BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

JANUARY, 1928.

General, Physical, and Inorganic Chemistry.

True and apparent width of spectral lines. P. H. van Cittert and H. C. Burger (Physica, 1927, 7, 149—156).—If *s* is the apparent width of a spectral line in a Fabry–Perot interferometer, *a* the apparent width for monochromatic light, and *b* the actual width, for $b > 0·42a$, $s^2 = a + 2·15b^2$; for $0·46a > b < 2a$, $s = 0·80a + 0·81b$. Also, $a = \varepsilon\lambda^2 2\pi d t^{\frac{1}{2}}$ for $\varepsilon = 1 - t$, *t* being the reflexion coefficient of the silver layer.

Chemical Abstracts.

Continuous spectra in hydrogen. G. Herzberg (Physikal. Z., 1927, 28, 727—728).—The continuous limit of the Balmer series, hitherto observed in emission only in solar prominences etc., has been produced in the laboratory with the aid of the electrodeless ring discharge. The continuous spectrum observed by Stark with canal rays is not the continuous limit in question. The work of Oldenburg (A., 1927, 177) on the ordinary hydrogen continuum and the many-lined spectrum is in general confirmed. Various hypotheses for the origin of the continuum have been suggested (cf. Schüler and Wolf, A., 1926, 213; Blackett and Franck, A., 1925, ii, 1097), but these are regarded as erroneous. The emission of the continuous spectrum is in some way connected with the decomposition of the H_2^+ ion, possibly as follows, $H_2^+ + H_2 = H_3^+ + H$ (Dorsch and Kallmann, A., 1927, 1001).

R. A. Morton.

Secondary spectrum of hydrogen and other spectra. H. Deslandres (Compt. rend., 1927, 185, 905—909).—The author's simple relationship between the number of atoms in a molecule and the frequency of the most intense radiation of each of the groups of bands emitted by the molecule (A., 1925, ii, 1114) is applied to results recently obtained for the intense radiations of the secondary spectrum of hydrogen. These radiations are due to H_3 molecules rather than to groups of three H_2 molecules, since the latter cannot exist at the high temperatures concerned and, moreover, have been identified with weaker radiations of the same spectrum. Similarly, the effect of a diatomic molecule (probably oxygen) is detectable in the ultra-violet band spectrum of water vapour. The universal constant $d(=1062·5)$ in the formula is also intimately connected with the principal bands of the absorption spectra of oxygen and the light gases, with the emission spectra of nitrogen, carbon, carbon dioxide, and cosmic bodies, and with many line spectra.

J. Grant.

Structure of the O II spectrum. C. Mihul (Compt. rend., 1927, 185, 937—939).—The terms of the O II spectrum derived from the normal electronic configuration of the O III spectrum are made up of systems *a* of quadruplets and of doublets corresponding with the O III multiplet ^3P, and of two systems *a'* of doublets corresponding with the O III terms ^1D and ^1S, respectively. A list of new terms and their combinations is given, thus completing the groups of the terms of the doublet system *a'*, corresponding with the $3p$ and $3d$ orbits of the emissive electron. The results are confirmed by the Zeeman effect.

J. Grant.

Arc and spark spectra of scandium (Sc I and Sc II). H. N. Russell and W. F. Meggers (U.S. Bur. Standards Sci. Paper 558, 1927, 22, 329—373).—The arc and spark spectra have been analysed and spectral term combinations have been assigned to 353 lines of Sc I and 142 of Sc II. Nearly all the observed lines in both spectra have been thus classified. In the spark spectrum (Sc II), which is the simplest, the terms with lowest energy content are ^3D, ^1D, arising from the electron configuration $3d\,.\,4s$, and these and other terms combine with spectral terms associated with the configurations $3d\,.\,4p$, $3d\,.\,4d$, and $3d\,.\,5s$. The ionisation potential of the Sc^+ atom is calculated to be 12·8 volts. The arc spectrum (Sc I) is much more complex. In this case, the lowest-energy term, representing the normal state of the scandium atom, is ^2D, originating with the three-electron configuration $3d\,.\,4s\,.\,4s$. This term and a $^4F'$ term arising from $3d\,.\,3d\,.\,4s$ begin two series from which an ionisation potential of 6·7 volts is calculated for the neutral scandium atom. Energy-level diagrams and tables are given for both spectra, and it is shown that in each case all details are in complete agreement with Hund's theory, which derives one or more specific spectral terms from each possible configuration of the electrons not in completed groups.

G. A. Elliott.

Analysis of the copper spectrum. II. Complex separations and quadruplet relations. W. M. Hicks (Phil. Mag., 1927, [vii], 4, 1161—1227).—Previous work on the copper spectrum (A., 1926, 766) is extended. An examination of the inverse *D*-lines indicates the possibility that these and the line at 5105 Å. with the frequency separation 2042 may not, as generally supposed, belong to the doublet system. Evidence is adduced for the existence of quadruplet systems depending on *d* terms with separations 2042, 1412, 894 and with these completely in accord with Landé's separation rules. The quadruplet systems are discussed in detail.

A. E. Mitchell.

Reversed spectra of metals produced by explosion under increased pressure. M. Fukuda (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, 6, 1—47).—Fine wires or strips of copper, silver, gold, mercury, calcium, zinc, cadmium, thallium, and tin were exploded in an enclosure under pressures of 1 and 8 atm. In general, the widths of the absorption and emission lines were found to be increased with the pressure. Forbidden lines were found in emission and absorption, their intensity increasing with the pressure. The characters of the lines obtained in explosion under two pressures are tabulated. The appearance of the lines could be correlated with the series classification of the ordinary type, but no satisfactory agreement was found between the theoretical classification of the copper, gold, and tin multiplets except in a few cases with copper. C. J. Smithells.

Arc spectrum of bismuth. G. R. Toshniwal (Phil. Mag., 1927, [vii], 4, 774—787).—The spectrum of bismuth has been examined in the heavy-arc and in the under-water spark. 183 lines in the region 1900—3550 Å. have been measured. The results are in general agreement with those of other observers, but include 57 lines not previously reported. The structure of the spectrum, from the point of view of theories of complicated spectra, is discussed, and it is shown that owing to the large atomic number of bismuth terms arising from the same level are widely separated; this increases the difficulty of interpretation. A. E. Mitchell.

Classical theories of absorption and refraction of X-rays. F. K. Richtmyer (Phil. Mag., 1927, [vii], 4, 1296—1302).—Although the relation between the index of refraction and atomic absorption coefficient of X-rays which may be developed by the classical method agrees in order of magnitude with the experimental data, the latter is too scanty to permit of an exact verification, and it seems quite probable that the relation applies to scattering rather than to fluorescent absorption. The equations of classical optics also lead to equations for scattering. R. Cuthill.

