 1930, ii, 2671; cf. B., 1931, 365).—Evaporation and dissolution of finely-divided mercury are much more marked than with compact mercury. Experiments on dissolution by artificial and natural gastric juice show that mercuric oxide is readily attacked; 0·1% hydrochloric acid dissolves it quickly and completely, but 0·8% sodium chloride solution has no action. Mercurous oxide is unattacked. A. A. Eldridge.

Excretion of mercury after ingestion of Hydrargyrum cum Creta. G. Vitte (Bull. Soc. Pharm. Bordeaux, 1930, **68**, 93—102; Chem. Zentr., 1930, ii, 2671).—After daily ingestion of finely-divided mercury (0·03 g.), the urine after the fifth to the eighth day contains mercury. The liver and kidneys of dogs which have received 2 g. of finely-divided mercury in a month contain mercury. A. A. Eldridge.

Effect of fluorine on the calcium metabolism of albino rats and the composition of the bones. F. J. McClure and H. H. Mitchell (J. Biol. Chem., 1931, **90**, 297—320).—The addition to the diet of rats of either calcium fluoride or sodium fluoride in quantities equivalent to 0·03% F inhibits growth independently of any effect on food consumption. The calcium balance is not influenced by calcium fluoride or sodium fluoride at concentrations equivalent to 0·01% and 0·03% F, but at a concentration equivalent to 0·06% the percentage of calcium retained is below normal. With concentrations of sodium or calcium fluoride equivalent to 0·03% or 0·06% F the ash content of the bones is increased, the calcium content of the ash is decreased, but the phosphate content is approximately normal. It appears that the administration of fluoride especially in the form of the more soluble sodium fluoride results in the deposition in the bone of some non-calcium constituent, possibly fluoride. Abnormalities are also produced in the structure of the teeth, but in this respect calcium fluoride is as effective as sodium fluoride. W. O. Kermack.

Hyperthermia. II. Acid–base equilibrium in hyperthermia induced by short radio waves. F. Bischoff, M. L. Long, and E. Hill. **III. Phosphorus equilibrium.** F. Bischoff, L. C. Maxwell, and E. Hill (J. Biol. Chem., 1931, **90**, 321—329, 331—339).—When the body temperature of a human subject is raised by the action of short radio waves the effect is the same as when the rise is brought about by external application of heat, except that a marked decrease in blood-volume occurs which is absent in the latter case. A loss of carbon dioxide and an increase in blood p_H were observed, but the urine was not markedly alkaline.

III. No phosphorus is eliminated in the perspiration during a hyperthermia induced by radio waves. The decrease in the excretion of phosphorus by the urine is due to the increase in metabolism associated with a change of inorganic to organic phosphate in the blood. Increased elimination of nitrogen occurs through the perspiration, and this accounts for the decrease in the nitrogen excretion in the urine.

W. O. Kermack.

Permeability of human epidermis to ultraviolet radiation. N. S. Lucas (Biochem. J., 1931, **25**, 57—70).—The apparent absorption of ultraviolet light by epidermis as determined by the usual methods of photometry is not entirely due to true absorption, but is in part due to scattering of the incident light by the epidermis. This scattering should, however, cause much less interference in transmission of the light to the underlying tissues when the skin is irradiated *in vivo*. For light of wave-length 300 mμ and less the effect of scattering is dwarfed by true absorption by the epidermis, since the shape of these absorption curves resembles those of many proteins and amino-acids. The percentage of ultra-violet light of physiologically active wave-lengths transmitted through the epidermis is higher than previously recorded by Hasselbalch (Skand. Arch. Physiol., 1911, **25**, 55) and is calculated to be about 1·5—30 times greater for wave-lengths from 404 to 289 mμ, respectively. S. S. Zilva.

Active group of catalase. II. K. Zeile (Z. physiol. Chem., 1931, **195**, 39—48).—After two adsorptions with tricalcium phosphate, liver-catalase gives a value for $k/[Fe_F]$ of 3430. The preparation of catalases from *Boletus scaber* and from pumpkin cotyledons is described. These catalases are spectroscopically identical with liver-catalase. After germination for 5 days between damp filter-paper, the cotyledons are ground in 5% disodium phosphate solution, kept on ice for an hour, and centrifuged. The middle layer has a *k*-value of about 250. The Fe_F of pumpkin-catalase has a value of about 0·0172. $k/[Fe_F]$ is about 8000. The activity of pumpkin-catalase, like that of liver-catalase (this vol., 123), can be suppressed by potassium cyanide. The dissociation constant of the enzyme–hydrogen cyanide complex is $2{\cdot}87\times10^{-7}$. A. Renfrew.

Ultra-violet irradiation and catalase. H. Koeppe (Arch. Kinderheilk., 1930, **89**, 70 pp.; Chem. Zentr., 1930, ii, 3585).—The amount of hydrogen peroxide decomposed by a definite amount of catalase is constant. The extent of decomposition of hydrogen peroxide by irradiation with a quartz lamp is proportional to the surface illuminated. The function of blood-catalase is to render possible the combination of oxygen with the fat envelopes; hence oxyhæmoglobin is reduced. A. A. Eldridge.

Determination of hydrogen peroxide and catalase in human blood. M. Rigoni (Atti Soc. med.-chir. Padova, 1928, 4 pp.; Chem. Zentr., 1930, ii, 3585).

Temperature coefficients and energy exchanges of the citric acid dehydrogenase of cucumber seeds. W. J. Dann (Biochem. J., 1931, **25**, 177—189).—At 25° the Michaelis constant of the citric acid dehydrogenase of cucumber seeds is $1{\cdot}65\times10^{-4}M$ and at 35° it is $8\times10^{-5}M$. Thus the temperature coefficient Q_{10} is 0·48 at 30° and the heat of formation of the citric dehydrogenase–citric acid compound is therefore 13,460 g.-cal. per mol. The temperature coefficient of the velocity of the reaction catalysed by the dehydrogenase has been measured; Q_{10} is 1·65 at 30°. The energy of activation of the citric dehydrogenase–citric acid compound is therefore 8790 g.-cal. per mol. S. S. Zilva.

Protective substances of amylase. IV. Protective action of yeast, malt, and barley extracts. V, VI. Purification of the protective substances. VII. Protective action of the purified substances and their identification. H. Nakamura (J. Soc. Chem. Ind. Japan, 1931, **34**, 16B—22B; cf. this vol., 391).—The filtrate from yeast, plasmolysed with toluene and autolysed, and water extracts of malt and barley protect taka-diastase against destruction by heat, as has been shown for proteases and peptones (this vol., 391). No activating action is shown. The amount of toluene and duration of autolysis have an almost inappreciable effect on the protective action of yeast extract. By rendering dilute solutions of the protective materials alkaline (p_H 8·5—11·7), precipitates are obtained which contain the whole of the actual protective substance. The ash from this material, and the calcium separated from it, exert a protective action equivalent to that of the original material. The protective action of calcium salts is proportional to the amount of calcium

contained in them. The action of these protective substances is not due to colloid protection nor to change of p_{H}; it is considered that amylase is a compound of calcium, the activity of which is lost on removal of calcium, and protected by its introduction.
F. E. Day.

Influence of cinchona alkaloids on the amylolytic enzyme. E. Ohlsson (Ar. Int. Pharm. Thér., 1930, **37**, 108—114; Chem. Zentr., 1930, ii, 2909).—Experiments were performed at constant p_{H}. Quinidine has no effect on taka-diastase or pancreatic amylase. Quinine, cinchonine, cinchonidine, and optoquin retard the enzymic hydrolysis of starch. Increased enzymic action in the presence of small concentrations of the alkaloids was not observed.
A. A. Eldridge.

Influence of citrates on the enzymic hydrolysis of starch. E. Ohlsson (Ar. Int. Pharm. Thér., 1930, **37**, 98—107; Chem. Zentr., 1930, ii, 2909).—Citrates do not affect taka-diastase at the optimum p_{H}, but at other p_{H} values they retard its action. In the absence of sodium chloride they retard the action of pancreatic amylase even at the optimum p_{H}; they have no effect at the p_{H} of the intestine.
A. A. Eldridge.

Mechanism of fermentation by invertases. E. Avtonomova (Biochem. Z., 1931, **231**, 13—24).—A mathematical formula independent of any theory of the process of fermentation has been worked out for the hydrolysis of sucrose by invertase; it is very similar to that deduced by Maximovitsch and Avtonomova (A., 1928, 549). It seems that the differences in behaviour which the various enzymes exhibit are due more to experimental conditions than to individual peculiarities of the enzymes, and that general formulæ based on the law of mass action, and taking into account the order of the reactions, can be found for all fermentative processes.
W. McCartney.

Kinetics of esterase action compared with acid catalysis. E. A. Sym (Biochem. Z., 1931, **230**, 19—50).—The action of esterase (from pig-pancreas powder) in acetone–water mixtures shows a minimum at a concentration of 6—8M of water. Esterification of acetic acid by the homologous series of alcohols is more active the greater is the mol. wt. of the alcohol used; this is also true for homologous acids of the aliphatic series. In the former the gradation of the ease of reaction is fairly independent of the medium, but in the latter the reaction velocities in esterase action are different from those in hydrochloric acid catalysis or thermal reaction. With butyl alcohol the equilibrium point is displaced by change of alcohol concentration (cf. Dietz, A., 1907, ii, 677) and the reaction velocity is considerably altered. Esterase action increases with increasing concentration of butyric acid up to 0·6M, but further increase results in the action remaining constant or even decreasing. Water activates esterase action but inhibits hydrochloric acid catalysis.
F. O. Howitt.

Enzymic production of mandelic esters. P. Rona, R. Ammon, and H. A. Oelkers (Biochem. Z., 1931, **231**, 59—66; cf. A., 1930, 373).—No stereochemical specificity in the production of esters can be observed when esterases (in the form of dried powders) from the pancreas, liver, or kidneys of the pig, from human liver, or from cat's liver are allowed to act on *n*-butyl alcohol and *d*-, *l*-, or *dl*-mandelic acid in equimolecular proportions.
W. McCartney.

Specificity of phosphatases. K. P. Jacobsohn and J. Tapadinhas (Biochem. Z., 1931, **230**, 304—311).—The preparation of menthylorthophosphoric, dimenthylorthophosphoric, and dimenthylpyrophosphoric acids is described and the action of animal and vegetable phosphatases on them investigated. Animal organ extracts (liver and kidney of sheep and rabbit), extracts of top yeast, or the juice of green leaves caused no hydrolysis of these substrates although the same samples of enzyme readily hydrolysed potassium diphenylpyrophosphate and bornylorthophosphate.
P. W. Clutterbuck.

Esterification of phosphoric acid, production of lactic acid, and phosphatase action in muscle-pulp and -powder. J. Bodnár and B. Tankó (Biochem. Z., 1931, **230**, 228—232; cf. A., 1929, 1106).—Lactic acid formation by fresh pulp of pigeon breast-muscle decreases on keeping in proportion to the decrease in the ability of the pulp to bring about esterification of phosphoric acid. The agents responsible for the latter reaction together with the total activity are found in the powder prepared from the pulp by alcohol–ether or acetone–ether treatment. The powder, however, exhibits a decreased power of lactic acid formation due to a reduced phosphatase content.
F. O. Howitt.

Refutation of Schutz' law and its analogous equations in the kinetics of enzyme action. K. Nakajima (J. Fac. Agric. Hokkaido, 1930, **28**, 329—356).—The Schutz equation is considered to hold only for dilute solutions of pepsin.
Chemical Abstracts.

Nature of proteases. VIII. Refractometric studies on the activity of different pepsin preparations. J. A. Smorodincev, A. N. Adova, and S. S. Drosdov (Z. physiol. Chem., 1931, **195**, 113—120).—The refractive indices of solutions of various pepsin preparations in hydrochloric acid are slightly higher for strong than for weak preparations; the values for 1% solutions of pepsin in varying concentrations (0·11—0·653%) of hydrochloric acid increase with rise in the concentration of the acid. The refractive indices of 1% solutions (p_{H} 1·26—1·50) of pepsin in hydrochloric acid do not alter during 72 hrs. at the ordinary temperature or during 24 hrs. at 38°; the values increase when the solutions are boiled. The activity of pepsin preparations can be determined by the alteration in the refractive index of a pepsin-hydrochloric acid digest of denatured fibrin; the enzyme solution is used as a control. There is generally a larger increase in the refractive index with strong than with weak preparations. Fibrin has no effect on the refractive index of hydrochloric acid.
H. Burton.

Specificity of animal proteases. Mode of action of peptidases. A. K. Balls and F. Köhler (Ber., 1931, **64**, [*B*], 294—301; cf. this vol., 392).—The action of aminopolypeptidase of the intestine is restricted by benzoyl-, bromo*iso*hexoyl-, and *p*-nitrobenzoyl-glycine, aceturic acid, phthalimide, and sarcosine, but not by allantoin, creatinine, or glycine anhydride. The action appears therefore to be due to the presence of an imino-group attached to an acid residue. The dependence of the reactivity of the imino-group on its acidic character is further illustrated by the behaviour of di- and amino-polypeptidase towards substituted di- and tri-peptides. Only the peptide group vicinal to the acid residue has a restricting action. Equivalent amounts of bromo*iso*hexoyl-glycine, -diglycine, and -triglycine exert the same action. Introduction of a second acidic group, for example tyrosine, increases this action, since more than one imino-group is enabled to react with the enzyme. In some cases it appears possible that the necessary activation of the imino-group is induced by the enzyme itself and that the union of the enzyme with the amino-group of the peptide molecule enables the imino-group to function as second point of attachment. The entry of the enzyme into the amino-group saturates its basic character to such an extent as is necessary for the activation of the imino-group. The tendency towards decomposition of the enzyme–substrate compound is considered to depend not on an increased instability to hydrogen-ion concentration, but on an enhanced reactivity of the imino-group.

H. Wren.

Proteolytic enzymes of green malt. II. Action of the proteinase on egg-albumin, caseinogen, edestin, and fibrin at different reactions. R. H. Hopkins and H. E. Kelly (Biochem. J., 1931, **25**, 256—264).—The optimum p_H at 46° is as follows: crystalline egg-albumin 3·3—3·6, caseinogen 3·35—5·57, fibrin 3·8 (or less) and at 6·0, edestin at 37° 4·3. These values approximate in most cases very closely to those of the maximum buffering power of the protein measured at 18°. The enzyme appears to act on ionised protein on both sides of the isoelectric point.

S. S. Zilva.

End-point of tryptase action. J. T. Groll (Pharm. Weekblad, 1931, **68**, 109—121).—The end-point of the action of tryptase on peptone can be regarded as reached when the Sørensen titration figure does not increase by more than 0·1 c.c. of 0·1*N*-sodium hydroxide solution in 24 hrs. This point is reached after a week, although only 20% of the peptone-nitrogen can be titrated; the value rises to about 30% after several weeks, but this occurs also in the absence of enzyme.