Vacuum spectrograph and its use in the long X-ray region. J. Shearer (Phil. Mag., 1927, [vii], 4, 745—753).—A description is given of an X-ray spectrograph employing a common vacuum in the X-ray tube and spectrograph, which permits of the rotation through known angles of the crystal and photographic film from outside the spectrograph while it is evacuated. Thus the difficulties, inherent in work with long X-rays, of absorption in the window between the spectrograph and the X-ray tube, of absorption in the air between the slit and the crystal and between the crystal and the photographic plate, and of the absorption in the covering over the photographic plate or film are obviated. The wave-length of the Ni $L\alpha$ line determined with this instrument is 14·5720 Å., which is in disagreement with the value of 14·528 Å. given by Thoræus. A determination of the $2d$ spacing of sucrose gave the value 21·1519 whilst that reported by Stenström is 21·141 Å. A. E. Mitchell.

X-Ray spectra of long wave-length. T. H. Osgood (Physical Rev., 1927, [ii], 30, 567—573).—A photographic method of obtaining X-ray spectra of wave-length greater than 20 Å. is described. About 15 lines have been measured between 40 and 200 Å., but as it is not yet possible to obtain a pure spectrum of any one element, the interpretation of the lines is uncertain. A. A. Eldridge.

L X-Ray absorption edges of tin, indium, cadmium, silver, palladium, rhodium, and ruthenium. G. D. Van Dyke and G. A. Lindsay (Physical Rev., 1927, [ii], 30, 562—566).—Values of the wave-length, ν/R, and $(\nu/R)^{\frac{1}{2}}$ for the L-absorption limits of the above elements are tabulated, together with energy level values. A. A. Eldridge.

Spectra of tin and their Zeeman effects. J. B. Green and R. A. Loring (Physical Rev., 1927, [ii], 30, 574—591).—The spectra of tin in the neutral state and in two stages of ionisation have been classified. The spectrum of neutral tin has five low levels, ${}^3P_{0,1,2}$, ${}^1D_2'$, ${}^1S_0'$, due to the configuration $5_2 5_2$. The configuration $5_2 6_1$ yields ${}^3P_{0,1,2}'$ and ${}^1P_1'$. The configuration $5_2 5_3$ yields 12 terms, of which the lowest four are definitely established. The ionisation potential of Sn I calculated from the value of the ${}^2p{}^3P_0$ term is $7{\cdot}37 \pm 0{\cdot}05$ volts, and the resonance potential computed from the resonance line 2863 Å. is 4·30 volts. The spectrum of Sn II is a doublet spectrum like that of In I. Several series are noted, including lines due to abnormal states, the electrons having the configuration $5_1 5_2 5_2$. The ionisation potential of Sn II is 14·5 volts, and the resonance potential 6·5 volts. The spectrum of Sn III consists of singlets and triplets, like that of Cd I. The ionisation potential is calculated to be about 30 volts, and the resonance potential 6·81 volts. A. A. Eldridge.

Zeeman effect in the band spectra of AgH, AlH, ZnH, and MgH. W. W. Watson and B. Perkins, jun. (Physical Rev., 1927, [ii], 30, 592—597).—The AgH bands exhibit no Zeeman effect. With AlH bands, only the first lines in each branch show an effect, in quantitative agreement with Van Vleck's predictions. With ZnH bands, the wide doublets found by Hulthén for the Q and R lines are shown to be quadruplets. With magnesium hydride bands, all the lines show broadening with a field of 10,000 gauss. There is no evidence of the existence of satellites splitting off from the main lines under the influence of the magnetic field. A. A. Eldridge.

Stark effect for the spectra of silver, copper, and gold. Y. Fujioka and S. Nakamura (Astrophys. J., 1927, 65, 201—213).—For silver the Stark effect of the doublet diffuse series lines was observed up to $2p-7d$. These and known data are discussed, and the components are classified as forbidden combinations. For copper, the effect was observed up to $2p-6d$; none of the $2p-mp$ combinations was observed. For gold, the effect was observed only for the $2p-4d$ lines. A. A. Eldridge.

Multiple ionisation in X-ray levels. H. R. Robinson (Phil. Mag., 1927, [vii], 4, 763—774).—A general discussion of work on X-ray measurement and multiple ionisation effects in X-ray levels. A. E. Mitchell.

Thermionic work function of tungsten. C. Davisson and L. H. Germer (Physical Rev., 1927, [ii], **30**, 634—638).—Corrected values are obtained; the conduction electrons within the filament do not possess normal thermal energies.

A. A. Eldridge.

Properties of atomic hydrogen. J. Kaplan (Physical Rev., 1927, [ii], **30**, 639—643).—Atomic hydrogen was passed from a discharge-tube into a 3-litre glass bulb, its presence being indicated by glowing thoria. The glow persisted for 3 sec. after interruption of the discharge, and white action spots on the glass for 6 sec. after interruption. Possibly atomic hydrogen can exist for 10 sec.

A. A. Eldridge.

Active nitrogen. IV. Independence of the afterglow and the chemical properties of active nitrogen. E. J. B. Willey (J.C.S., 1927, 2831—2842; cf. A., 1926, 893; 1927, 431, 635).—Four methods are described by which it is shown that chemically active nitrogen which exhibits no visible luminosity may be prepared. "Active" nitrogen has probably a metastable diatomic or acetylenic molecule, since, when it reacts with other substances, it gives rise to compounds which, on hydrolysis, liberate ammonia. Substances of this type are produced in the few reactions of ordinary inert nitrogen, so that the two cannot be very different in structure.

M. S. Burr.

Electrodeless discharge through gases. (Sir) J. J. Thomson (Phil. Mag., 1927, [vii], **4**, 1128—1160).—The theory of the electrodeless discharge, produced when a vessel containing gas at a low pressure is placed inside a solenoid through which rapidly alternating currents are passed, is discussed. It is shown that the discharge requires a maximum magnetic force inside the solenoid depending on the nature of the gas, its pressure, the frequency of the currents, and the size of the vessel. The force is infinite when the pressure is either infinite or zero, and is a maximum when the pressure is such that $\lambda p=c$, where λ is the free path of the electron in the gas, p the frequency of the alternating current, and c the electron velocity when its energy is that required for ionisation of the gas. Thus it follows that there is a critical pressure when the discharge passes most easily. It is shown also that in the electrodeless discharge very heavy currents may pass through the gas without producing visible luminosity. The effects produced on the discharge by placing certain solids at the centre of the ring discharge are discussed.

A. E. Mitchell.

Spectroscopic determination of e/m. W. V. Houston (Physical Rev., 1927, [ii], **30**, 608—613).—The wave-lengths of the hydrogen lines at 6563 and 4861 Å., respectively, measured with reference to the helium line 5015·6750 Å. are 6562·7110±0·0018, 6562·8473±0·0009; 4861·2800±0·0013, 4861·3578±0·0022, and those of the ionised helium line 4686 are 4685·7030±0·0012, 4685·8030±0·0026. The Rydberg constant for hydrogen is thence computed as 109677·759±0·008, and that for helium 109722·403±0·004. The ratio e/m is evaluated as 1·7606±0·0010±10^7 *E.M.U.* per g.

A. A. Eldridge.

Diffraction of cathode rays by thin films of platinum. G. P. Thomson (Nature, 1927, **120**, 802).—Previous work on celluloid (A., 1927, 605) has been extended to platinum, as well as to gold and aluminium.

A. A. Eldridge.

Duration of the existence of doubly-charged positive ions in gases and their detection. L. B. Loeb (Proc. Nat. Acad. Sci., 1927, **13**, 703—707).—Theoretical. It is concluded that the experimental evidence for the existence of doubly-charged positive gas ions is not conclusive.

W. E. Downey.

Ionisation by collision. L. G. H. Huxley (Phil. Mag., 1927, [vii], **4**, 899—902).—A reply to Taylor's criticisms (A., 1927, 1001).

C. J. Smithells.

Atomic structure and the magnetic properties of co-ordination compounds. II. L. C. Jackson (Phil. Mag., 1927, [vii], **4**, 1070—1080).—The previous discussion on uninuclear co-ordination compounds (A., 1926, 773) has been extended to the multinuclear co-ordination compounds. It is concluded that the scheme proposed by Cabrera is better able to account for the magnetic properties of co-ordination compounds than those of Welo and Baudisch or of Bose.

A. E. Mitchell.

Preparation of radiothorium. D. K. Yovanovitch (Arh. Hemiju, 1927, **1**, 89—94).—A preparation extremely rich in radiothorium is obtained by repeated precipitation with concentrated hydrochloric acid from concentrated solutions of mesothorium-1. This preparation is freed from traces of barium, mesothorium-1, and radium by fractional crystallisation.

R. Truszkowski.

Behaviour of small quantities of radon at low temperatures and low pressures. A. F. Kovarik (Phil. Mag., 1927, [vii], **4**, 1262—1275).—The vapour pressure, P, of radon has been measured between 79° and 114° Abs., and found to be connected with the temperature, T, by the expression $\log P=-968{\cdot}479/T+0{\cdot}3021\log T+1{\cdot}158$. Considerable irregularities were, however, observed, suggesting that the product of condensation may be in the form both of small frozen drops and of a monatomic layer on the cooled surface. The volatilisation temperature of small amounts of radon condensed in a glass tube is apparently either 116° or 121° Abs.

R. Cuthill.

Effect of radon on the solubility of lead uranate. A. Holmes (Phil. Mag., 1927, [vii], **4**, 1242).—A misinterpretation by Bailey (A., 1927, 928) of the author's previous statements (A., 1926, 654) is corrected.

A. E. Mitchell.

Efficiency of β-recoil of thorium-*B*. K. Donat and K. Philipp (Physikal. Z., 1927, **28**, 737).—Barton (A., 1926, 553) found the efficiency of β-ray recoil of radium-*C* from radium-*B* to be not more than 6%, and only 2% with a perfectly clean surface; Muszkat (Phil. Mag., 1920, [vi], **39**, 690) found much higher values. Thorium-*B* has certain advantages as a test-substance for this problem, and investigation shows the efficiency to be between 2% and 6·5%. Gurney (A., 1926, 990), however, has shown that the primary β-particles from thorium-*B* have smaller velocities than those from radium-*B*; thus the β-recoil should show a smaller efficiency. The present work is therefore not completely in agreement with that of Barton. The discrepancy may be due to reflexion of recoil atoms from the collecting surface.

R. A. Morton.

Half-period of radium-*E*. L. F. Curtiss (Physical Rev., 1927, [ii], **30**, 539—542).—An extension of previous work (A., 1926, 771). The mean value given by new preparations is 4·975 days.

A. A. Eldridge.

Radioactivity of potassium. G. Hevesy (Nature, 1927, **120**, 838—839).—In order to ascertain which of the isotopes of potassium is responsible for the emission of β-rays, 1 litre of the metal was submitted to ideal distillation, the distance between the hot and cold surfaces being less than 1 cm. The at. wt. of the residual fraction was reported by Hönigschmid to be 0·005 (±1) unit greater than the normal value. Using Hofmann's vacuum electrometer method, the difference between the feeble radioactivities of the heavy fraction and ordinary potassium (as chloride) was determined as 4·2±0·7%. This result is in accord with the at. wt. determination if the radioactivity is assumed to be due to the isotope of at. wt. 41. It is concluded that this isotope is mainly, if not solely, responsible for the observed radioactivity of potassium. Cæsium, a pure element, does not exhibit radioactivity, whilst if the radioactivity of rubidium (85, 87) is due to the heavier isotope, the greater activity of rubidium is quantitatively accounted for. Holmes and Lawson's value (A., 1926, 554) of $1 \cdot 5 \times 10^{12}$ years as the half-value period of potassium now requires correction to their alternative value, $7 \cdot 5 \times 10^{10}$ years (A., 1927, 86), since before the consolidation of the earth's crust about 2% of the potassium isotope 41 has disintegrated. If it is assumed that the emission of β-rays effects an alteration in the nuclear charge, the transformation product will be a calcium isotope of at. wt. 41; the maximum amount of this which has accumulated in potassium minerals during the whole of geological time will thus be 0·1% of the potassium content, an amount which should permit of detection.

A. A. Eldridge.

Collision of α-particles with helium atoms. S. Ghosh (Bull. Calcutta Math. Soc., 1926, **17**, 99—104).—Of 1203 Wilson cloud photographs of α-particle tracks in helium, 44 were forked. The range of the recoil atoms was 0·94—3·2 cm., and the angle between the tracks was 1° 23′—6° 17′. It is concluded that the helium nucleus is oblate spheroidal in shape, and (since the recoil tracks were not longer than the original α-particle tracks) the recoil atoms do not exist as singly-charged particles during the whole course of their existence as ionising agents.

Chemical Abstracts.

Accurate determination of ion-formation by single α-particles and detection of new activities. G. Hoffmann (Physikal. Z., 1927, **28**, 729—731).—The formation of ions by α-particles in the neighbourhood of metal surfaces has been investigated and the statistical results of a large number of α-ionisations are expressed by plotting the number of ions formed against the number of collisions per unit time. Both by electrometric readings and by a specially designed recording instrument, the curves show sharp maxima corresponding with uranium I and uranium II, using uranium as the source of α-particles. Ion-formation is at a maximum at the saturation potential. Metal surfaces of lead, gold, aluminium, zinc, copper, and brass have been studied, and particularly interesting results obtained with a copper surface coated with zinc residues left after treating the metal with sulphuric acid. A large number of maxima are observed in the ionisation, and these may be due to α-particles of very short range or else to another phenomenon, possibly H-rays.