S. I. Levy.

Effect of heat on the activating efficiency of enterokinase. J. Pace (Biochem. J., 1931, **25**, 1—7).—The heat-inactivation of enterokinase, like that of purified trypsin, proceeds according to the unimolecular formula. The stability is influenced considerably by the p_H of the medium, but there is an optimum region between p_H 6 and 7. The critical increment of the process at p_H 6·5, 5·12, or 3·2 is of the order of 40,000 g.-cal.

S. S. Zilva.

Hitherto undescribed proteolytic action of intestinal extract. A. K. Balls and F. Köhler (Ber., 1931, **64**, [*B*], 383—387).—The enzyme is prepared from the glycerol extract of the intestine of the pig. After adsorption by aluminium hydroxide at p_H 4·5—5, it remains in the residual solution, from which it can be isolated by adsorption with aluminium hydroxide *C* at p_H 7·0, followed by elution with secondary phosphate. It can be freed from ereptic enzymes by treatment with hydrogen sulphide or hydrocyanic acid. It is stable towards the two last-named substances and formaldehyde, but is completely destroyed at 70° within 2—3 min. It exerts hydrolytic action on peptide-like substances which do not contain a free amino- or carboxyl group. With "aniline peptides" the increase in acidity is very slight, but the hydrolysis can be followed readily with the aid of the diazo-reaction. With chloroacet-*o*-nitroanilide the incidence of hydrolysis is shown by the yellow colour of the free *o*-nitroaniline, but increase of acidity is scarcely noticeable, since the base impedes the action of the enzyme; addition of formaldehyde, which combines with the base, causes a marked increase in hydrolysis. The activity of the enzyme preparation towards chloroacetyl-*dl*-alanine, chloroacetyl-*dl*-leucine, and benzoyltriglycine but not towards benzoyl-glycine or -diglycine has been established.

H. Wren.

Proteolytic action of papain and cathepsin. H. A. Krebs (Naturwiss., 1931, **19**, 133).—A defence of the author's work against the criticisms of Waldschmidt-Leitz (A., 1930, 1217; this vol., 124).

A. J. Mee.

Structural conceptions of the action of enzymes in leather chemistry. M. Bergmann (Collegium, 1930, 516—520).—Certain enzymes hydrolyse the hide proteins into amino-acids, others oxidise the amino-acids by removing two hydrogen atoms, and a third class produces the final products of putrefaction. A hydrogen acceptor is necessary for the functioning of the oxidising enzymes. Using chloroacetic acid as the acceptor, it has been combined with phenylalanine, and in presence of acetic anhydride as catalyst the acid $CHPh{:}C(CO_2H){\cdot}NHAc$ has been obtained. The resemblance to the enzyme action is shown by the similarity of the end-products of the reaction and by the readiness with which the reaction proceeds in presence of a catalyst. Thus at the ordinary temperature an unsaturated dipeptide containing two hydrogen atoms less than glycyl-*l*-phenylalanine which could not be hydrolysed by any of the known pancreatic enzymes has been prepared, but was hydrolysed by commercial pancreatin, thus indicating the presence in the latter of a hitherto undescribed proteolytic enzyme.

D. Woodroffe.

Chemical nature of urease. E. Waldschmidt-Leitz and F. Steigerwaldt (Z. physiol. Chem., 1931, **195**, 260—266).—Addition of varying amounts of amino-acids, peptides, and potassium cyanide to crude and purified urease preparations usually causes an alternation in their activity; pure amino-acids need not be used, since a tryptic digest of caseinogen has a greater activating power than either alanine or cystine. Contrary to the statement of Tauber (A., 1930, 1217), crystalline urease (Sumner, A., 1926, 1061, 1176) is not inactivated by trypsin or by other proteolytic enzymes; hydrolysis of the admixed globulin occurs, since no precipitate occurs with sulphosalicylic acid.

H. Burton.

Influence of neutral-red on the respiration of yeast. M. Geiger-Huber (Proc. K. Akad. Wetensch. Amsterdam, 1930, 33, 1059—1068).—The respiration of baker's yeast at 20° and between p_H 5·0 and 8·1 is independent of the hydrogen-ion concentration. Addition of neutral-red (1 in 10) increases the respiration immediately by 20—30% in an acid medium and 10—20% in an alkaline medium, but a subsequent decrease occurs, and about 1 hr. after addition of the dye the value is the same for all p_H values and is only about 80% of that of the undyed cells. With increasing age of the cells the change in respiration on addition of the dye increases and a final steady value is attained only after a much longer period. Since changes are observed in the respiration of the yeast in the presence of insufficient dye to colour the cells. it is suggested that the neutral-red influences the protoplasmic boundary wall. J. W. Smith.

Selective fermentation. Alcoholic fermentation of mixtures of dextrose and lævulose by brewer's and Sauterne yeasts. R. H. Hopkins (Biochem. J., 1931, 25, 245—255).—The factor $K_{G/F}$ (the relative degree of fermentation of the two sugars) for brewer's yeast is not appreciably influenced by the relative proportions of dextrose and lævulose in the original solution nor by modification of the invertase activity of the yeast. The invertase of Sauterne yeast resembles that of brewer's yeast in that it is inhibited more strongly by lævulose than by dextrose. The addition of invertase to a mixture of dextrose and lævulose undergoing fermentation by zymin from brewer's yeast does not affect the selectivity. $K_{G/F}$ for brewer's yeast decreases with rise in temperature of fermentation, whilst that for Sauterne yeast increases. Brewer's yeast ferments dextrose faster than lævulose in separate solutions when the concentration of sugar is less than 1%. Sauterne yeast ferments lævulose faster than dextrose in separate solutions at all concentrations up to 10%, but especially at low concentrations. The mutarotation of partly fermented solutions of the sugars is for dextrose by brewer's yeast in the positive direction, dextrose by Sauterne yeast in the negative, lævulose by brewer's yeast in the positive, and lævulose by Sauterne yeast in the negative direction. S. S. Zilva.

Biochemistry of zinc. Zinc and fermentation by yeast. A. Zlatarov, M. Andreïtscheva, and D. Kaltscheva (Biochem. Z., 1931, 231, 123—134).—At a dilution of 0·002N solutions of zinc sulphate or nitrate inhibit completely the fermentation of dextrose by yeast. More dilute solutions (0·002N—0·0011N) restrict the fermentation, which, however, is not affected by solutions of still greater dilution. The action of the zinc salts alone is quantitatively and qualitatively different from that of mixtures of these salts with salts of other metals (nitrates of calcium, potassium, manganese, and iron, and sodium succinate). Of the salts of the other metals potassium and calcium nitrates always stimulate fermentation, manganese and iron nitrates stimulate or restrict, according to the degree of dilution, and sodium succinate always restricts fermentation, dilute solutions (not more concentrated than 0·1N) being considered in all cases. Calcium nitrate is the salt which stimulates most strongly, sodium succinate that which restricts most strongly, the effects being proportional to the degree of dilution. Zinc sulphate at a dilution of 0·001N converts the stimulating action of other salts into a restricting action and increases the action of sodium succinate. In the presence of 0·001N-calcium nitrate solution or of 0·001N-sodium succinate solution fermentation is completely suppressed by 0·00139N-zinc nitrate solution. Similar effects are observed with other mixtures, but the inhibiting action of 0·002N-zinc nitrate solution is not affected by the presence of any of the other salts. W. McCartney.

Rôle of iron and copper in the growth and metabolism of yeast. C. A. Elvehjem (J. Biol. Chem., 1931, 90, 111—132).—Baker's yeast has been grown on a medium containing sucrose 2·5%, magnesium sulphate 0·25%, potassium chloride 0·25%, ammonium chloride 0·25%, disodium hydrogen phosphate 0·25%, and calcium chloride 0·05%, but deficient in iron and copper, the content in these elements being less than 0·0025 mg. and 0·001 mg. per 100 c.c., respectively. The yeast grew at an abnormally slow rate, was pale in colour, possessed an abnormally low total iron content, was completely devoid of free inorganic iron, had a low cytochrome content, and showed a low oxygen consumption. The addition of a small amount of iron increases the rate of growth, the cytochrome content, and the oxygen consumption. When copper is added as well as iron a distinctly high rate of growth is obtained and the yeast produced is particularly rich in the cytochrome-*a* component. In old cultures the oxygen consumption decreases owing to the acidity of the medium. In 48 hrs.' old cultures at least 80% of the respiration is inhibited by potassium cyanide, but in 7 days' old cultures the oxygen uptake is completely unaffected by potassium cyanide. The potassium cyanide-stable system metabolises dextrose, is destroyed at 60°, and is inhibited to the extent of 70% by urethane. The respiration of yeast grown on beer wort, which prevents the development of high acidity, is largely inhibited by cyanide. In this medium the total respiration may be low, due to an insufficient supply of iron in the wort. The addition of bios to the synthetic media used in this work stimulated the rate of growth to a small extent, but had no effect on the respiratory activity of the yeast. The concentration of copper which gives maximum stimulation of cytochrome-*a* is 0·01 mg. per 100 c.c. Higher concentrations of copper inhibit growth during the first 48 hrs., but the toxic effect disappears as the concentration of cells in the medium increases. Yeast low in inorganic iron cannot assimilate iron from a phosphate buffer at p_H 7·0, but readily takes up iron at p_H 4·0. W. O. Kermack.

Staining of yeast-cells with methylene-blue and the permeability of the yeast-cell membrane. I. H. Fink (Z. physiol. Chem., 1931, 195, 215—240; cf. von Euler and Florell, A., 1920, i, 267).—The influence of hydrogen-ion concentration, neutral salts, and various sugars on the adsorption of methylene-blue by yeast-cells has been studied. Little methylene-blue is adsorbed by washed, dry bottom yeast from an acid solution, whilst at p_H 7·4—9·0 about 92% of the dye is adsorbed. Conversely, the dye is eluted from the stained cells much more readily by an acid than by an alkaline medium. The influence of small amounts of salts on the staining is particularly noticeable when yeast is suspended in distilled water, whereby the number of cells stained increases rapidly with time; in tap water, the number remains constant. There is a marked increase in the number of stained cells when salt-free solutions of dextrose, lævulose, sucrose, or galactose are used; maltose is somewhat less active, mannitol is inactive, whilst glycerol has only a slight action. It is suggested that the yeast-cell membrane is altered so as to allow the methylene-blue to permeate the cell. The above effect with sugars is not obtained if the sugar solution contains small amounts of salts. Yeast-cells, suspended in dextrose solution and then treated with methylene-blue, could not be grown on wort–gelatin plates; growth occurred in absence of the dye or when potassium chloride was added prior to the dye. Subsequent staining of the colonies with methylene-blue shows that those grown from the dextrose solution alone are mainly dead, whilst those from a suspension of cells in tap water are living to the extent of about 95%.

Fermentation of dextrose by yeast in salt-free solution occurs much less readily than in presence of salts; addition of methylene-blue causes a retardation in the evolution of carbon dioxide which is much more pronounced in the salt-free medium. This retardation is almost completely abolished by addition of salts; the effect for anions is acetate<citrate<tartrate<nitrate<sulphate and bromide<thiocyanate<iodide<chloride, and for cations lithium<sodium<potassium<ammonium. H. Burton.

Activator-*Z*. H. von Euler and T. Philipson (Z. physiol. Chem., 1931, **195**, 81—100).—Using the autolysate of bottom yeast (this vol., 263) as the source of *Z*-activity, the acceleration of fermentation due to caffeine, theobromine, xanthine, tryptophan, adenosine, thymidine, or hæmin is found to be zero. The *Z*-activity of malt-germ extract is comparable with that of boiled yeast extract; the *Z*-activities of extracts of fresh barley cotyledons, rutabagas, moulds, tea, and coffee are weak.

The *Z*-factor is practically insoluble in 95% acetone, but dissolves in 90% acetone. Colloidal ferric hydroxide treatment does not alter the activity of activator-*Z*. "Fe-Extract" prepared by precipitating the dialysate with lead acetate and mercuric chloride, treating with hydrogen sulphide, neutralising, adding iron hydrosol, centrifuging, concentrating, suspending in 1% monopotassium phosphate solution, and again centrifuging, is not, at any p_H, adsorbed by blood-charcoal. Phosphate in neutral and alkaline solutions adsorbs the active substance. By extracting the aluminium phosphate extract with acetic acid, a solution having half the activity of "Fe-Extract" is obtained. Silicic acid does not adsorb the active substance.

The absorption capacity of top yeast for activator-*Z* is unaltered by, and independent of, the state of saturation. Bottom yeast is activated in exactly the same way by dialysate and "Fe-Filtrate," and is only influenced by that part of activator-*Z* which is not adsorbed by ferric hydroxide. A. Renfrew.

Hexosemonophosphoric esters. R. Robison and E. J. King (Biochem. J., 1931, **25**, 323—338).—An aldosemonophosphoric ester, $[\alpha]^{20}_{5461}$ +41·4° (barium salt $[\alpha]^{20}_{5461}$ +21·2°), has been isolated from the hexosemonophosphoric ester produced by fermentation of hexoses with yeast juice. The reducing power of the ester measured by an iodometric method is equal to that of the equivalent amount of dextrose, or by the Hagedorn and Jensen method 80% of that of dextrose. The Selivanov reaction is not appreciably greater than that given by dextrose. The phenylhydrazine salt of the osazone of aldosemonophosphoric ester is identical in m. p. (154—154·5°) and rate of hydrolysis with the corresponding salt of the osazone of fructosemonophosphoric ester. The ester is very resistant to hydrolysis by acids at 100°. Hydrolysis proceeds more rapidly when the free aldosemonophosphoric acid is heated alone than in presence of sulphuric acid. The sugar product of acid hydrolysis has the character of *d*-dextrose. Hydrolysis by bone-phosphatase proceeds rapidly at the ordinary temperature and p_H 7·0, but the sugar product contains both dextrose and lævulose. Oxidation of the aldosemonophosphoric ester with bromine yields a phosphohexonic acid, from which gluconic acid has been obtained by hydrolysis with bone-phosphatase. The constitution of the ester is that of a dextrose-6-phosphate. The specific rotations of the free ester and of its barium salt differ considerably from those of the synthetic ester prepared by Levene and Raymond (this vol., 63). A ketosemonophosphoric ester similar in most respects to Neuberg's fructosemonophosphoric ester has also been isolated from the fermentation products, whilst evidence has been obtained of the presence of another ester as yet unidentified. S. S. Zilva.

Easily cleavable phosphoric acid compound in yeast. H. von Euler and R. Nilsson (Z. physiol. Chem., 1931, **195**, 273—276).—Yeast contains an easily cleavable phosphoric acid compound which is not completely precipitated by magnesia mixture and ammonia, and gradually gives a precipitate with Embden's reagent. H. Burton.

Behaviour of yeasts and some *Hyphomycetes* towards quinic acid. W. W. Perwozwansky (Zentr. Bakt. Par., 1930, II, **81**, 372—392).—All fungi examined developed normally when quinic acid was the sole source of carbon. Benzene derivatives were produced in all cases, protocatechuic acid being prominent. In the presence of sugars, organisms utilising quinic acid could not produce a typical alcoholic fermentation. Organisms utilising quinic acid produced organic acids (notably oxalic) when grown in sugar media containing calcium carbonate. Oxidation of dextrose to gluconic acid occurred in cultures of *Dermatium pullulans*. A. G. Pollard.