R. A. Morton.

Determination of the range of the α-particles of uranium I and II. G. C. Laurence (Proc. Nova Scotian Inst. Sci., 1927, **17**, 103—106).—The ranges of the α-particles of uranium I and II have been redetermined by the Wilson cloud chamber method. The value 2·72 cm. for uranium I, with a probable error of 1·5%, falls on the Geiger–Nuttall curve within the limits of experimental error and is close to Geiger and Nuttall's value of 2·67 cm. The value 3·29 cm. for uranium II, with a probable error of 1%, is, however, considerably greater than Geiger and Nuttall's value of 3·07 cm. Neither is it in agreement with that deduced from measurements of pleochroic haloes. The disintegration constant of uranium II, calculated by applying the Geiger–Nuttall relationship to the range 3·29 cm., is $2 \cdot 1 \times 10^{-11}$ per sec.

M. S. Burr.

Ionisation and stopping power of various gases for α-particles from polonium. I. G. E. Gibson and E. W. Gardiner (Physical Rev., 1927, [ii], **30**, 543—552).—Determinations of the differential ionisations and stopping powers of hydrogen, neon, nitrogen, oxygen, argon, and methyl iodide for α-particles from polonium indicate that the energy lost by the α-particle per ion is nearly independent of the speed throughout the range.

A. A. Eldridge.

Ionisation and stopping power of various gases for α-particles from polonium. II. G. E. Gibson and H. Eyring (Physical Rev., 1927, [ii], **30**, 553—561).—The molecular ionisation and stopping power of cyanogen, hydrogen cyanide, carbon monoxide, carbon dioxide, nitrous oxide, methyl iodide, oxygen, nitric oxide, and azomethane and the stopping power of hydrogen for α-particles from polonium are tabulated. Such unstable molecules as nitric oxide and azomethane give strictly additive stopping powers. Values are obtained of α for air in the straggling equation $y=e^{-(x/\alpha)^2}/\pi^{\frac{1}{2}}\alpha$ which agree with those given by other methods.

A. A. Eldridge.

Atomic disintegration. G. Stetter (Physikal. Z., 1927, **28**, 712—723).—A review. See A., 1927, 494, 495.

R. A. Morton.

Scattering of radiation from atoms. I. Waller (Phil. Mag., 1927, [vii], **4**, 1228—1237).—Mathematical.

A. E. Mitchell.

Structure of an atom of nitrogen. V. H. Collins (Chem. News, 1927, **135**, 341—346).—Speculative.

Quantum emission and stationary states. N. H. Kolkmeijer (Z. physikal. Chem., 1927, **130**,

95—99).—Mathematical. Space–time considerations are applied to certain aspects of the Bohr atom.
L. L. Bircumshaw.

Light quanta and interference. A. J. Dempster and H. F. Batho (Physical Rev., 1927, [ii], 30, 644—648).—By means of interference experiments with the helium line 4471 Å. it is shown that a single quantum of radiation obeys the classical laws of partial transmission and reflexion at a half-silvered mirror and of subsequent combination with the phase difference required by the wave-theory of light.
A. A. Eldridge.

Experimental technique of photochemistry. IV. Critical examination of certain filters for the 365 mercury line. L. T. M. Gray (J. Physical Chem., 1927, 31, 1732—1736).—Winther's filter (A., 1913, ii, 458) and the Luther–Forbes G1 filter (A., 1909, ii, 632) are both shown to be efficient filters for the mercury line 365 μμ, measurements of transmission having been made. Both filters are very sensitive to hydrogen-ion concentration, addition of acid to the latter moving the bands towards the visible end of the spectrum, and addition of alkali in the opposite direction. The Goerz glass filter has also been examined. With all three filters, however, measurements of transmission before and after use should be made.
L. S. Theobald.

Metals as semi-transparent layers in the interferometer. P. Zeeman (Z. physikal. Chem., 1927, 130, 237—240).—The behaviour of transparent layers of silver, treated in various ways, of platinum, copper, and gold, and of gold alloys is described.
L. S. Theobald.

Absorption experiments on excited molecular hydrogen. L. A. Sommer (Nature, 1927, 120, 841).—Search has been made for a metastable state of H_2, corresponding with the 2^3S state in the helium spectrum, by absorption experiments in excited molecular hydrogen. A number of intense lines located in definitely bounded regions show self-reversal, whilst other intense lines scattered over the whole spectrum do not show any absorption.
A. A. Eldridge.

Absorption of ultra-sonic waves by hydrogen and carbon dioxide. T. P. Abello (Proc. Nat. Acad. Sci., 1927, 13, 699—701).—An ultra-sonic beam, generated by a piezo-electric crystal, was passed through a mixture of air and carbon dioxide (or hydrogen). The energy of the emergent beam was measured by the pressure it exerted on a torsion vane.
W. E. Downey.

Absorption spectra of chromic acid, potassium chromate and dichromate in aqueous solution. E. Viterbi and G. Krausz (Gazzetta, 1927, 57, 690—703).—The extinction coefficients of these substances have been determined for 0·001*M*- and 0·0001*M*-solutions. The absorption of chromic acid is similar to that of potassium dichromate, and solutions of these substances obey Beer's law whilst a solution of potassium chromate does not. It is thought, therefore, that in potassium dichromate solution only a little dichromate ion is dissociated into chromate or $HCrO_4'$ ions, and that in potassium chromate solution the failure of Beer's law is due to the formation of dichromate ions.
R. W. Lunt.

Absorption spectra of various alkaloids and their salicylates and of other derivatives of salicylic acid. J. E. Purvis (J.C.S., 1927, 2715—2719; cf. A., 1926, 108, 557; 1927, 496).—The absorption spectra of the following substances have been examined and the results compared with previous data relating to other derivatives of salicylic acid: salicylamide, salicylanilide, benzene-5-azosalicylic acid, *o*-salicyloyloxybenzoic acid, the alkaloids atropine, pilocarpine, colchicine, and eserine and their salicylates. The specific absorptive capacity of compounds containing centres of different chemical type, *e.g.*, acid and basic, appears to depend not only on their chemical nature, but also on the more or less intimate chemical combination of the various centres. When the chemical combination is not so close, as in the salicylates of the alkaloids, both the acid and basic nuclei retain their own specific absorption to a considerable extent. In such compounds as salicylanilide, or benzene-5-azosalicylic acid, where, on the contrary, there is closer chemical combination of the absorbing centres, each centre is influenced by the other to a much greater extent and the specific absorption of each is not so sharply defined.
M. S. Burr.