New substances produced by action of moulds. N. Wijkman (Annalen, 1931, **485**, 61—73).—Two new acids are produced by growth of *Penicillium* *glaucum* on sucrose media, and may be separated by fractional crystallisation from alcohol. *Glauconic acid* 1, $C_{18}H_{20}O_7$, m. p. 202°, titrates with alkali in the cold between a di- and tri-basic acid, and in the warm as a tetrabasic acid; it is considered, therefore, to contain one or more lactone rings. It is unaffected by methyl-alcoholic hydrogen chloride, and is converted by diazomethane into oily unidentified products. It gives *mono-acetyl*, m. p. 175°, and *-benzoyl*, m. p. 170°, derivatives, a *nitro*-derivative, m. p. 159°, by nitration in concentrated sulphuric acid, and a *dihydro*-derivative (a tribasic acid), m. p. 235°, by reduction with zinc and acetic acid. Thermal decomposition at 215° gives an unsaturated *ketone*, $C_7H_{12}O$, b. p. 146°/720 mm. (*dinitrophenylhydrazone*, m. p. 173°; *semicarbazone*, m. p. 183°), and a *substance*, m. p. 171°, which on titration with alkali behaves similarly to the original acid, is unaffected by bromine, methylating agents, or acetic anhydride, and is reduced to a tribasic acid by zinc and acetic acid. The ketone absorbs two atoms of bromine, but rather more than two atoms of hydrogen, and is oxidised by alkaline permanganate to propionic acid. *Glauconic acid* 2, $C_{18}H_{20}O_6$, behaves as a tetrabasic acid when titrated with alkali in the warm, can be distilled undecomposed in a high vacuum, and does not react with acetic anhydride and pyridine.

H. A. Piggott.

Determination of enzyme yield in fungus cultures. Z. I. Kertesz (J. Biol. Chem., 1931, **90**, 15—23).—A method is described for determining the amounts of invertase in the mycelium of a mould, and in the medium in which it is grown. Although with cultures of *Penicillium glaucum* grown under apparently identical conditions, the total dry matter in the mycelium varies greatly, the enzyme content of the whole mould is approximately constant. When the salt content of the medium is adequate, the enzyme content of the mould increases as the sucrose content of the medium is increased, but in the absence of either potassium, phosphorus, or magnesium the enzyme content remains approximately constant with variations of sucrose concentration. In the case of normal cultures of *P. glaucum* the total enzyme content of the culture reaches a maximum in the first few days.

W. O. Kermack.

Biochemistry of micro-organisms. XIX. 6-Hydroxy-2-methylbenzoic acid, a product of the metabolism of dextrose by *Penicillium griseo-fulvum*, Dierkx. W. K. Anslow and H. Raistrick (Biochem. J., 1931, **25**, 39—44).—This compound was obtained by ether extraction of the medium. The medium on treatment with bromine water yields a precipitate consisting principally of 2 : 4 : 6-tribromo-*m*-cresol.

S. S. Zilva.

Formation of citric acid by moulds. IV. Conversion of saccharic acid. K. Bernhauer, H. Siebenäuger, and H. Tschinkel (Biochem. Z., 1931, **230**, 466—474).—The formation of saccharic acid as an intermediate in the conversion, during fermentation with *Aspergillus niger*, of dextrose and gluconic acid into citric acid (claimed by Challenger, Subramaniam, and Walker, A., 1927, 228) is investigated, using 21 strains of the mould, including the culture employed by these authors. In no case could either the formation of saccharic acid from dextrose or gluconic acid or the formation of citric from saccharic acid or its salts be detected. With some of the cultures, a precipitate was obtained with Denigès' reagent, but this was shown to be mercuric oxalate.

P. W. Clutterbuck.

Characterisation of the group of *Aspergillus niger*. III. Comparison of different strains. K. Bernhauer, F. Duda, and H. Siebenäuger (Biochem. Z., 1931, **230**, 475—483).—The formation of citric and gluconic acids by a number of strains of *A. niger* is determined. Acid-forming power is increased by removing the ripe spores and storing dry or by subculturing on a natural acid medium (lemon juice). Good acid-forming strains spore relatively late, sporing being inhibited by the high acidity. The best yield of citric acid represents 76·3% on the original sugar or 96·8% on the sugar fermented and of gluconic acid 66·53% on the sugar used or 96·42% of theory (cf. A., 1929, 472).

P. W. Clutterbuck.

Relationships between organic acids elaborated by *Aspergillus niger*. Molliard (Compt. rend., 1931, **192**, 313—315).—When *A. niger* is cultivated on media containing sucrose and only small amounts of ammonium nitrate and other essential salts, gluconic acid formation is rapid during 10 days, does not alter appreciably during the next 50 days, and then diminishes; the amount of citric acid produced increases steadily during 90 days. At the end of the experiment, reducing sugar (formed by inversion of the sucrose) is present, but oxalic acid is not. The citric acid is not produced from the gluconic acid. The use of sodium gluconate or citrate in the media causes formation of oxalic acid, which is considered to be a definite excretion. Gluconic and citric acids are oxidation products of the sugar; these can be metabolised by the fungus.

H. Burton.

Enzymic conversion of guanidine into urea. N. N. Ivanov and A. N. Avetissova (Biochem. Z., 1931, **231**, 67—78).—In the presence of dextrose *Aspergillus niger* grown on peptone produces an enzyme *guanidase* which decomposes guanidine into urea and ammonia, the guanidine serving as a nitrogen source for the growth of the mould. The decomposition is quantitative if a dried preparation of the dead micro-organism containing guanidase (but no urease) is used. Guanidase is destroyed by boiling with water.

W. McCartney.

Production of kojic acid by *Aspergillus flavus*. O. E. May, A. J. Moyer, P. A. Wells, and H. T. Herrick (J. Amer. Chem. Soc., 1931, **53**, 774—782).—The effects of the amount and source of nutrient nitrogen, temperature, sugar concentration, and depth of the culture medium on the production of kojic acid from dextrose by *A. flavus* are investigated. Ammonium nitrate is the most satisfactory source of nitrogen and the best yields of acid are obtained at 30—35°. Maximum amounts of the acid are obtained most conveniently from 20% dextrose solutions after 12 days; the yield of acid is about 55% (on the sugar consumed).

H. Burton.

Kojic acid: formation from trioses by *Aspergillus oryzæ*. F. Challenger, L. Klein, and T. K. Walker (J.C.S., 1931, 16—23).—The authors agree with Corbellini and Gregorini (A., 1930, 959) that the formation of kojic acid from pentoses and hexoses is best explained by assuming a preliminary breakdown to the triose followed directly by condensation to kojic acid, and not passing through dextrose. *A. oryzæ* grows on 5% dihydroxyacetone and 5% glycerol in the standard medium (A., 1929, 1042), producing kojic acid, in the case of dihydroxyacetone in 30% yield, and grows also on 2% calcium gluconate, 2% potassium hydrogen saccharate, 2% potassium citrate containing 0·5% citric acid, 1% glyceric acid, and 5% trimethylene glycol without producing kojic acid. On rhamnose it yields minute quantities of a substance, probably kojic acid.

A. niger grows on 5% glycerol, but the product of its action varies with the strain of mould, one strain producing glyceraldehyde, and another oxalic acid. No citric acid was identified in either case, and the second strain gave oxalic acid from arabinose.

G. Discombe.

Allantoinase in fungi. A. Brunel (Compt. rend., 1931, 192, 442—444).—The presence of allantoinase in a fungus extract is demonstrated by incubating at 40° with a 0·2% solution of allantoin containing 0·125% of ammonium hydrogen carbonate. The allantoic acid formed is hydrolysed by hydrochloric acid at 100° to glyoxylic acid and urea, the former being recognised by a colour reaction and the latter isolated as xanthylcarbamide. Alternatively, allantoic acid is isolated as its silver salt. A list of fungi containing allantoinase is given. P. G. Marshall.

Specific polysaccharides from fungi. H. D. Kesten, D. H. Cook, E. Mott, and J. W. Jobling (J. Exp. Med., 1930, 52, 813—822).—When tested by direct precipitation against the corresponding antisera the polysaccharides from the yeast-like fungi exhibit only partial specificity. Cross-precipitin reactions are frequent. A relatively high degree of specific precipitability can, however, be demonstrated by absorption of precipitin on the intact mycotic bodies. Chemical Abstracts.

Effects of carbon dioxide, hydrogen sulphide, methane, and of the absence of oxygen on water organisms. J. Nikitinsky and F. K. Mudrezowa-Wyss (Zentr. Bakt. Par., 1930, II, 81, 167—198).—Carbon dioxide and hydrogen sulphide are toxic to the majority of water organisms. Methane and hydrogen are non-poisonous. Many organisms can withstand the absence of oxygen for periods up to 20—30 days. The resistance of organisms to carbon dioxide and hydrogen sulphide and (to a smaller extent) to the absence of oxygen is closely related to their saprophytic activities. Such resistance decreases with the complexity of the organism, *i.e.*, in the order crustaceæ < rotifers < protozoa.

A. G. Pollard.

Wall structure and mineralisation in coralline algæ. L. G. M. Baasbecking and E. W. Galliher (J. Physical Chem., 1931, 35, 467—479).—The cell walls of *Corallina officinalis*, L., and *Amphirora dorbigniana*, Dec., are non-cellulosic but contain pectin-like substances. They are birefringent in longitudinal section and isotropic in cross-section. *X*-Ray examination [by O. L. Sponsler] of decalcified and natural *Amphirora* showed that calcite is the only mineral deposited by the living coralline. The deposition of magnesium is a secondary phenomena.

L. S. Theobald.

Fermentation of cellulose at high temperatures. P. A. Tetrault (Zentr. Bakt. Par., 1930, II, 81, 28—45).—Organisms capable of fermenting cellulose at 60° are described and a new type of organism from pigmented cultures is separated. Dextrose is the principal product. A. G. Pollard.

Biological oxidation of carbohydrate solutions. I. Oxidation of sucrose and ammonia in sectional percolating filters. S. H. Jenkins (Biochem. J., 1931, 25, 147—160).—A mixture of 0·033% sucrose, 0·033% acetic acid, and 0·033% lactic acid, when fed at a suitable rate of flow, is readily oxidised by a mixed microbial population. A biological film is built up and the organic matter is oxidised even if the C : N ratio of the nutrient solution is 80—1. Acid and invert-sugar are formed if a 0·1% sucrose solution is allowed to trickle through a mature portion of the sectional filter. The maximum drop observed is from p_H 7·0 to 6·6. Oxidation of ammonia proceeds best in the lower sections where the concentration of sugar is least. It is not inhibited by concentrations of sugar up to 0·05—0·06%. Both nitrites and nitrates are produced by micro-organisms in the presence of 3—4 parts per 100,000 parts of nitrogen as ammonia. Each section rapidly shows nitrifying activity when placed in a suitable part of the filter. S. S. Zilva.

Biological oxidations in the succinic acid series. J. H. Quastel and A. H. M. Wheatley (Biochem. J., 1931, 25, 117—128).—The biological oxidation of fumaric acid proceeds largely if not entirely through *l*-malic acid. Fumarate and *l*-malate inhibit the oxidation of succinate in presence of various bacteria and of muscle- and brain-tissue. Strict aërobes, *B. alkaligenes*, *B. subtilis*, and *M. lysodeikticus*, and muscle-tissue attack *l*-aspartate in a different manner from the facultative anaërobes *B. coli*, *B. proteus*, and *B. acidi lactici*. The latter oxidise the acid through fumaric and *l*-malic acids. Malonate inhibits the oxidation of succinate not only by bacteria, but also by muscle- and brain-tissue, the degree of inhibition being greatest with these tissues. The wide variation with different cells in the degrees of inhibition by malonate is associated with difference between velocities of oxidation of fumarate and those of succinate. Neither malonate nor oxalate inhibits the velocity of oxidation of *p*-phenylenediamine by brain-tissue. S. S. Zilva.

Hydrogenase: a bacterial enzyme activating molecular hydrogen. I. Properties. II. Reduction of sulphate to sulphide by molecular hydrogen. M. Stephenson and L. H. Stickland (Biochem. J., 1931, 25, 205—214, 215—220).—I. The enzyme has been found in some strains isolated from a mixed culture from river mud as well as in *B. coli*, *B. acidi lactici*, etc. It is not present in baker's yeast or in sheep's-heart muscle. At a hydrogen pressure of one atmosphere the enzyme is saturated. The maximum velocity of the action of the enzyme is at $p_{\rm H}$ 6·0. The shape of the $p_{\rm H}$–velocity curve suggests the possibility of the existence of two hydrogenases. In its reactions to cyanide and urethane hydrogenase behaves as a typical dehydrogenase. By means of the enzyme hydrogen reduces molecular oxygen, methylene-blue, nitrate, and fumarate. *B. coli* in a buffer solution at $p_{\rm H}$ 6·5 does not take up molecular hydrogen.

II. An organism from river mud reduced sulphate quantitatively to sulphide by means of molecular hydrogen. It also reduced sulphite and thiosulphate to sulphide. The curve obtained by plotting the hydrogen-ion concentration against the velocity of reduction of methylene-blue is of the same character as that obtained with other organisms containing hydrogenase. The optimum reaction for the activation of hydrogen in this case is $p_{\rm H}$ 6·3.

S. S. Zilva.

Mechanism of the degradation of citric acid by *B. pyocyaneus* (*Pseudomonas pyocyanea*). II. Action of *B. pyocyaneus* on succinic acid. T. K. Walker, V. Subramaniam, H. B. Stent, and J. Butterworth (Biochem. J., 1931, 25, 129—137; cf. Butterworth and Walker, A., 1929, 1493; Challenger, Subramaniam, and Walker, A., 1927, 228).—The addition of small quantities of acetone to cultures of *B. pyocyaneus* on calcium acetate media is followed by the formation of lactic acid. The action of this organism on succinates leads to the formation of *dl*-malic acid and *l*-malic acid. When the organism acts on *dl*-malic acid dextrorotatory activity is developed in the medium. *l*-Malic acid is therefore not formed by resolution, but by the action of *B. pyocyaneus* on ammonium succinate. *dl*-Malic acid most probably arises by direct hydroxylation of succinic acid and the *l*-malic acid by dehydrogenation of succinic acid to fumaric acid followed by asymmetric addition of water to the latter.

S. S. Zilva.

Oxidation–reduction potentials of pneumococcus cultures. II. Effect of catalase. L. F. Hewitt (Biochem. J., 1931, 25, 169—176).—Some of the characteristic differences in behaviour between pneumococci and catalase-forming bacteria disappear when catalase preparations are added to the former. The electrode potential of aërobic pneumococci cultures remains at a low level after the addition of the enzyme. In aërated cultures the potential falls to a much lower level and growth is much more luxuriant when it is added. Bacteria differ in oxidation–reduction behaviour in respects other than that of peroxide formation. Bacterial peroxide and hydrogen peroxide possess many properties in common. There are indications of an acceleration of reduction effect by killed aërobic bacteria (*M. lysodeikticus*) and of a poisoning effect by erythrocytes. S. S. Zilva.