Absorption spectra of some anthocyanidins. S. A. Schou (Helv. Chim. Acta, 1927, 10, 907—915).—The absorption spectra of pelargonidin, cyanidin, delphinidin, pæonidin, syringidin, and syringidin diglucoside (malvin) in the visible and ultra-violet regions have been investigated and the results correlated with the structure of these compounds. In addition to the absorption maximum in the visible region, all these substances exhibit a band at about 2700 Å. The absorption spectra of alkaline solutions of syringidin diglucoside are quite different from those of neutral solutions, and it is suggested that in alkaline media the substance has a quinonoid structure.
J. S. Carter.

Fluorescence in mixtures of ammonia and mercury vapour. A. C. G. Mitchell (J. Amer. Chem. Soc., 1927, 49, 2699—2703).—Mercury atoms excited by the absorption of the resonance line 2537 Å. of mercury are necessary for the production of the above fluorescence band having a maximum at 3370 Å. (cf. A., 1927, 217). Ammonia and mercury atoms in the 2^3P_1 or 2^3P_0 states are necessary for the production of the ultra-violet portion of the band. The intensity of the diffuse band varies with the ammonia and hydrogen pressure in the same manner as the rate of sensitised decomposition of ammonia, which is readily explained on the assumption that the emitter is an ammonia molecule activated by a collision of the second kind with an excited mercury atom.
S. K. Tweedy.

Ionisation of hydrogen chloride by electron impacts. H. A. Barton (Physical Rev., 1927, [ii], 30, 614—633).—By a mass-spectrographic method, the products of electron impact ionisation in hydrogen chloride were found to be: H^+, H_2^+, $(H_2O)^+$, $(HCl)^+$, and Cl_2^+. The type Cl_2^+ is considered to be a secondary product, and the hot tungsten filament in the hydrogen chloride produced molecular hydrogen in quantities sufficient to account for the hydrogen ions. When further resolved, the peak ascribed to (HCl)$^+$ was found to consist of peaks corresponding with the ions (Cl^{35})$^+$, (HCl^{35})$^+$, (Cl^{37})$^+$, (HCl^{37})$^+$. Hydrogen ions were not observed when time was given for the water vapour adsorbed by the walls of the vessel to be removed. Negative ions can be formed in hydrogen chloride without electron impacts of more than 2—3 volts energy. The results indicate the process of ionisation of hydrogen chloride by electron impacts to be $W+\text{HCl}\longrightarrow(\text{HCl})^{+}+e$, and not $W+\text{HCl}\longrightarrow\text{H}^{+}+\text{Cl}^{-}$. A. A. Eldridge.

Band spectra and dissociation of iodine monochloride. G. E. Gibson and H. C. Ramsperger (Physical Rev., 1927, [ii], **30**, 598—607).—The wave-lengths and frequencies of 33 band-heads of iodine monochloride are tabulated, and the frequencies are arranged in two series; two faint heads of a third series were also observed. The maximum of continuous absorption is about 4800 Å. The variation of intensity with wave-length accords with Franck's theory; hence iodine monochloride dissociates in light into unexcited atoms, and into an unexcited iodine atom and a chlorine atom in the 2^2P_1 state. The results require an evolution of 3·8 kg.-cal. for the reaction $\text{ICl}=0{\cdot}5\text{I}_2+0{\cdot}5\text{Cl}_2$. Thermodynamic calculations support the former process, so it is concluded that dissociation by the former process takes place with greater intensity than by the latter. A. A. Eldridge.

Excitation of the spectra of carbon monoxide by electronic impacts. O. S. Duffendack and G. W. Fox (Astrophys. J., 1927, **65**, 214—237).—The ionisation potential of carbon monoxide, as determined by the low-voltage arc, is 14·3 volts. For the neutral molecule, two sets of levels were determined as 6·0, 10·34, 11·35 and 8·0, 10·73 volts, and the band systems are correlated to transitions between these levels. Deslandres' third positive carbon bands are due to carbon monoxide. The ionised carbon monoxide molecule has three levels at 16·9, 20·0, 22·9 volts, and the negative band systems have been correlated to transitions between these levels. A. A. Eldridge.

Absolute measurement at high frequency of the dielectric constants of liquids. R. Darbord (Compt. rend., 1927, **185**, 1193—1195).—The new type of condenser described for the measurement of ε by the Wheatstone bridge method consists of a cylindrical vessel divided into an upper and a lower portion, the latter containing two shaped, horizontal armatures, one of which is fixed, whilst the other rotates inside it. If c_1 and c_2 are the capacities of the empty lower portion for the two extreme positions of the armatures, and εc_1 and εc_2 are the corresponding capacities after the addition of the liquid, then $\varepsilon=(\varepsilon c_2-\varepsilon c_1)/(c_2-c_1)$. If the armatures are fixed, the instrument must be standardised against a liquid of known ε. The apparatus avoids the influence of dispersion of the lines of force, and may be used with liquids for the vapours of which ε is nearly unity. J. Grant.

Variation of the specific inductive capacity of fluids in intense electric fields. L. Cagniard (Compt. rend., 1927, **185**, 1195—1197).—Herweg's calculations of electrical induction (Z. Physik, 1920, **3**, 36) are extended to include the effect of electrostriction, and it is shown that for an isothermal transformation there is an increase in the dielectric constant. The calculations do not apply to liquid dielectrics and do not afford evidence for or against the existence of dipoles. J. Grant.

Contraction in the formation of volatile hydrides. C. del Fresno (Anal. Fís. Quím., 1927, **25**, 363—368).—The contraction in the formation of the volatile hydrides increases with diminution in the atomic number of the negative element present. Within each period, the contraction varies approximately inversely with the atomic number of the negative element and directly with the number of hydrogen atoms in the hydride. G. W. Robinson.

Refractive index of sulphur trioxide. R. Nasini (Gazzetta, 1927, **57**, 667—669).—Attention is directed to certain errors in the data in Abegg's "Handbuch" relating to the refractive index of this substance and notice is given of a forthcoming paper on this subject. R. W. Lunt.

Magnetic rotation in optically active substances. G. Calcagni (Gazzetta, 1927, **57**, 713—716).—The change in rotation of a number of optically active substances produced by an external magnetic field depends on the direction of the field and is independent of the concentration of the solution in the cases examined. R. W. Lunt.

Dispersion of methane. T. H. Havelock (Phil. Mag., 1927, [vii], **4**, 721—725).—A comparison is made of the approximate dispersion formulæ for neon, hydrogen fluoride, water, ammonia, and methane. It is shown that methane does not belong to this sequence and that its molecule is not equivalent to a C^{----} ion with four hydrogen nuclei. This argument is substantiated by an examination of the ionisation potentials. It is shown that the dispersion formula is in support of a molecular structure with a C^{++++} ion and four H$^-$ ions. A. E. Mitchell.