Dissociation of the diphtheria anatoxin–antitoxin complex and recovery of the anatoxin. G. Ramon, R. Legroux, and M. Schoen (Compt. rend., 1931, 192, 512—514; cf. A., 1924, i, 1149).—A solution of anatoxin is obtained when the anatoxin–antitoxin flocculate, after washing in isotonic saline, is dissolved in slightly acidulated water at $p_{\rm H}$ 6—6·5.

C. C. N. Vass.

Purification and concentration of diphtheria toxin and anatoxin. S. Schmidt, A. Hansen, and K. A. Kjaer (Ann. Inst. Pasteur, 1931, 46, 202—221).—The methods utilised include adsorption by alumina or charcoal and elution by sodium hydrogen phosphate solution, precipitation by alcohol or acetone, precipitation by acids, dialysis through cellophane membranes, and evaporation in a vacuum.

F. O. Howitt.

Lipins of tubercle bacilli. XXII. Carbohydrates of the purified wax. E. G. Roberts and R. J. Anderson. **XXIII. Separation of the lipoid fractions from the timothy bacillus.** E. Chargaff, M. C. Pangborn, and R. J. Anderson (J. Biol. Chem., 1931, 90, 33—43, 45—55).—XXII. From the water-soluble fraction obtained by hydrolysis with alcoholic hydrochloric acid of the purified wax (cf. A., 1929, 1342) there have been isolated *d*-arabinose, and traces of glucosamine hydrochloride and inositol. When the wax is hydrolysed by alcoholic potassium hydroxide an amorphous alcohol-insoluble polysaccharide fraction is obtained which on acid hydrolysis yields mannose, *d*-arabinose, and galactose together with unidentified reducing sugars. A barium salt containing barium (27·88%) and phosphorus (5·06%) was also obtained.

XXIII. Timothy-grass bacilli (*Mycobacterium phlei*) grown on the Long's medium have been analysed, the methods previously adopted in the case of the tubercle bacillus being followed closely. The following results were found: phosphatide 0·59%, acetone-soluble fat 2·75%, chloroform-soluble wax 4·98%, total lipins 8·37%; polysaccharide 3·90%, dried bacterial residue 87·70%. The acetone-soluble fat had saponification value 231·8, acid value 62·7, iodine value 72·3. The timothy-grass bacillus contains less lipin than does the avian or bovine strain and much less than the human strain of the tubercle bacillus, whilst the polysaccharide content is considerably greater than that of the tubercle bacillus.

W. O. Kermack.

Nucleic acid of the timothy bacillus. R. D. Coghill (J. Biol. Chem., 1931, 90, 57—63).—By extraction with 2% sodium hydroxide solution of the residue from timothy-grass bacilli after treatment with alcohol–ether and chloroform, an impure nucleic acid was obtained in a yield of about 2%, which on hydrolysis yields guanine, uracil, and cytosine, but no thymine. It contains at least 20% of pentose. It was therefore apparently a nucleic acid of the plant type, in contradistinction to the nucleic acid of the tubercle bacillus which is of the animal type.

W. O. Kermack.

Tuberculosis. I. Reaction of the connective tissues of the normal rabbit to lipins from the tubercle bacillus, strain H 37. F. R. Sabin, C. A. Doan, and C. E. Forkner. **II. Reaction of the connective tissues of the normal rabbit to a water-soluble protein and a polysaccharide from the tubercle bacillus, strain H 37; spontaneous pseudo-tuberculosis aspergillina as a complication in fraction testing.** C. A. Doan, F. R. Sabin, and C. E. Forkner (J. Exp. Med., 1930, 52, Suppl. 3, 3—72, 73—87). Chemical Abstracts.

Fermentation in a heterogeneous and discontinuous medium. A. Demolon and G. Barbier (Compt. rend., 1931, **192**, 514—515).—Comparison of the rates of fermentation due to motile and non-motile organisms shows that in sand containing 6—8% of water, diffusion and migration readily occur; in an argillaceous medium similar results are observed only when the medium contains 17·0—21·5% of water. C. C. N. Vass.

Gas–metal electrode potentials in sterile culture media for bacteria. E. M. Boyd and G. B. Reed (Canad. J. Res., 1931, **4**, 54—68).—A method is described for determining the gas–metal electrode potential of media and for the preparation of a standard buffered medium for the purpose. The passage of air through sterile media caused an increase in potential at platinum and gold electrodes. Hydrogen produced a decreased potential at a platinum electrode and little change at a gold electrode. Carbon dioxide and nitrogen produced little change in either case. The observed potentials were in agreement with those recorded for electrodes immersed in potassium chloride solutions. Mercury electrodes reacted with the media (cf. French and Kahlenberg, A., 1928, 1330). A. G. Pollard.

Conditions of antibacterial and antitoxic action of the bile. I. A. Clementi. **II.** A. Clementi and A. Castelli (Arch. Sci. biol., 1929, **13**, 211—220, 221—234; Chem. Zentr., 1930, ii, 3588).—Retardation of coagulation in lactic fermentation of milk in presence of bile salts is due to combination of the latter with the acid. Bile and sodium taurocholate retard the development of *Bacillus coli*. A. A. Eldridge.

Action of intestinal disinfectants. F. Eichholtz and R. Wigand (Arch. exp. Path. Pharm., 1931, **159**, 81—92).—Trichlorocresol and tetrachloro-derivatives of certain hydrocarbons were highly active as intestinal disinfectants in the sense of reducing the number of living bacteria and yeasts in the fæces of various animals. Creolin and guaiacol were less active, whilst a number of the accepted intestinal disinfectants appeared to be without effect. W. O. Kermack.

Bactericidal action of sodium salicylate. M. Garofeanu and E. Ioan (Compt. rend. Soc. Biol., 1930, **104**, 513—514; Chem. Zentr., 1930, ii, 2663).—The growth of *B. coli*, streptococci, and staphylococci is arrested or inhibited by sodium salicylate. A. A. Eldridge.

Influence of pituitrin on the ionic excretion. L. T. Poulsson (Z. ges. exp. Med., 1930, **72**, 232—243; Chem. Zentr., 1930, ii, 2910).—After intramuscular injection of pituitrin the reaction of human urine is displaced towards alkalinity; the ammonia content falls and the total fixed base rises relatively to the sodium content. A. A. Eldridge.

Effect of pituitary preparations on the blood-lipin. E. George (Z. ges. exp. Med., 1930, **72**, 303—312; Chem. Zentr., 1930, ii, 2910).—Raab's observation (Z. ges. exp. Med., 1928, **62**, 366) of the fall in blood-lipins after injection of pituitrin was not confirmed. A. A. Eldridge.

Substance resembling anterior pituitary extract in human urine. Pregnancy reaction. M. Aron and M. Klein (Compt. rend. Soc. Biol., 1930, **103**, 702—704; Chem. Zentr., 1930, ii, 3165).—Injection of the urine of man, woman, or pregnant woman into rabbits caused thyroid changes qualitatively resembling, but less marked than, that of anterior pituitary extract. Zondek's anterior pituitary hormone differs from that which affects the thyroid. A. A. Eldridge.

Anterior pituitary hormone. W. Falta and F. Högler (Klin. Woch., 1930, **9**, 1807—1812; Chem. Zentr., 1930, ii, 2794).—"Prähormon" caused reduced basal metabolism and frequently increased specific dynamic protein action. This hormone, but not "Prolan," greatly increased growth in infantilism, although both hormones had the usual effect on sexual development. A. A. Eldridge.

Anterior pituitary hormones. II. B. Zondek (Klin. Woch., 1930, **9**, 393—396; Chem. Zentr., 1930, ii, 3049).—Normal male or female urine contains less than 110 mouse units of prolan-A. In the climacteric three stages associated with different hormone production are distinguished. Ten days after operative castration prolan-*A* appears in the urine and may be detected during a year; after *X*-ray sterilisation, in spite of amenorrhœa, it is first observed after 1—1·5 years, and remains for 1·5 years. A. A. Eldridge.

Relation between the anterior pituitary body and the gonads. III. Fractionation and dilution of ovary-stimulating extract. M. Hill and A. S. Parkes (Proc. Roy. Soc., 1931, B, **107**, 455—463).—Saline suspensions of pituitary tissue, "alkaline" extracts of ox anterior lobes, and extracts of urine of pregnancy all give (*a*) follicular luteinisation and (*b*) follicular maturation and ovulation, in one or more of the species of animals used, viz., mice, rats, rabbits, and ferrets, the relative intensities of the two effects varying with different extracts and in different animals. Dilution experiments with urine extracts gave no evidence that the two reactions are due to the same hormone at different concentrations. By alcohol fractionation of urine extracts, partial separation of luteinising and maturating actions appears to be effected, the 50% alcohol-soluble material being predominantly luteinising, whilst the 30% alcohol-soluble fraction was mainly follicle-maturing. W. O. Kermack.

Separation of the male sexual hormone from the female hormone (menformone). E. Dingemanse, J. Freud, S. Kober, E. Laqueur, A. Luchs, and A. W. P. Münch (Biochem. Z., 1931, **231**, 1—5).—The male sexual hormone possesses basic properties and can be separated from the female hormone (menformone) by adding water to a concentrated benzene extract of male urine, the extract having first been mixed with alcoholic sodium hydroxide. The liquid separates into two layers, the male hormone passing into the benzene layer. Since the male hormone distils in a high vacuum at 90° separation by distillation is also possible. W. McCartney.

Male sexual hormone. J. Freud, S. E. de Jongh, E. Laqueur, and A. P. W. Münch (Klin. Woch., 1930, 9, 772—774; Chem. Zentr., 1930, ii, 3048).—By means of methods corresponding with those for the preparation of menoformone, ox testicles and male human urine afforded extracts which were active towards the combs of castrated cocks and hens and the seminal vesicles of castrated or infantile rats. A. A. Eldridge.

Action of parathyroid hormone on the magnesium content of blood. H. G. Scholtz (Arch. exp. Path. Pharm., 1931, 159, 233—235).—The administration of parathyroid extract to adult dogs results in a rise in the magnesium content of the serum, which reaches its maximum more quickly than does the rise in calcium content. W. O. Kermack.

Calcium metabolism and parathyroid hormone in various animal species. M. Thölldte (Krankheitsforsch., 1930, 6, 397—430; Chem. Zentr., 1930, ii, 2666).—Injection of parathyroid hormone into the dog, cat, or rabbit leads to a rise in serum-calcium of about the same percentage. A. A. Eldridge.

Antagonism between adrenaline and insulin. R. Cario (Klin. Woch., 1930, 9, 1623—1624; Chem. Zentr., 1930, ii, 2277).—Injection of 6% dextrose solution into the pancreatico-duodenal artery even after removal of the adrenals does not lead to rise in blood-sugar, presumably owing to increased secretion of insulin. A. A. Eldridge.

Effect of insulin on growth, nitrogen excretion, and respiratory metabolism. M. W. Goldblatt and R. W. B. Ellis (Biochem. J., 1931, 25, 221—235).—The injection of 2—50 units of insulin did not influence the growth of rats on restricted and unrestricted amounts of food. Insulin has no effect on the urinary nitrogen excretion of rats consuming an exclusively fatty diet or during starvation. Insulin hypoglycæmia in a starving human subject is associated with a marked increase in the respiratory quotient. This effect ceases when the blood-sugar recovers. Progressive fall in blood-sugar and disappearance of glycosuria may be induced in a glycosuric patient without any change in the respiratory quotient or caloric output. Insulin can increase the liver-glycogen of young dogs during starvation without any change in muscle-glycogen. This may be accompanied by marked hypoglycæmia. The attainment of blood-sugar values of vanishing proportions may be accompanied by an acute fall in respiratory quotient. S. S. Zilva.

Influence of large doses of insulin on the lipins of blood and organs. I. H. Page, L. Pasternak, and M. L. Burt (Biochem. Z., 1931, 231, 113—122).—Subcutaneous administration of large doses of insulin to rabbits causes a 30% decrease in the phosphate content of their blood-serum and less pronounced alterations in the cholesterol content of the blood and of some of the organs (kidneys, brain). The amount of fatty acids in the brain and blood and the degree of unsaturation of the fats of the brain, liver, and blood are also affected. The cholesterol content of the blood-serum of hares is increased by the administration of large doses of insulin. W. McCartney.

Action of insulin on the glycogen content of the perfused rabbit's liver. N. A. Nielsen (Biochem. Z., 1931, 230, 259—268).—By perfusion of rabbit's liver with defibrinated blood without addition of insulin, a gradual decrease of dextrose in blood and a corresponding deposition of glycogen in the liver are observed, the glycogen being distributed very unevenly. Addition of insulin ($\frac{1}{3}$ to 20 international units) brings about an increase of dextrose in the perfusing blood and a decrease of glycogen in the liver. No action is detectable using less than one third of a unit of insulin. P. W. Clutterbuck.

Initial insulin hyperglycæmia. A. von Koranyi (Deut. med. Woch., 1930, 56, 1683; Chem. Zentr., 1930, ii, 2911).—Extracts of the muscle of rabbits in hypoglycæmia (strychnine, phloridzin, or insulin) or of diabetic animals cause hyperglycæmia in rabbits. The cause of initial insulin hyperglycæmia is discussed. A. A. Eldridge.

"Insulin diabetes." P. Wichels and H. Lauber (Z. klin. Med., 1930, 114, 20—26, 27—32; Chem. Zentr., 1930, ii, 2277).—When insulin (5 units) is administered intravenously to a rabbit at 10 min. intervals, marked hyperglycæmia continues for 1 hr., the liver being free from glycogen. The effect with dogs and man is similar, but less marked. It is not due to direct action of insulin on the liver. Although increased secretion of adrenaline may be partly responsible it is not the only cause, since the hyperglycæmia is observed after removal of the adrenals or thyroid gland. A. A. Eldridge.

Inhibition of the formation of insulin by excessive administration of carbohydrate. F. Verzár and A. von Kúthy (Pflüger's Archiv, 1930, 225, 606—612; Chem. Zentr., 1930, ii, 2795).—Dogs received for a long period sufficient sucrose or dextrose to appear constantly in the urine. When the sugar diet was discontinued excretion of dextrose continued for several days, the blood-sugar being practically normal. With renewal of the sugar diet for a short time the hyperglycæmic curve was longer and flatter than normally, simulating that observed in diabetes. Hence exhaustion of the pancreas by excessive administration of sugar is possible; this may be a cause of diabetes. A. A. Eldridge.

Growth factors. W. J. Boyd, J. Latter, and W. Robson (Nature, 1931, 127, 308).—A growth-inhibiting substance extracted from the flesh of vertebrates is thermo-stable, is not a sterol, and probably contains nitrogen. L. S. Theobald.

Plant colouring matters and vitamin-*A*. E. Bürgi (Deut. med. Woch., 1930, 56, 1650—1652; Chem. Zentr., 1930, ii, 3166).—Identity of, or close relation between, chlorophyll and vitamin-*A* is indicated by experiments with phæophytin, sodium chlorophyllin, and chlorophyll free from carotene. A. A. Eldridge.

Carotene and vitamin-*A*. Conversion of carotene into vitamin-*A* by fowl. N. S. Capper, I. M. W. McKibbin, and J. H. Prentice (Biochem. J., 1931, 25, 265—274).—Chickens can be reared successfully to maturity on a synthetic vitamin-*A*-free diet to which carotene or cod-liver oil concentrate is added. The carotene is not stored in the liver as such, but is converted into vitamin-*A* (cf. Moore, A., 1929, 1343; 1930, 962). The beaks and shanks of chickens which had become colourless through the absence of carotenoids from the diet did not become more yellow when carotene was added to it. The disease known as visceral gout is curable by the administration either of carotene or of cod-liver oil. The vitamin-*A* contents of hen-liver oils are very high and the vitamin-*A* requirements of the fowl are large.

S. S. Zilva.

Vitamin-*A* and carotene. VII. Distribution of vitamin-*A* and carotene in the body of the rat. T. Moore (Biochem. J., 1931, **25**, 275—286).—An excess of carotene was found throughout the alimentary tract in albino rats fed on large quantities of red palm oil or carrot-fat for prolonged periods. The pigmented fat derived from the fæces was biologically active proportionately to its carotene content. The liver oils gave higher colorimetric values for vitamin-*A* than those characteristic for cod-liver oil concentrates. Small amounts of carotene were also found in the liver oils of rats which received the pigment up to the time of killing. This was, however, almost absent after 68 days on the deficient diet. The concentration of vitamin in the "storage" fats of the body was only about 1/100,000 of the concentration of the liver oils. Other tissues gave very weak or no reactions for the vitamin. The conversion of carotene most probably takes place in the liver. S. S. Zilva.

Spectrographic data concerning vitamin-*A* and liver oils. R. A. Morton, I. M. Heilbron, and A. Thompson (Biochem. J., 1931, **25**, 20—29).—The vitamin-*A* band at 328 mμ is free from fine structure. Nearly all cod-liver oils exhibit selective absorption in the region 260—295 mμ. The blue solutions obtained in cod-liver oils with antimony trichloride give a clear band at 328 mμ and a single sharp band at 604—608 mμ. In the case of crude cod-liver oils of high potency an additional selective absorption between 565 and 585 mμ is frequently observed in the blue solution. In the blue solutions obtained with concentrates the main band is at 620—624 mμ, but on dilution with an inactive oil to the approximate concentration of cod-liver oil it reverts to 604—608 mμ. In many cases the colour test with concentrates shows a less intense band at 582—593 mμ. Vitamin-*A* is decomposed on treatment with sodium ethoxide and concentrates yield in consequence acids characterised by a series of well-defined absorption bands with maxima near 394, 375, 350, 330, 316, 302, 282, 271, and 260 mμ. Similarly, absorbing acids which are not present as simple glycerides in the oil itself are produced by ordinary saponification.

S. S. Zilva.

Spectrographic data of natural fats and their fatty acids in relation to vitamin-*A*. A. E. Gillam, I. M. Heilbron, T. P. Hilditch, and R. A. Morton (Biochem. J., 1931, **25**, 30—38).—Fatty acids (or esters prepared therefrom) produced in the ordinary hydrolysis of vitamin-*A*-containing liver oils or of some other fatty oils from animals the liver of which contains vitamin-*A*, yield highly characteristic banded absorption spectra which are absent from the corresponding acids of vitamin-*A*-free oils.

S. S. Zilva.

Colour reactions of substances containing vitamin-*A*. N. I. Orlov (Z. Unters. Lebensm., 1930, **60**, 254—267).—The Bezssonoff reaction is unspecific and of little use. That with sulphuric acid appears to be related to the vitamin-*A* content, but it is not sufficiently sensitive and it is too evanescent for colorimetric purposes. The antimony trichloride reaction is the most useful, but it fails in the presence of pigments and other substances. The removal of these results in loss of vitamin-*A*. A solution prepared by mixing 1 c.c. of crystal-violet solution (0·040 g. in 100 c.c. of 95% alcohol), 0·6 c.c. of methylene-blue solution (0·040 g. in 100 c.c. of 95% alcohol), and 25 c.c. of 95% alcohol is used as standard. Numerous solutions of the oil of varying concentration are examined and the concentrations are plotted against the readings. A similar series of tests is carried out on the standard oil and the curves obtained are compared. The method is only approximate.

W. J. Boyd.

Colour reactions of sterols with nitric acid. O. Rosenheim and R. K. Callow (Biochem. J., 1931, **25**, 74—78).—Nitric acid or a solution of mercuric acetate in nitric acid ("mercury reagent") gives characteristic colour reactions with certain sterols. A red colour with the mercury reagent is characteristic of the $\Delta^{1:2}$ (or $\Delta^{1:13}$) linking in sterols. A greenish-blue colour is given by ergosterol in dilute solutions, whilst a yellow colour results when concentrated solutions of ergosterol are employed. The latter reaction can be used as an index of the purity of ergosterol, since oxidised or otherwise changed specimens give finally an intense green reaction. Certain liver oils and the unsaponifiable fraction from cod-liver oil which are sources of vitamin-*A* give a gentian-blue colour with the reagent. S. S. Zilva.

Chemical nature of the antixerophthalmic vitamin-*A*. H. Seel (Arch. exp. Path. Pharm., 1931, **159**, 93—110).—Highly-active preparations of vitamin-*A* have been obtained from the unsaponifiable fraction of shark-liver oil. The purified material, which is active when administered to rats in doses of 0·1—1·0 γ, is very unstable, being readily destroyed by exposure to atmospheric oxygen. This instability increases with purification. Oxidation of cholesterol with benzoyl peroxide yields oxycholesterol, possessing an apparent vitamin-*A* activity and giving a blue antimony trichloride reaction. The greater stability of the blue reaction in the case of oxycholesterol as compared with natural vitamin-*A* may be due to the presence of interfering substances associated with the natural vitamin. The ultra-violet absorption spectra of vitamin-*A* derived from a natural source and of suitably oxidised cholesterol have been determined and show distinct similarity, both possessing bands at 327 mμ and 293 mμ. W. O. Kermack.

Destructive action of finely-divided solids on vitamin-*A*. J. K. Marcus (J. Biol. Chem., 1931, **90**, 507—513).—Measurement of the antimony trichloride colour reaction shows that vitamin-*A* of cod-liver oil concentrates undergoes considerable destruction when intimately mixed with several powders and stored for some days under air or carbon dioxide. Finely-divided vegetable charcoal (" nuchar ") destroys 90% of the vitamin in 3 hrs. even if the charcoal is previously reduced. The destructive action of lactose is markedly inhibited by quinol and, to a smaller extent, by water.

A. Cohen.

Absorption and retention of vitamin-*A* in young children. J. I. Rowntree (J. Nutrition, 1930, 3, 265—287).—The antimony chloride test is not specific; biological assay methods were employed. Vitamin-*A* is not excreted in the urine; the fæcal loss is 2—12% of the intake. The vitamin-*A* of cod-liver oil and egg-yolk was equally well utilised; inconclusive results were obtained with that from carrots. Chemical Abstracts.

Antineuritic vitamin. II, III. A. G. van Veen (Rec. trav. chim., 1931, 50, 200—207, 208—220; cf. this vol., 270).—The extraction of this vitamin from rice-bran by Jansen and Donath's method (A., 1926, 644) has been investigated both by physiological effects (on birds) and by determination of the nitrogen content of the various fractions. Approximately 33% of the rice-bran (1·6% nitrogen) goes into solution on extraction, whilst acid clay absorbs most of the vitamin with only a relatively small proportion (25%) of the material precipitated with phosphotungstic acid (nitrogen, 1·6%). Only 25% of the adsorbed material is recovered by elutriation of the clay with barium hydroxide (p_H 12—13), and the remaining 75% cannot be removed even by treatment with hot concentrated alkali or with strong acids. If the alkaline extract is immediately acidified with sulphuric acid (to p_H 4) almost no destruction of the vitamin by the alkali occurs.

III. The fractions obtained by fractional precipitation of the acid clay extract with silver nitrate and barium hydroxide at various hydrogen-ion concentrations have been investigated. The fraction precipitated at p_H 4·5 affords xanthine, guanine, adenine, and hypoxanthine. Of the fraction precipitated at p_H 4·5—7, the portion not precipitated by silicotungstic acid contains histidine and uracil, and gives two unidentified picrolonates, m. p. 260° (decomp.) (nitrogen 31·7%), and m. p. 220—224° (decomp.) (nitrogen 20·4%). The third fraction precipitated at p_H 6·5—7, which is partly precipitated in fraction 2, contains guanidine and arginine, and gives a picrate, m. p. 247—250° (decomp.) (nitrogen 22·5%), a picrolonate, and an amorphous substance (nitrogen 16%). The portion not precipitated by silver nitrate and barium hydroxide contains a small quantity of monoamino-acids, betaine, choline, and an unidentified hydrochloride (nitrogen 16·3%). J. W. Baker.

Further fractionation of yeast nutrilites and their relationship to vitamin-*B* and Wildiers' "bios." R. J. Williams and E. M. Bradway (J. Amer. Chem. Soc., 1931, 53, 783—789).—The " bios " of Wildiers is not adsorbed to any marked extent on fuller's earth and it is apparently identical with that previously described (A., 1925, i, 342; 1929, 1339). No evidence is available that this bios is other than a single substance. The growth of the yeast used by Miller (Science, 1924, 59, 197) and Eastcott (A., 1928, 1056) is stimulated to a marked extent by inositol, whilst Wildiers' is not. Old process baker's yeast and yeast 578 (A., 1927, 592) require more complex growth-stimulants than Wildiers' yeast. Evidence is now brought forward to show the existence of a fourth nutrilite concerned in the growth-stimulation of yeast 578. Some of the nutrilites may be components of vitamin-*B* (cf. A., 1930, 1222).

H. Burton.

Vitamin-B_1 and -B_2 contents of yeast. E. J. Quinn, F. B. Whalen, and J. G. Hartley (J. Nutrition, 1930, 3, 257—263).—The vitamin-*B* content of various American and Canadian yeasts varied considerably, whilst the vitamin-B_2 content was uniform. The antineuritic vitamin was the limiting factor in two samples of brewer's yeast. Chemical Abstracts.

Complex nature of vitamin-*B*. II. Evidence that a third factor exists. C. H. Hunt and W. Wilder (J. Biol. Chem., 1931, 90, 279—291).—For the normal growth of the rat and for the prevention and cure of pellagra in that animal a third fraction in the vitamin-*B* complex is required which is non-adsorbable on fuller's earth and thermolabile in an alkaline medium when autoclaved for 5 hrs. at 15 lb. pressure. It is distinguished from the antineuritic fraction B_1 (*B*), which is thermolabile both in an acid and in an alkaline medium, and from the pellagra-preventive factor B_2 (*G*), which is relatively thermostable at both acid and alkaline reactions. All three factors are necessary for the normal growth of the rat. W. O. Kermack.

Effect of nitrous acid on components of the vitamin-*B* complex. H. C. Sherman and M. L. Whitsitt (J. Biol. Chem., 1931, 90, 153—160).—When either vitamin-B_1 (*B*) or -B_2 (*G*) is treated with nitrous acid by aspirating the gases generated by the action of hydrochloric acid on sodium nitrite through the solution the activity is not reduced, but when subjected to more drastic treatment by generating the nitrous acid directly in the solution, considerable reduction of potency takes place in the case of B_1 and a less marked reduction in the case of B_2. It is considered probable that B_2 itself is unaffected by nitrous oxide, but that some of the other more recently discovered but not yet completely differentiated factors may be destroyed by the treatment.

W. O. Kermack.

Esterification of phosphoric acid and phosphatase action in avitaminosis-*B*. J. Bodnár and A. Karell (Biochem. Z., 1931, 230, 233—237).—The musculature and liver of pigeons suffering from avitaminosis-*B* exhibit a power to esterify phosphoric acid 77—146% greater than that of the organs from healthy birds. No such difference, however, exists between the respective phosphatase activities.

F. O. Howitt.

New diet for the study of avitaminosis-*B*. L. Randoin and R. Lecoq (Compt. rend., 1931, 192, 444—447).—The following avitaminous diet, resembling in composition dried cows' milk, has been found suitable for pigeons: purified caseinogen 8, purified fibrin 8, ovalbumin 8, purified butter-fat 8, lard 18, purified carbohydrate 35, saline mixture (Osborne and Mendel) 5, agar-agar 8, and filter-paper 2%. Daily addition of 0·35—0·50 g. of dried brewer's yeast produces a complete diet. The above regime possesses the advantage that the rate of development of polyneuritis is not appreciably affected by the nature of the carbohydrate, whilst with those containing 66% of carbohydrate and only 4% of fat the rate of development of symptoms varies with the ease and rapidity of the intestinal absorption of the carbohydrate. P. G. Marshall.

Relation of a fat-free diet to the scaly tail condition in rats described by Burr and Burr. E. M. Hume and H. H. Smith (Biochem. J., 1931, **25**, 300—306).—The condition developed when the rats were kept on coarse wire grids with highly purified caseinogen and usually when extracts of yeast were used as a source of *B*-vitamins, and could be cured by whole dried, but not by autoclaved, yeast. The condition may be correlated with some deficiency in the yeast–vitamin complex.

S. S. Zilva.

Antiscorbutic potency of apples. II. M. F. Bracewell, F. Kidd, C. West, and S. S. Zilva. III. M. F. Bracewell, T. Wallace, and S. S. Zilva (Biochem. J., 1931, **25**, 138—143, 144—146).—II. Newton Wonder apples possess a vitamin-*C* content of the order of that possessed by Cox's Orange Pippin, whilst Lane's Prince Albert occupies an intermediate position between the latter and the much more potent Bramley's Seedling. This last variety can be frozen at −20° and kept at this temperature for 4 months without losing appreciably in antiscorbutic activity. Immature small apples of this variety gathered in July are not more active per g. than the ripe apples gathered normally. Bramley's Seedling apples stored at 3° in air for 5 months do not lose any of their antiscorbutic activity. The concentration of vitamin-*C* in the tissue of the apple increases as the skin is approached from the core, and is more than six times as great in the peel as in the flesh near the core.

III. King Edwards containing about 0·0307% N were about 1·5 times as potent antiscorbutically as apples of this variety containing about 0·0387% N. No significant disparity in the vitamin-*C* content was found between Bramley's Seedlings containing high and low quantities of nitrogen. S. S. Zilva.