Thermal degeneration of the *X*-ray haloes in liquids. C. V. Raman (Nature, 1927, **120**, 770).—The predicted degeneration of the diffraction halo with rise of temperature has been demonstrated experimentally. A. A. Eldridge.

Crystal structure of Cu_3Sn and Cu_3Sb. W. M. Jones and E. J. Evans (Phil. Mag., 1927, [vii], **4**, 1302—1311).—When the crystal structure of alloys corresponding in composition with the above formulæ is examined by *X*-ray methods, the results are the same as would be obtained with a pure metal possessing a close-packed hexagonal structure, so that it is not possible from these experiments to decide whether the alloys are true compounds or merely solid solutions. In each instance, the shortest interatomic distance is equal to the sum of the atomic radii of the component elements. R. Cuthill.

Crystal structure of some of the alums. J. M. Cork (Phil. Mag., 1927, [vii], **4**, 688—698).—*X*-Ray measurements of a number of alums have yielded the following values (in Å.) for the dimensions of the unit cubic cell: 12·18 for $\text{NH}_4\text{Al}(\text{SO}_4)_2,12\text{H}_2\text{O}$, 12·14 for $KAl(SO_4)_2,12H_2O$ and for $KCr(SO_4)_2,12H_2O$, 12·20 for $RbAl(SO_4)_2,12H_2O$, 12·31 for $CsAl(SO_4)_2,12H_2O$, and 12·21 for $ThAl(SO_4)_2,12H_2O$. Four molecules are ascribed to the unit cell. The eight metal atoms take positions at the corners, centre, centre of faces, and mid-points of edges of the cell, making a rock-salt arrangement of univalent and tervalent metals. The space-group is T_h^6. From a Fourier analysis of the electron distribution and a critical survey of the atomic absorption coefficients, alternative arrangements of the atoms along the trigonal axis have been deduced.

A. E. MITCHELL.

Structure of the isomorphic substances tetramethylammonium iodide, bromide, and chloride. L. VEGARD and K. SOLLESNES (Phil. Mag., 1927, [vii], **4**, 985—1001).—The dimensions of the unit cell and the space-group D_{4h}^{7} previously found for tetramethylammonium iodide by Bragg's method (*ibid.*, 1917, [vi], **33**, 395) have been confirmed by the powder method. The investigation of the chloride and bromide compounds has made it possible to fix the position of the nitrogen and carbon atoms more accurately. They form groups NC_4, where nitrogen is at the centre of a tetrahedron of carbon atoms. The centre distance of these groups is 1·50 Å. Regarding the crystal as a packing of spheres, it is assumed that there is one group of 8 and one group of 16 hydrogen atoms in a unit cell. The diameter of the hydrogen atom is 1·70 Å. The arrangement of the atoms suggests that the crystal has an ionic constitution $NMe_4^+Cl^-$ (or Br^- or I^-).

C. J. SMITHELLS.

New kinds of mixed crystals. V. D. BALAREV [with R. KAISCHEV] (Z. anorg. Chem., 1927, **167**, 237—240).—It is suggested that in the mixed crystals of barium sulphate and potassium permanganate prepared by Geilmann and Wünnenberg (A., 1927, 120) the permanganate was merely held in capillaries in the sulphate. The possibility of the formation of such crystals and of the removal of the permanganate from them with oxalic and sulphuric acids will depend on the experimental conditions. In the co-precipitation of zinc and copper sulphides, where a similar explanation has been advanced (A., 1927, 925), the amount of the former sulphide present in the precipitate has been found to depend on the temperature and acidity of the solution. R. CUTHILL.

Change of ionic refraction in crystal lattices. K. FAJANS (Z. physikal. Chem., 1927, **130**, 724—731).—An attempt has been made to obtain a quantitative expression for the change of the refraction of ions when composing a crystal lattice. For the change ΔR_a of the refraction R_a of the anion of the alkali halides the equation $\Delta R_a = CR_a^2/r^4$ (r the distance between the positive and negative ions and C a constant) should be valid. For the lithium halides, a fairly satisfactory constant is obtained. Calculations for the other alkali halides indicate qualitatively that ΔR_c, the change of refraction of the cation, increases for a given cation as the distance between the ions decreases, and for different cations increases with their ease of deformation.

H. F. GILLBE.

Temperature variation of the elasticity of Rochelle salt. E. P. HARRISON (Nature, 1927, **120**, 770).—Attention is directed to the analogy between piezo-electric phenomena and the reciprocal relations between strain and magnetic properties shown by ferromagnetic metals. A. A. ELDRIDGE.

Temperature–electrical resistivity relationship in certain copper α-solid solution alloys. A. L. NORBURY and K. KUWADA (Phil. Mag., 1927, [vii], **4**, 1338—1341).—The electrical resistivity, R, of alloys of copper with aluminium, tin, and silicon has been determined between −191° and 438°, the results showing that R is related to the resistivity at 0°, R_0, and the temperature, t, by the equation $R = R_0 + \alpha t$, where α is a linear function of R_0, and increases with it. Alloys of copper with nickel or manganese deviate somewhat from this relationship.

R. CUTHILL.

Iron carbide (Fe_3C). G. TAMMANN and K. EWIG (Z. anorg. Chem., 1927, **167**, 385—400).—The temperature–magnetisation curves of steels containing 0·15—3·9% of carbon show that the magnetisation decreases sharply between 200° and 220° by an amount which is proportional to the carbon content, and increases with it. Since the steels which are richer in carbon contain carbide formed from the molten metal as well as from the γ-mixed crystals, the two forms must be identical. A sample of cementite lost its magnetisation completely at 210°, but after having been heated at 500° for 5 hrs., there was no change in the magnetisation at 200—215°, and the magnetisation–temperature curve corresponded with that of pure iron. This relatively low decomposition temperature, however, appeared to be due to the presence of occluded gases. A cooling curve showed no irregularity at the transition point at 210°, but a volume change could be detected dilatometrically. Aluminium and titanium do not affect the transition temperature, but silicon, manganese, and boron depress it considerably, the effects increasing in this order. R. CUTHILL.

Theory of the magnetic properties of iron and other metals. R. H. DE WAARD (Phil. Mag., 1927, [vii], **4**, 641—667).—A mathematical theory of magnetism based on the result obtained by Barkhausen (Physikal. Z., 1919, **20**, 401) that during the magnetisation of a body the magnetic moment changes partly discontinuously, and the extension of Barkhausen's work by van der Pol to show that hysteresis curves in iron wires show discontinuities. A. E. MITCHELL.

Magnetic properties of thin films of electrolytic iron. E. P. T. TYNDALL (Physical Rev., 1927, [ii], **30**, 681—691).—Magnetisation curves and hysteresis cycles were obtained for films of iron electrolytically deposited on brass tubes.