Chemical nature of vitamin-*D*. E. Takamiya (J. Dept. Agric. Kyushu, 1930, **3**, 1—27).—Irradiation of various vegetable oils with ultra-violet light results in a decrease in the rates of hydrolysis by lipase, which increases with the time of exposure and with the degree of unsaturation of the oil as measured by its iodine value. The decrease in the rate of enzyme hydrolysis after irradiation is accompanied by a decrease in the iodine value, probably due to ozonide formation. Irradiation also produces an increase in the viscosity of the oils, but the non-irradiated oils which are the most viscous are also most rapidly hydrolysed by lipase. Ozonisation of the oils causes a decrease in iodine value, increase in viscosity, and a decrease in the rate of hydrolysis by lipase, and in general the effects of ozonisation and of irradiation by ultra-violet rays both of cholesterol and of unsaturated oils are strikingly similar. Ozone exerted some definite curative action on rachitic rats fed in an ozonised atmosphere and it also activated ergosterol. An excessive exposure of ergosterol to ozone diminished the activity and ultimately resulted in loss of activity. It is suggested that vitamin-*D* is the mono-ozonide of ergosterol.

W. O. Kermack.

Sterol content and antirachitic activatibility of mould mycelia. L. M. Pruess, W. H. Peterson, H. Steenbock, and E. B. Fred (J. Biol. Chem., 1931, **90**, 369—384).—Various moulds have been grown on a synthetic medium containing 4% of dextrose as the source of carbon. The yields of dry pad varied from 7·3 to 35·0% of the dextrose consumed. When the concentration of dextrose in the medium was increased to 10—20%, the yield of dry pad was more than doubled. The autoclaved, dried, and finely-ground pads of twelve moulds and also five types of mushrooms grown in the open were irradiated with ultra-violet light. When these products were tested on rats, those from eight moulds and three mushrooms showed distinct antirachitic activity in doses of 10 mg. of irradiated material per rat over a period of 7 days. The total alcohol-soluble sterol determined by the digitonin method in eleven moulds and four mushrooms varied from about 0·1 to 1·0% of the dry weight of the fungus. The amount of sterol unextracted by alcohol ranged from 0·01 to 0·40% of the dry pad. In most cases 90% or more of the alcohol-soluble sterol was present in the free state. The effect of various factors on the growth and sterol content of the moulds has been investigated.

W. O. Kermack.

Vitamin-*D*. I. Action of ozone and ultra-violet light on cholesterol and oils. II. Rickets and ozone. E. Takamiya (Bull. Agric. Chem. Soc. Japan, 1929, **5**, 71, 72—73).—Ozone activates ergosterol. Rachitic rats are cured by ozonised air without treatment with vitamin-*D* or ultra-violet rays.

Chemical Abstracts.

Antirachitic vitamin unit. Standardisation of commercial vitamin-*D* preparations. O. K. Schultz (Z. Vitamin-Kunde, 1930, 51—54, 81—83; Chem. Zentr., 1930, ii, 2799).—It is proposed that there should be produced a definite degree of rachitis which is eliminated by the preparation in a certain time. The unit is defined as the smallest quantity of an antirachitic material which within 21 days will convert + + + + rachitis in rats into — rachitis.

A. A. Eldridge.

Evaluation of vitamin-*D* preparations. M. Schieblich (Biochem. Z., 1931, **230**, 312—319).—Comparative investigation with rats of the antirachitic action of vitamin-*D* preparations shows that the curative dose is usually much greater than the protective dose (cf. A., 1929, 1111; B., 1929, 996).

P. W. Clutterbuck.

Critique of the line test for vitamin-*D*. C. E. Bills, E. M. Honeywell, A. M. Wirick, and M. Nussmeier (J. Biol. Chem., 1931, **90**, 619—636).—A review, in which it is claimed that certain graphic relations between the degree of healing and dosage may be applied to assays with greater accuracy than has hitherto been considered possible. A. Cohen.

Toxicology of the irradiation products of ergosterol. W. Heubner (Nachr. Ges. Wiss. Göttingen, 1930, 149—163; Chem. Zentr., 1930, ii, 2798).—Experiments on the effects of various preparations in high doses on rabbits, including the determination of blood-phosphate, indicate that several different active substances are present. Moreover the antirachitic potency can be diminished to a much greater extent than the toxicity by suitable treatment of a preparation. A. A. Eldridge.

Calcifying and toxic actions of large doses of irradiated ergosterol on animals. Separation of the two actions. H. Simonnet and G. Tanret (Compt. rend., 1931, **192**, 586—588; cf. A., 1930, 506, 1071).—Administration of irradiated ergosterol to rabbits in doses of 40 mg. per day causes death in 6—18 days and 8—12 days when the irradiation periods are 45 min. and 6 hrs., respectively. 20 Mg. per day of the former irradiation product are fatal in 15—25 days. The calcium content of the thoracic aorta reaches a maximum value of 23·6%. The active material is stable to oxidation and reduction. Resistance is observed in some animals which survive for many months. Survival may also be maintained by treatment on alternate days. Rabbits receiving potassium iodide at the same time as irradiated ergosterol survive much longer than controls, and show only slight calcification of the aorta. The toxic and calcifying actions may be separated by employing massive doses (0·1 and 0·2 g. per day) when death occurs in 6—8 days, whilst the calcium content of the aorta shows only a slight increase to 1—4%. A. Cohen.

Local calcification of tissue after subcutaneous injection of irradiated ergosterol. T. von Brand and F. Holtz (Z. physiol. Chem., 1931, **195**, 241—247).—Subcutaneous injection of large doses of irradiated ergosterol in soya-bean oil causes calcification at the site of injection. This is due to the specific action of a conversion product of ergosterol, namely, the " calcinosis factor " (A., 1930, 1481). H. Burton.

Calcification of the bones of rats on a diet low in ergosterol. E. M. Hume and H. H. Smith (Biochem. J., 1931, **25**, 292—299).—Rats subsisting on vitamin-*D*-free diet which were irradiated by exposure to a mercury quartz lamp, rats which were receiving ergosterol and irradiation, and rats which were receiving no irradiation but ergosterol in their diet showed about the same percentage of ash in their bones. Animals which received neither ergosterol in their diet nor irradiation had a lower ash content. All the rats used which received a fat-free diet developed the " scaly tail " condition (cf. Burr and Burr, A., 1929, 853). S. S. Zilva.

[Effect of] white phosphorus and " vitasterin " [on animals]. C. R. H. Rabil (Arch. exp. Path. Pharm., 1931, **159**, 47—53).—Experiments on mice give no support to the view that the administration of white phosphorus promotes calcification in presence of vitamin-*D*. W. O. Kermack.

Poisoning by metallic salts during vitamin-*D* feeding. H. Hoff (Med. Klin., 1930, 26, 1560—1562; Chem. Zentr., 1930, ii, 3308—3309).—Guinea-pigs receiving much vitamin-*D* were less susceptible to poisoning by basic lead carbonate or mercury succinate than normal animals. Resistance was diminished by theophylline or alcohol. A. A. Eldridge.

Spierer lens and what it reveals in cellulose and protoplasm. W. Seifriz (J. Physical Chem., 1931, **35**, 118—129).—The Spierer lens, an oil-immersion objective carrying a mirror, smaller than the lens, which reflects all the direct light coming into the objective, is described, together with the structure which it reveals of certain tissues of *Sambucus*, *Allium*, and *Apium*. Cellulose and protoplasm are seen to consist of minute rods or super-micelles, 1—2 μ in length and 0·5—0·7 μ in thickness, arranged end to end to form long, parallel striæ. L. S. Theobald.

Carbon dioxide dissolved in plant sap and its effect on respiration measurements. J. J. Willaman and W. R. Brown (Plant. Physiol., 1930, 5, 535—542).—Dissolved carbon dioxide in plant sap is determined by immersing plant material in boiling 95% alcohol and removing the gas under reduced pressure. The importance of distinguishing between carbon dioxide formation and the release of dissolved carbon dioxide in plant tissue is emphasised. Apples having greatest winter hardiness have the lowest output of carbon dioxide. A. G. Pollard.

Respiration of apple twigs in relation to winter hardiness. W. A. de Long, J. H. Beaumont, and J. J. Willaman (Plant. Physiol., 1930, 5, 509—534).—Carbon dioxide production from excised apple twigs is conditioned by previous temperature environment. If the previous temperature was higher a constant rate of carbon dioxide production is assumed, whereas if the previous temperature was lower there is a peak of carbon dioxide production prior to reaching the constant rate. This is ascribed in part to the liberation of carbon dioxide formed during cold storage and dissolved in the cell-sap. Hardier varieties have a lower peak production than more tender ones. Low-temperature storage of twigs without aspiration results in a slight gain in sugar content, but with aspiration there is a small decrease in sugars and an increase in starch. A. G. Pollard.

Respiration of the seeds of oil-bearing plants. A. I. Ermakov and N. N. Ivanov (Biochem. Z., 1931, **231**, 79—91).—The respiration of oil-bearing seeds (linseed, castor, almond) does not differ from that of seeds in which carbohydrate is the reserve material, and in the early stages of germination of the oil-bearing seeds the respiratory coefficient is approximately 1. During the same period there is no increase in the dry weight of the seeds and both the quantity and quality of the oil remain unaltered. Since the iodine value of the oil does not change even in the later stages of germination when its amount decreases as a result of conversion into carbohydrate, it follows that the oil does not undergo direct atmospheric oxidation. In the early stages of the germination the amount of mono- and di-saccharides present in the seeds increases as a result of enzymic hydrolysis of the polysaccharides. W. McCartney.

Function of hexuronic acid in the respiration of the cabbage leaf. A. Szent-Györgyi (J. Biol. Chem., 1931, 90, 385—393).—The oxygen uptake of finely-minced cabbage leaf decreases rapidly during the first 5 min. This decrease is correlated with the disappearance of reduced hexuronic acid (cf. A., 1929, 98) as the result of oxidation in the air. The fresh pulp reduces Folin's phenol reagent without addition of alkali, but after a short exposure to the air this reducing power, which depends on the presence of the reduced hexuronic acid, is lost. The mechanism which effects the reduction of hexuronic acid is damaged by the mincing to a greater extent than the mechanism effecting its oxidation. If the original concentration of reduced hexuronic acid is restored by addition of this substance a vigorous uptake of oxygen again takes place, which lasts until the theoretical quantity is taken up. The thermolabile catalyst is present to a large extent in the cell sap uncombined with the formed elements of the cell. By precipitation with barium acetate, which does not remove the hexoxidase from the juice, followed by salting out of the hexoxidase by ammonium sulphate, and repeated redissolution and reprecipitation, the enzyme may be obtained in a purified condition exhibiting no oxygen uptake until hexuronic acid is added to it. The enzyme in a phosphate buffer solution (p_{H} 5·9) is relatively stable, resisting the action of 1% acetic acid, sodium carbonate, or formalin for 5 min. and capable of being kept for 1 week in an ice-chest without loss of activity. It is, however, relatively sensitive to alcohol or acetone and to heat. Low concentrations of sodium cyanide (0·005% or less) have no effect on the oxidation; 0·01% slightly and 0·1% largely inhibits the activity. As small quantities of cyanide are not inhibitory, it appears that oxygen activation is not involved (cf. Dixon, A., 1927, 901; Szent-Györgyi, A., 1926, 867). The reduction of methylene-blue by hexuronic acid is not increased by the presence of hexoxidase nor is the action of this enzyme inhibited by 5% urethane or chloroform. These facts indicate that hydrogen activation is not involved. The kinetics of the oxidation of hexuronic acid in presence of hexoxidase also indicates that the mechanism involved is different from that of any other known enzyme. Hexoxidase appears to act on no substrate except hexuronic acid. Glutathione is oxidised in presence of both hexoxidase and hexuronic acid, although hexoxidase itself is without effect.

W. O. Kermack.

The benzidine reaction in potatoes. F. Yoshioka (Biochem. Z., 1931, 231, 233—238; cf. Boas, this vol., 122).—The enzyme from potatoes described by Boas is very stable towards changes in reaction, but is also very unstable towards heat. Although at 50° its activity is unaffected, at 60° it is reduced, and at 70° destroyed. It readily loses its solubility in water and is precipitated from solutions by alcohol or acetone, by half saturation with ammonium sulphate, or by complete saturation with magnesium sulphate. The precipitated insoluble material even when dried retains all the activity of the enzyme. Although it can be precipitated by kaolin it cannot be recovered from this material by elution and it cannot be adsorbed by aluminium hydroxide. Potassium cyanide, mercuric chloride, and mercuric oxycyanide inhibit its action, but nickel powder has no effect on it.

W. McCartney.

Effect of various methods of storage on the chlorophyll content of leaves. P. A. Harriman (Plant Physiol., 1930, 5, 599—606).—Losses of chlorophyll during the drying of leaves of soya bean and nasturtium were least when temperatures of 45—60° were used. At 88° the loss approximated to 70% and at 18—24° to 20—30%. Low-temperature drying was ineffective in preventing chlorophyll losses unless the leaves were actually frozen. Leaves frozen in carbon dioxide "snow" retain all their chlorophyll.

A. G. Pollard.

Effect of fertility on the carbohydrate : nitrogen relation in the soya bean. F. A. Welton and V. H. Morris (Plant Physiol., 1930, 5, 607—612).—Comparison of soya beans grown in sand cultures and soil showed that with increasing fertility the total dry matter and carbohydrate content of the stems decreased, the principal constituents affected being the easily hydrolysable carbohydrates, cellulose, and lignin. High carbohydrate contents were not associated with low proportions of nitrogen as in non-legumes. High nitrogen contents were associated with heavy nodulation of the roots. The stems of plants grown in poor soil or sand were tough and rigid and did not lodge.

A. G. Pollard.

Transport in the cotton plant. I. Transport of phosphorus, potassium, and calcium. T. G. Mason and E. J. Maskell (Ann. Bot., 1931, 45, 125—173).—Analyses are made on samples from normal plants and from a group in which a ring of bark has been removed. Two regions (upper and lower) are distinguished, depending on their situation immediately above or below the first fruiting branch. A downward movement of phosphorus by way of the bark is definitely established, whilst a similar mechanism for the transport of ash and potassium seems probable. There is no evidence of a similar transport of calcium. Although the content of all constituents of the leaves is increased in the "ringed" group, there is no evidence as to what elements are responsible for the significant increase of ash, since the increases of phosphorus, potassium, and calcium are too slight to be significant. Upward movement of phosphorus and potassium to the leaves probably occurs normally by way of the wood, whilst no evidence of such a movement of calcium has been obtained. From data obtained with two groups of plants, in which the upper and lower regions, respectively, were deprived of leaves, it is shown that upward (as well as downward) transport of phosphorus and ash may occur by way of the bark. A significant increase in the phosphorus content of the wood and bark (about 20%) occurs, on removal of the growing bolls, in both the upper and lower regions, whilst the ash content shows a similar increase in the upper region only, and calcium no significant increase in either. The effect of fertilisation in increasing the uptake of phosphorus, ash, potassium, and, to a smaller extent, calcium by the ovules and carpels lends support to the view that phosphorus and

potassium travel to the boll by way of the phloem, whilst calcium does so by way of the xylem.
P. G. Marshall.

Effect of light on the migration of nutritive material at the opening of buds. E. Michel-Durand (Compt. rend., 1931, **192**, 440—442).—Buds of *Æsculus hippocastanum* were investigated. In the dark, the total glucosides and protein-nitrogen increase during the first fortnight and diminish thereafter, whilst the soluble nitrogen increases in a regular manner. When exposed to light, the buds show a slower, but more regular, increase in both simple and complex glucosides, combined with a larger increase in protein-nitrogen particularly after the first fortnight; the increase in dry weight is also greater. Both synthetic and hydrolytic phenomena occur more rapidly in the presence of light and are related to the formation of chlorophyll.
P. G. Marshall.

Diffusion of certain solutes through membranes of living plant cells and its bearing on certain problems of solute movement in the plant. F. C. Steward (Protoplasma, 1930, **11**, 521—557).—Apparatus for examination of the diffusion of fluids through cell membranes is described. Plasmolysis markedly affects the extent of diffusion through membranes. Rates of diffusion may be expressed mathematically in terms of membrane thickness. The coefficient of diffusion of dextrose through tissue is approximately 0·01 of that in water. The value for potassium phosphate is still lower. The general problem of solute movement in tissues is discussed.
A. G. Pollard.

Permeability of the cell wall. I. Membrane of the reed-grass (*Arundo phragmites* var. *pseudodonax*, Asch and Graeb); its use as osmometer and its permeability to sucrose. V. Úlehla (Protoplasma, 1930, **11**, 574—600).—Manipulative details are recorded. The membrane is less permeable to water, sucrose, and salt solutions than is collodion. Theoretical values were obtained for sucrose solutions, but with salt solutions some anomalous osmosis occurs.
A. G. Pollard.

Penetration of α-naphthol-2-sulphonate-indophenol, *o*-chlorophenol-indophenol, and *o*-cresol-indophenol into *Valonia*. M. M. Brooks (Proc. Nat. Acad. Sci., 1931, **17**, 1—3).—The penetration of 0·000048—0·000384M solutions of the dyes in sea-water into the sap of *Valonia* at 25° has been studied. The results indicate that the sulphonic acid group inhibits penetration. The non-sulphonated dyes are absorbed in a colourless form, and although penetration is more rapid from acid than from alkaline solutions, the equilibrium concentration is independent of the external p_H, and varies with the nature of the buffer salts used; borates appear to interfere with the process.
H. F. Gillbe.

Thermodynamics of ion concentration by living cells. F. P. Zscheile (Protoplasma, 1930, **11**, 481—496).—Free energy changes during the accumulation of ions by plant-cells are calculated from published data and values for different plants compared. The radioactive energy of potassium is inadequate to supply the energy necessary for its accumulation in plants.
A. G. Pollard.

Effect of nitrate fertiliser on stomatal behaviour. A. L. Pleasants (J. Elisha Mitchell Sci. Soc., 1930, **46**, 95—116).—Nitrates made the stomata of bean plants more responsive to light; the rate of loss of water was diminished.
Chemical Abstracts.

Negative correlation between nitrate-nitrogen in the juice of beet leaves and the weight of the leaves. D. E. Frear (J. Agric. Res., 1931, **42**, 53—56).—A negative correlation exists between the nitrate content of the leaf-juice and the weight of the leaves of beet. Juice from the midrib contains more nitrate than that from other parts of the leaf. Leaves for examination should be of approximately the same size, since the proportional weight of midrib to whole leaf decreases with increasing leaf size.
A. G. Pollard.

Nature of drought-resistance in crop plants. R. Newton and W. M. Martin (Canad. J. Res., 1930, **3**, 336—427).—The bound water in a solution of a hydrophilic colloid, such as plant press-juice, is determined by cryoscopic observation of the apparent sucrose content when sufficient of the sugar has been added to give a molar solution in the total water. This value is not independent of the concentration of sucrose employed, and is, in the case of gum-arabic, considerably greater with molar solutions of sucrose than with similar solutions of dextrose. The bound water in sols of gelatin, agar, albumin, blood-fibrin, dextrin, and gum-arabic increases with the concentration of the solute, but in all cases except the last the rate of increase diminishes with increasing concentration.

By fine grinding and pressing at a pressure not exceeding 3—4 atm. at 0° a fluid is obtained which is substantially identical with the original tissue fluids. The concentration of solute in this juice is conveniently determined in a sugar refractometer by the application of a suitable factor; in the cereal group this factor is 0·83. Hydrolysis of added sucrose by the enzymes of the press-juice increases with rise of temperature and time of storage, but is insufficient in amount to vitiate bound water determinations.

Dialysis of the press-juice in a collodion sac leads, with the progressive removal of the salts, to a partial coagulation of the colloids. This coagulation is not entirely prevented by dialysing against 1% sodium chloride solution. During the course of the dialysis the gold number tends to rise, whilst changes in the bound water correspond generally with changes in p_H. In both fresh and dialysed juice, the reaction of which has been modified by the addition of lactic acid or sodium carbonate, the bound water shows a minimum value at p_H 7—8.

The concentration, osmotic pressure, bound water, and properties of the colloidal constituents of the leaf press-juice of various crop plants have been determined. It is considered, in the case of the wheats and grasses, that the bound water content gives a satisfactory indication of adaptation to drought-resistance.

The loss of moisture from cactus segments is in extreme cases but 5% in 148 days. The rate of loss is not widely different at 0, 25, and 50% R.H., but is greater than in an atmosphere of 75 or 100% humidity.

The leaves of the grasses, *Phleum pratense* and *Agropyron tenerum*, lose water rapidly at zero humidity, almost complete desiccation occurring in 4 days. The course of the dehydration is similar notwithstanding great differences of the two plants in resistance to drought. T. H. MORTON.

Selective cultivation of beetroot and the fixity of the composition of the vegetation as postulated by Liebig. E. SAILLARD (Compt. rend., 1931, **192**, 504—507).—An examination of the analytical data obtained over a period of 30 years discloses no constant ratio between the sugar content and the basic oxides or phosphorus content. The amounts of the bases combined with the organic acids decrease as the sugar concentrations increase. Selective cultivation has produced varieties which require a decreased mineral content to elaborate the same amount of sugar. C. C. N. VASS.

Maintenance of moisture equilibrium and nutrition of plants at and below the wilting percentage. J. F. BREAZEALE (Arizona Agric. Exp. Sta. Tech. Bull., 1930, No. 29, 137—177).—There is a continuous film of moisture between the soil and the growing plant at all moisture contents above the wilting point; this is the point of equilibrium between the suction force of the plant and the adhesive forces of the soil. The available moisture of a soil is that held by the soil with a force less than the suction force of the plant (approximately 5 atmospheres). Water may pass from soil to plant-root or *vice versa*, according to the relative magnitude of the forces involved. Plants take up nutrient ions as a result of their electrical charges, and the actual passage of water into the plant-root is not essential to the process. The intake of nutrients by plants may continue at the wilting point. Plants may absorb moisture from a particular soil area, and transport and exude this in drier areas in which nutrients may be dissolved and absorbed by the plant.
A. G. POLLARD.

Formation of oil in plants. S. IVANOV (Chem. Rund. Mitteleuropa Balkan, 1930, 7, No. 1, 115—117, No. 2, 9—11; Chem. Zentr., 1930, ii, 2662—2663).—Similarity of the oils produced indicates that the process of formation is similar in a genus of plants. Plants of northern habitat always contain a larger proportion of unsaturated glycerides than those of southern habitat; oils containing oleic acid, however, are unaffected by climate. A. A. ELDRIDGE.

Glyceride structure of laurel fats. G. COLLIN (Biochem. J., 1931, **25**, 95—100).—Laurel-kernel fat contains 43·1% of lauric, 6·2% of palmitic, 32·3% of oleic, and 18·4% of linoleic acid. There is, however, present in it 36% of saturated glycerides, of which trilaurin is the predominant constituent. Apparently the unsaturated unlike the saturated acids do not link up with each other, but distribute themselves among the residual palmitic and lauric acids. The laurel-kernel fat, therefore, does not resemble other kernel fats. Laurel-pulp fat, on the other hand, resembles analogous specimens of other origin.
S. S. ZILVA.

Starch in plant seeds. A MÜHLDORF (Bot. Arch., 1930, **30**, 167—194; Chem. Zentr., 1930, ii, 2791).—The starch grain of sphagnum seed consists of two components; one, deposited chiefly in the outer layer, may probably be regarded as analogous to amylopectin, and the other, present within the grain, to amylose. A. A. ELDRIDGE.

Iodometric determination of reducing sugars in the apple. H. K. ARCHBOLD and E. M. WIDDOWSON (Biochem. J., 1931, **25**, 101—116).—Dextrose is quantitatively oxidised to gluconic acid by alkaline iodine in 2 hrs. at 1° and some oxidation of lævulose also occurs. In mixtures of dextrose and lævulose the amount of iodine reduced per g. of lævulose increases from 0·013 to 0·017 g. as the latter to the former increases from 1/1 to 5/1, and then decreases slowly as this ratio is further increased. The value 0·017 can be used for determination of lævulose and dextrose in apples by combination of the iodometric and copper reduction methods. The treatment of extracts of mature apples with basic lead acetate and subsequent deleading with disodium phosphate or potassium oxalate removes oxidisable material other than sugar under certain conditions.
S. S. ZILVA.

Gums. II. Tragacanthin—the soluble constituent of gum-tragacanth. A. G. NORMAN (Biochem. J., 1931, **25**, 200—204).—Tragacanthin may be separated by ordinary filtration in extreme dilution. Uronic acid units constitute about one half of the molecule. Arabinose was the only sugar found. A portion of the arabinose is possibly united to the uronic acid to form a resistant nucleus and the residue is attached by a glucosidic linking and is therefore easily removable. S. S. ZILVA.

Catechin of the cacao bean. W. B. ADAM, F. HARDY, and M. NIERENSTEIN (J. Amer. Chem. Soc., 1931, **53**, 727—728).—*l*-Acacatechin is present in cacao beans from various sources to the extent of about 0·8%. H. BURTON.

Algin from *Laminaria*. H. COLIN and P. RICARD (Bull. Soc. Chim. biol., 1930, **12**, 1392—1400).—The solution obtained by the hydrolysis of algin with water under pressure or sulphuric acid does not contain any appreciable amount of reducing sugars. From this liquid, a barium salt having approximately the composition indicated by the formula $(C_6H_9O_7)_2Ba$ was isolated. The authors conclude that algin is a glucoside containing glycuronic acid as part of the molecule, and that the reducing action of the hydrolysis product is due to the formation of this acid. B. LEVIN.

Rye mucilage. E. BERLINER and R. RÜTER (Z. ges. Mühlenwesen, 1930, 7, 52—57; Chem. Zentr., 1930, ii, 1790).—A 10% aqueous suspension of the flour at 27° is shaken at 5 min. intervals for 30 min.; 3 c.c. of 15% sodium tungstate solution are added, and concentrated sulphuric acid until thymol-blue is reddened. Enzymic activity may be inhibited by addition of these substances at first. The filtrate is treated with 6 vols. of methyl alcohol; the precipitate of mucilage still contains N×5·7=6·7%, traces of reducing sugar, α_D before inversion −77° or −90°, after inversion +77°, η^{20} 7 in 0·2% solution. It is non-fermentable; hydrolysis affords non-fermentable reducing sugars (11% of dry weight). Various strains of rye were examined. The viscosity of the clarified aqueous extract affords the best indication of the mucilage content, and may serve for evaluation of the quality of rye flour. A. A. ELDRIDGE.

Chemical composition of pollen. E. ELSER and J. GANZMÜLLER (Z. physiol. Chem., 1931, **194**, 21—32).—Methods are described for the determination of moisture, sugar, fat, protein, total ash and its constituents, and enzymes in pollen. Analytical data are presented for the alder, pine, and hazel, and the results are discussed in relation to the nutritional value of the pollen to the honey-bee. A. COHEN.

Membranes of spores and pollen. II. *Lycopodium clavatum*, L. III. *Picea orientalis*, *Pinus sylvestris*, L., and *Corylus avellana*, L. F. ZETZSCHE and H. VICARI. **IV. Fossil sporopollens from Tasmanite and Moscow lignite.** F. ZETZSCHE, H. VICARI, and G. SCHÄRER (Helv. Chim. Acta, 1931, **14**, 58—62, 62—67, 67—78).—II. Digestion of the spore membrane of *L. clavatum* with 75% sulphuric acid at the ordinary temperature gives a cellulose-free sporonin (cf. A., 1928, 524) which has, however, undergone some change. Prolonged treatment of the membrane with 85% phosphoric acid at about 30° removes the cellulose completely; subsequent treatment of the residue with hydrofluoric acid affords sporonin, probably $C_{90}H_{142}O_{27}$ (cf. *loc. cit.*), which is nearly ash-free. Boiling acetic anhydride converts this into an *acetylsporonin*, $C_{90}H_{127}O_{12}(OAc)_{15}$, hydrolysed by 0·1*N*-alcoholic potassium hydroxide to the original substance. Acetylation of the acetylsporonin in presence of zinc chloride at 70—80° causes degradation of part of the substance to resinous material; the insoluble residue contains 35·4% Ac.

III. Successive treatment of the pollens from *P. orientalis*, *P. sylvestris*, and *C. avellana* with potassium hydroxide, 85% phosphoric acid, and hydrofluoric acid affords *substances* of the probable formulæ $C_{90}H_{146}O_{25}$, $C_{90}H_{131}O_{11}(OH)_{13}$, and $C_{90}H_{138}O_{22}$, respectively, resembling sporonin.

IV. Details are given for the extraction of *tasmanin*, $C_{90}H_{134}O_{15}(OH)_2$, and *bothrodendrin*, $C_{90}H_{111}O_{12}(OH)_9$, from Tasmanite and Moscow lignite, respectively.

H. BURTON.

Phytochemical studies of Oregon plants. I. H. M. BURLAGE (J. Amer. Pharm. Assoc., 1931, **20**, 33—40).—*Artemisia heterophylla*, Nutt. ("Golden-rod sage"): the leaves and tops of this herb (7 samples) on steam-distillation gave 0·77—1·72% of oil having d^{20} 0·9187—0·9639, $[\alpha]_D^{20}$ −0·91° to +39·95°, n_D^{20} 1·4196—1·4994, acid value 2·75—12·63, saponif. value 23·36—51·97, acetyl value 40·44—201·43, ester value 20·34—39·34, free acids 4·0—21·0%, phenols 4·0—8·0%, aldehydes and ketones 0—4·0%. *Heracleum lanatum*: distillation of the fruits (3 samples) yielded 0·26%—0·57% of oil having d^{20} 0·8640—0·8698, $[\alpha]_D^{20}$ −0·07° to +0·93°, n_D^{20} 1·4268—1·4290, soluble in 1·2 vols. of 80% alcohol, acid value 2·40—5·30, saponif. value 249·70—266·90, acetyl value 33·20—48·00, ester value 244·40—263·50, free acids 1·0—5·0%, phenols 1·0—2·0%, aldehydes and ketones 1·0—2·0%. Constants of oils of the same genus are given for comparison. *Melissa officinalis*, L. (Lemon mint): steam-distillation yielded 0·13% of oil having d^{20} 0·9632, $[\alpha]_D^{20}$ −10° 6′, n_D^{20} 1·4999, acid value 9·20, saponif. value 34·41, acetyl value 43·30, ester value 25·13, free acids 2·0%, phenols 4·0%, aldehydes and ketones 17·0%; it was insoluble in 20 parts of 80% alcohol. *Micromeria douglasii*, Benth. (Tea vine): distillation of the fresh herb gave 0·25% of oil having d^{20} 0·9217, $[\alpha]_D^{20}$ −21° 3′, n_D^{20} 1·4572, acid value 6·06, saponif. value 27·01, acetyl value 55·54, ester value 20·95, solubility in 80% alcohol 1 : 10. Chemical investigations of the whole plants of the above species are also recorded. E. H. SHARPLES.