A. A. ELDRIDGE.

Production of metallic single crystals. J. A. M. VAN LIEMPT (Amer. Inst. Min. Met., Tech. Pub., 1927, No. 15, 8 pp.).—Four methods are reviewed, viz., from the liquid state, from the gaseous state, electrolytically, and by recrystallisation in the solid state. CHEMICAL ABSTRACTS.

Photo-electric threshold of single bismuth crystals. T. J. Parmley (Physical Rev., 1927, [ii], 30, 656—663).—The photo-electric threshold of single-crystal bismuth after a new surface had aged for 1 hr. at 10^{-6} mm. was 2567 Å., and immediately after a new surface had been cut in a vacuum of the order of 10^{-7} mm. was 2835 Å. Values for the polycrystalline form were 2560 and 2830 Å.

A. A. Eldridge.

Photo-electric effect and surface structure in zinc single crystals. E. G. Linder (Physical Rev., 1927, [ii], 30, 649—655).—The photo-electric current obtained varies when the surface of a single crystal of zinc, illuminated with ultra-violet light, is rotated; it is maximal when the hexagonal axis is normal to the illuminated surface and minimal when parallel.

A. A. Eldridge.

Photo-electric conduction in selenium. R. J. Piersol (Physical Rev., 1927, [ii], 30, 664—672).—With the aid of a specially constructed cell, a linear relation between the square of the photo-current and the light intensity is established; hence photo-conduction in selenium is due to a photo-electric liberation of electrons rather than to an allotropic change. Experiments on the effect of immersing a cell in liquid air indicate that the mechanism of the current conduction under dark conditions is entirely different from that of the photo-conduction.

A. A. Eldridge.

Cohesion at a crystal surface. J. E. Lennard-Jones and (Miss) B. M. Bent (Trans. Faraday Soc., Nov. 1927, advance proof).—Theoretical. A mathematical investigation of the cohesive forces outside a (100) surface plane of a crystal of the rock-salt type, the problem being idealised in the sense that the boundary is assumed to be perfectly plane and unlimited in extent. The cohesive forces between an outside particle and the (100) surface plane are dealt with under four headings. (1) If the outside particle is charged there is an electrostatic force between the particle and the valency charges of the ions in the crystal. At a given distance from the plane surface this force is a maximum above the lattice points of the crystal, and is zero at all points of those planes normal to the surface which bisect the lines joining adjacent ions. An expression is deduced for this force which diminishes rapidly with the distance from the surface; thus with sodium chloride the maximum forces on a charge ε at distances 2·815 and 5·63 Å. are $8{\cdot}46\times10^{-5}$ and $9{\cdot}87\times10^{-7}$ dynes, respectively. (2) If a neutral atom approaches the crystal surface, there is no direct electrostatic attraction, but an induced attraction is set up owing to the polarisation of the atom by the charged ions in the crystal. An expression is deduced for this effect, which is much less than the electrostatic force in (1), and falls off much more rapidly with increasing distance. Thus in the case of a neutral atom of argon approaching the (100) surface of sodium chloride, the forces at distances 2·815 and 5·63 Å. are $8{\cdot}19\times10^{-6}$ and $1{\cdot}1\times10^{-9}$ dynes, respectively. (3) Attractions similar to those of van der Waals exist between neutral atoms and similar forces are supposed to exist in the case of charged particles in addition to the forces in (1) and (2). An expression is deduced for this attraction, which, in the case of an argon atom, at distances 2·815 and 5·63 Å., amounts to $1{\cdot}92\times10^{-5}$ and $3{\cdot}04\times10^{-7}$ dynes, respectively. This attraction thus falls off much less rapidly with distance, and the van der Waals' forces may thus act as the first agents in the process of adsorption. (4) The fourth problem is the polarisation of a crystal by a charge outside it, and the difficulties in the solution are indicated.

W. Hume-Rothery.

Cohesion in the crystalline state. F. I. G. Rawlins (Trans. Faraday Soc., Nov. 1927, advance proof).—The applications of the new wave mechanics to ionic or heteropolar crystals (cf. Pauling, A., 1927, 399), and the work of Hund (Z. Physik, 1925, 34, 833) on "stratified" lattices are briefly reviewed. An explanation of the cohesion in other special crystal lattices may be sought in a combination of the theories valid for truly heteropolar and truly homopolar lattices.

W. Hume-Rothery.

Effect of rolling on single crystals of aluminium. S. Tanaka (Mem. Coll. Sci. Kyōtō, 1927, 10, 303—309).—Single crystals of aluminium, in the form of plates 1 mm. thick, were rolled to varying degrees, and the orientations of the small crystals produced by the destruction were investigated by *X*-ray methods. Three types of fibrous structures were observed. In the first type the fibre axes correspond with the [110] direction, and most of the (001) planes are nearly parallel to the rolled surface. The maximum deviation from this orientation, which is produced by rotation of the crystals about the fibre axis, is about 26°. The second type has an orientation of the micro-crystals such that the fibre axis corresponds with the [112] direction, and the (110) planes coincide with the rolled surface; the maximum deviation from this orientation is about 28°. In the third type, the [111] direction and the (110) planes are nearly parallel to the fibre axes and the rolled surface, respectively; the deviation is here about 10°. Another arrangement similar to the third type but with the (112) plane parallel to the surface may exist, but the proof is incomplete. No simple relation could be traced between the initial orientation of the single crystal, the direction of rolling, and the final state of the fibrous structure.

W. Hume-Rothery.

Effect of grain boundary on the hardness of aluminium. K. Yamaguchi (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, 6, 271—300).—Aluminium test pieces cut from sheet 1 mm. thick were strained by a tensile load of 5 kg./mm.^{2} and annealed at 600° to form large crystals occupying the full cross-section of the material. Reference lines were drawn at intervals of 1 mm. at right angles to the major axis, from which the extension in different parts of the test piece, when loaded in tension, could be determined. The elongation took place almost entirely in the crystals and diminished rapidly in the neighbourhood of a grain boundary. The percentage elongation varied widely in crystals of different orientation. The results are in agreement with the slip-interference theory of hardening.

C. J. Smithells.

Deformation, rupture, and hardening of crystals. M. Pólányi (Trans. Faraday Soc., Nov. 1927, advance proof).—The deformation and rupture of crystals of zinc, cadmium, tin, and other metals with special reference to the work of the author and his collaborators (cf. A., 1923, ii, 768; 1924, ii, 298; 1925, ii, 252, 370, 371; 1926, 666) is described. The mechanism of the strengthening and weakening of crystals by deformation is described, and the theory of the "bent crystal" is discussed.