Anthocyans in [grape] hybrids. E. PARISI and I. COSMO (Ital. Agric., 1930, No. 5, 10 pp.; Chem. Zentr., 1930, ii, 2971—2972)—The anthocyans of European and American grapes and their hybrids, when isolated by Willstätter's method, give similar red solutions, but differentiation may be accomplished by means of ferric chloride. The aqueous hydrochloric acid extract is shaken with amyl alcohol, and the red alcoholic solution is shaken with water containing a trace of ferric chloride. American grapes give a dark blue precipitate at the interface, the violet colour of the amyl alcohol vanishing after a few hours. German grapes give no precipitate, and the solution long remains coloured. With hybrids the amyl alcohol remains reddish-violet and the characteristic precipitate appears. A. A. ELDRIDGE.

Anthocyanins in the etiolated shoots of buckwheat and wheat. S. JONESCO (Compt. rend., 1931, **192**, 438—440).—The chromogen obtained from etiolated shoots of buckwheat is a yellow powder which yields galactose on hydrolysis. When boiled in alcoholic solution for 5—10 min. with 20% hydrochloric acid, it gives rise to the red anthocyanin. The chromogen from etiolated wheat shoots reduces ammoniacal silver nitrate and Fehling's solution and yields arabinose on hydrolysis. It can be transformed into the pigment by oxidation with a mixture of barium peroxide and manganese dioxide, but not by boiling with alcoholic hydrochloric acid.

P. G. MARSHALL.

Biochemistry of the colouring matter of tomatoes. H. VON EULER, P. KARRER, E. VON KRAUSS, and O. WALKER (Helv. Chim. Acta, 1931, **14**, 154—162).—When green tomatoes are allowed to ripen at 20—21°, the normal ripening process (formation of red colouring matter) occurs. At 30°, ripening is accompanied by an orange-yellow pigmentation, and the colouring matter consists mainly of flavones or flavonols together with small amounts of carotene and xanthophyll. Lycopene formation is probably an enzymic process taking place at an optimum temperature below 30° (the enzyme is thermolabile at this temperature). The colouring matter of "Golden Queen" tomatoes does not contain lycopene. Light appears to have no function in the formation of lycopene. H. BURTON.

***Leonurus sibericus*, L. I. Leonurine.** S. KUBOTA and S. NAKASHIMA (Folia Pharmacol. Japon., 1930, **11**, No. 2, 153—158).—The plant contains about 0·05% of the alkaloid *leonurine*, $C_{13}H_{19}O_4N_4$, m.p. 238°, soluble in amyl alcohol. CHEMICAL ABSTRACTS.

Source of error in determination of amide-nitrogen in plant extracts. H. B. Vickery and G. W. Pucher (J. Biol. Chem., 1931, **90**, 179—188).—When the amide-nitrogen in extracts of fresh tobacco leaf which contains a large amount of nitrate-nitrogen is determined by hydrolysis in presence of excess of hydrochloric acid and measurement of the ammonia formed, a result is obtained which is too large on account of the reduction of nitrate to ammonia by some unknown substance present in the leaf. This substance largely disappears during curing of the leaf. Octyl alcohol is found to have the same effect. A second error in the determination of amide-nitrogen occurs as the result of the oxidation of the ammonia by the mixture of hydrochloric acid and nitric acids. Under the conditions proposed by Sachsse (J. pr. Chem., 1873, **6**, 118) these two actions almost exactly counterbalance and approximately accurate results may be obtained. When no hydrochloric acid and only sulphuric acid is used in the hydrolysis, more latitude is allowable both in the concentration of acid and in the time of boiling. It is suggested that 2*N*-sulphuric acid should be employed and that hydrolysis should be continued for 6 hrs.

W. O. Kermack.

Proteins of Indian foodstuffs. III. Globulins of Bengal Gram (*Cicer arietinum*, Linn.) and Horse Gram (*Dolichos biflorus*). N. Narayana (J. Indian Inst. Sci., 1930, **13a**, 153—158; cf. Sundaram and others, A., 1930, 260).—The arginine content of Bengal Gram protein was considerably higher than that of other Indian pulses. The two proteins examined contained sufficient proportions of arginine, tyrosine, and lysine, but were deficient in cystine and tryptophan. A. G. Pollard.

Hydrogen cyanide in the *Leguminosæ*. P. Guérin (Bull. Soc. Chim. biol., 1930, **12**, 1338—1354). A review. B. Levin.

Enzymes of tobacco. C. Neuberg and M. Kobel (Biochem. Z., 1930, **229**, 455—463).—Neither the enzymes (amylase, invertase, phosphatase, pectase, glycolase, keto-aldehyde mutase) nor the carbohydrates (pectin) of tobacco leaves are damaged or otherwise appreciably affected when these are rapidly dried in a current of air heated at temperatures not exceeding 100°. W. McCartney.

Lignin as a possible factor in lodging of cereals. J. Davidson and M. Phillips (Science, 1930, **72**, 401—402).—Wheat grown on a plot heavily fertilised with sodium nitrate showed characteristic lodging close to the " milk " stage of the grain. The silica and ash contents of the straw were lower than those of the control, but, contrary to expectations, the lignin content was markedly higher. A high lignin content thus appears to favour lodging by making the straw brittle. L. S. Theobald.

Magnesium content of certain foods. Joachimoglu and G. Panopoulos (Med. Welt, 1929, **3**, 1538; Chem. Zentr., 1930, ii, 1789).—Olives and raisins are particularly rich in magnesium. The following magnesium contents ($MgCl_2$%) are recorded : milk 0·0428, wholemeal flour 0·1248, mutton 0·0129, olive 0·1132, currants 0·0764—0·2145, white wine 0·0037. The magnesium resides chiefly in the skin of the grape. A. A. Eldridge.

Toxic action. I. Swelling and shrinkage of plant tissue in solutions of toxic substances. W. Stiles (Protoplasma, 1930, **11**, 349—381).—The rate of swelling of tissues of potato tuber in toxic solutions is best examined by direct weighing of the liquid intake. Two types of toxic action may occur, viz., that characterised from the commencement of the test by a continuous reduction in the rate of swelling as compared with that in distilled water, and that in which there occurs an initial increase in the rate of swelling, followed by a decline. Mercury cyanide, copper sulphate, quinine hydrochloride, and chloroform have the former effect, whilst the latter is produced by sulphuric and osmic acids, mercuric chloride, and primary aliphatic alcohols. No acceleration of the rate of intake of water was observed in red-beet tissue immersed in mercuric chloride. The order of toxicity of the substances named was quinine hydrochloride > mercuric chloride > chloroform > copper sulphate > ethyl alcohol. A. G. Pollard.

Toxic effects of iodine and nickel on buckwheat grown in solution cultures. M. Cotton (Bull. Torrey Bot. Club, 1930, **57**, 127—140).—Iodine (1·27 in 10^6) caused depression of growth; 40 parts in 10^6 killed the plants. Nickel was highly toxic at concentrations of 5·87 in 10^6.

Chemical Abstracts.

Microscopy and microchemistry of common indigenous fruits. A. Niethammer (Planta [Z. wiss. Biol.], 1930, **12**, 399—413).—Calcium oxalate crystals are commonly found in unripe fruits. These gradually dissolve as the fruit ripens. The acetaldehyde content of the fruit increases during the ripening process. The nature and distribution of organic acids in the fruits are examined. A. G. Pollard.

Increased permeability of barley due to acetylene. F. F. Nord and J. Weichherz (Protoplasma, 1930, **11**, 440—446).—The permeability of barley grain to methylene-blue is increased by the presence of acetylene. A. G. Pollard.

Spike disease of *Dodonæa viscosa*. B. N. Sastri and N. Narayana (J. Indian Inst. Sci., 1930, **13a**, 147—152).—The nitrate, nitrite, ammonia, and amide contents of diseased tissues of *D. viscosa* were higher than those of corresponding healthy tissue. The diseased tissues were characterised by a tendency to accumulate sugars and starch and by a deficiency of calcium (cf. Rao and Sreenivasaya, A., 1929, 1204). A. G. Pollard.

Association of biochemical products with cellulose esters. J. Loiseleur and L. Velluz (Compt. rend., 1931, **192**, 159—160; cf. this vol., 167).—Membranes containing a protein and a cellulose derivative can be prepared by mixing a solution of the protein in a suitable amount of anhydrous formic acid with one of cellulose acetate in a mixture (10 : 7) of acetone and methyl alcohol, the methyl alcohol preferably containing 10—40% of formaldehyde. C. A. Silberrad.

Determination of oxygen consumption of a single cell. R. B. Howland and A. Bernstein

(J. Gen. Physiol., 1931, **14**, 339—348).—An improved apparatus which gives consistent results under constant conditions is described. The oxygen consumption of a single *Actinosphærium eichhornii* is 0·00113 mm.^{3} per hr., and that of a single *Paramecium caudatum* 0·00049 mm.^{3} P. G. Marshall.

Determination of oxygen in sea-water and fresh water. M. Nicloux (Bull. Soc. Chim. biol., 1930, **12**, 1326—1337).—The method previously described for sea-water (A., 1930, 1143) has also been applied to fresh water. B. Levin.

Determination of carbon dioxide by Van Slyke's method. F. Mainzer (Biochem. Z., 1930, **229**, 311—314).—In Van Slyke and Neill's method (A., 1924, ii, 872) for the determination of carbon dioxide in urine loss of the gas by dissolution in the paraffin and by diffusion is avoided if the paraffin is first saturated with carbon dioxide at the same pressure as that maintained over the urine during the measurement and if the temperature is reduced to 5°. If the measuring vessel of Van Slyke's apparatus is replaced by one of a type described by the author, volumes up to 6·0 c.c. can be measured, although the accuracy of measurements in excess of 2·0 c.c. decreases in proportion to the volume measured. W. McCartney.

Determination of dextrose by electrometric titration: application to blood-sugar. L. Maricq (Bull. Soc. Chim. biol., 1930, **12**, 1366—1381).—Dextrose may be determined by utilising the method for the electrometric titration of iodomercurates (cf. A., 1929, 1259) under the following optimum conditions. To 5 c.c. of a dextrose solution containing 0·2 g. per litre are added water (10 c.c.), 1 c.c. of *N*-sodium hydroxide, and 5 c.c. of a reagent prepared by adding about 6 g. of mercuric iodide to a solution of 4·150 g. of potassium iodide in 100 c.c. of water. The mixture is heated on the water-bath for 5 min., cooled, diluted with 30 c.c. of water, and then acidified with 2 c.c. of *N*-nitric acid. It is then titrated electrometrically with mercuric chloride. Blood-sugar may be determined as follows. To 1 c.c. of blood in 7 c.c. of water are added 1 c.c. of 10% sodium tungstate solution and 1 c.c. of 0·66*N*-sulphuric acid. The mixture is shaken, filtered, and 2 c.c. of the filtrate are added to 13 c.c. of water, 1 c.c. of *N*-sodium hydroxide solution, and 5 c.c. of the reagent prepared as before, but diluted five times. The mixture is shaken, heated for 5 min. on the water-bath, cooled, acidified with 2 c.c. of *N*-nitric acid, and titrated as before. B. Levin.

Volumetric determination of sugars by the mercurimetric method. A. Ionesco-Matiu and M. Vitner (Bull. Soc. Chim. biol., 1930, **12**, 1414—1422).—The authors have applied the method of determination of mercury to the volumetric determination of sugars (cf. A., 1928, 1230; B., 1929, 698). The method is based on the reduction of mercuric iodide to mercury by the sugar in alkaline solution, separation of the mercury by centrifuging, dissolving in a mixture of nitric and sulphuric acids, and determining the mercury as in the method previously described. The method is satisfactory for the determination of dextrose, lactose, maltose, and for sugar in urine and blood. B. Levin.

Fate of lævulose in the animal organism. I. Determination of lævulose by the diphenylamine method. W. W. Oppel (Biochem. Z., 1930, **229**, 85—99).—Lævulose, in amounts from 0·085 to 0·438 mg., can be determined by heating at 100° for 20 min. 1 c.c. of a solution mixed with 0·1 c.c. of a 20% alcoholic solution of diphenylamine and 1 c.c. of 25% hydrochloric acid, extracting the cooled liquid with 2—2·5 c.c. of *iso*amyl alcohol, diluting the extract to 30 c.c. with ethyl alcohol, and comparing the colour of the liquid so obtained with that produced by a simultaneously prepared and approximately equally concentrated solution containing a known weight of lævulose. The error of the method varies from 3 to 10%. W. McCartney.

[Analysis.] XII. [A. Extraction apparatus for liquids. B. Determination of bromine in urine. C. Micro-determination of ammonia and urea by the urease method.] L. Pincussen (Biochem. Z., 1930, **229**, 233—237). A. A description is given of an apparatus for the continuous ether extraction of liquids. B. Filtered urine (5—10 c.c.) is treated with 6—12 drops of concentrated sodium hydroxide solution and evaporated to dryness at 100°. The residue is ignited at red heat in a nickel crucible, cooled, and dissolved in water. After filtration into a distilling flask the solution is made strongly acid with concentrated sulphuric acid, potassium hydrogen sulphate (20 c.c. of 10% solution) is added, potassium permanganate solution (2%) is run in drop by drop until a permanent red colour appears, and, for 1·5 hrs., air is then drawn through the flask into two bottles containing potassium iodide (10—20 c.c. of 2% solution). The contents of the bottles are titrated with 0·01*N*-sodium thiosulphate solution, starch (1% solution) being used as indicator. C. The substances are determined by the method described in the author's "Mikromethodik," 5th Ed., 1929, except that the removal of the ammonia from the solution is facilitated by increasing to saturation its sodium chloride content. This saturation has no effect on the determination of urea. W. McCartney.

Micro-determination of iodine in organic materials [blood and urine.] T. von Fellenberg [with C. Burckhardt] (Mitt. Lebensm. Hyg., 1930, **21**, 183—188; Chem. Zentr., 1930, ii, 1893).—Oxalated blood (10 c.c.) is evaporated with saturated potassium carbonate solution (1 c.c.) and the residue is carbonised in a muffle furnace just below red heat or in a closed tube; after extraction with water it is again ignited. Potassium nitrate is not employed to facilitate ashing. On addition of 50 γ of iodine to slaughterhouse blood containing 1·50—1·37 γ, 41·2—44 γ was found; on addition of a like amount to urine containing 2·45—2·37 γ of iodine 44·6—46·6 γ was found. A. A. Eldridge.