W. Hume-Rothery.

Effect of iron and oxygen on the electrical conductivity of copper. R. P. Heuer (J. Amer. Chem. Soc., 1927, 49, 2711—2720).—Thermodynamic calculations indicate that the effect of the presence of oxides on the conductivity of copper cannot be neglected (cf. Hanson and Ford, B., 1924, 833, whose copper is shown to have contained ferrous oxide). The conductivity of copper is reduced at the rate of 630% of the standard value for 1% of iron. Iron, also, may be completely oxidised in alloys containing cuprous oxide eutectic. S. K. Tweedy.

Hall effect and resistance in sputtered tellurium films. F. W. Warburton (Physical Rev., 1927, [ii], 30, 673—680).—Except when the film is heated in a gas, and apart from an ageing process, the Hall *E.M.F.* is proportional to the resistance of the film. A. A. Eldridge.

Hall effect in aluminium crystals in relation to crystal size and orientation. (Miss) P. Jones (Phil. Mag., 1927, [vii], 4, 1312—1322).—Determinations of the Hall coefficient with aluminium crystals have given the absolute value $3\cdot44\times10^{-4}$, this being independent of the crystal size and of the direction of the primary current in relation to the lattice planes. R. Cuthill.

Magnetic differentiation of hydrated ferric oxides. II. E. Wedekind and W. Albrecht (Ber., 1927, 60, [*B*], 2239—2243; cf. A., 1926, 1196).—Examination of the susceptibility of hydrated ferric oxides indicates a probable maximum in specimens containing less than 22% of water. Such specimens cannot be prepared below 45° or by means of acetone. Dehydration under water at 100° in sealed tubes or open vessels yields products which have maximum susceptibility when containing 14—15% and 10—11% of water, respectively, but the experiments are not strictly reproducible and the process is complicated by ageing phenomena which occur slowly even at the atmospheric temperature. It appears valid to conclude that at least one definite hydrate is responsible for the high magnetic susceptibility of the products. Ageing of the specimens is accompanied by the appearance of interference lines in their *X*-ray spectra. A hydrate, obtained by ultrafiltration of a solution of ferric chloride which had been dialysed as far as possible and subsequently dried by acetone and ether, was not remarkably magnetic. Further specimens were obtained by the interaction of iron pentacarbonyl with hydrogen peroxide in alcoholic solution and by the addition of anhydrous ferric sulphate or ferric ammonium sulphate to 35% ammonia solution. Although having almost identical water content, the hydrates differ greatly in their magnetic properties. H. Wren.

Magnetic susceptibilities of positive vanadium ions. S. Freed (J. Amer. Chem. Soc., 1927, 29, 2456—2468).—The magnetic susceptibilities of quadrivalent, tervalent, and bivalent positive vanadium ions, measured by a null method, indicate that these ions contain 1, 2, and 3 Bohr magnetons, respectively. This is not in agreement with published theories based on the quantum theory and the anomalous Zeeman effect on atomic ions, possibly because the latter should be replaced by magnetic influences on band spectra (molecular ions). Measurements on sodium perchlorate, sodium chloride, perchloric acid, and sulphuric acid solutions are recorded.

S. K. Tweedy.

Liquid wires and their surface films. W. B. Pietenpol and H. A. Miley (Physical Rev., 1927, [ii], 30, 697—704).—When a wire of a metal of low m. p. is heated in air or oxygen, it may glow without breaking, owing to the support afforded by a thin oxide film of considerable strength. Wires with clean surfaces when heated in nitrogen break at the m. p. of the metal. Experiments with sulphide, bromide, and chloride films indicate that (*a*) if there is not a firm coat at the m. p. of the metal the wire breaks at that temperature, (*b*) if the m. p. of the coat is between the m. p. of the metal and the glowing temperature the wire breaks at the m. p. of the coat, (*c*) if the m. p. of the film is above the glowing point, the wire can be made to glow when freely suspended. A. A. Eldridge.

Thermal expansion of cobalt–nickel, cobalt–iron, and iron–nickel alloys. A. Schulze (Physikal. Z., 1927, 28, 669—673).—The measurements have been carried out for the complete series of these alloys, using the glass-tube method of Henning, and operating within the range from the ordinary temperature to 100°. In each case, the expansion–composition curves for these metal pairs show remarkable peaks corresponding with the compositions of intermetallic compounds which were detected previously from measurements of electrical conductivities (A., 1927, 196), or otherwise. The results are of special interest, since non-ferromagnetic alloys do not give expansion curves of this type.

G. A. Elliott.

Thermal expansion at low temperatures of metals crystallising in regular systems. W. H. Keesom (Z. physikal. Chem., 1927, 130, 658—661).—The cubical expansion coefficients of silver and copper have been calculated according to Grüneisen's formula, and although the results in general show fair agreement with observed values, at the lowest temperature-intervals considerable discrepancies occur. H. F. Gillbe.

Theory of specific heat, with consideration of the latent heat of fusion and vaporisation. Y. Doi (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, 6, 129—147).—The latent heat accompanying the change of state of a substance is treated from the point of view of the quantum theory. By regarding the thermal agitation of an atom of a non-gaseous substance as being composed of simple harmonic motions, and giving it an expression analogous to that of the energy of the Bohr atom, the following approximate expression is deduced for the latent heat of vaporisation: $L=3Nph\nu/2J$, where N is Loschmidt's number, J the mechanical equivalent of heat, h is Planck's constant, and ν the frequency of atomic oscillation in the state corresponding with the quantum number p. ν is given by $2^{\frac{1}{2}}N_0^{\frac{1}{3}}V/2\pi$, V being the velocity of propagation of longitudinal waves along a thin rod of the substance under consideration and N_0 the number of atoms contained in a unit cube of the substance. It is further shown that the product of the latent heat of vaporisation L, and the temperature coefficient of linear expansion α, equals a constant, and by calculation for a number of metals, using data for L and α taken from the tables, it is found that $\alpha L=1$ approx. By means of this relation, the following expressions are obtained: $x=\sqrt{3Nm_{\text{H}}\alpha AV^2/1{\cdot}008J}$, where x is the ratio of the mean distance between two neighbouring atoms to the mean amplitude of the supposed simple harmonic motions executed by the atoms, A is the at. wt., and m_{H} the mass of the hydrogen atom; and $p=2\sqrt{2}\,.\,\pi mV/x^2N_0^{\frac{1}{3}}h$, m being the mass of the atom under consideration. x and p are calculated for fourteen metals. In every case, x is greater than 2, or the mean value of the amplitude of the thermal oscillations of an atom in a non-gaseous substance is less than half the mean distance between two neighbouring atoms. L. L. Bircumshaw.

Electrical conductivity and specific heat of solid metals, and the occurrence of transition points. C. Drucker (Z. physikal. Chem., 1927, **130**, 673—690).—The method described previously (A., 1925, ii, 24) for the determination of the ratio between the temperature coefficient a of the electrical resistance and the specific heat c has been applied to bismuth and nickel. The method forms a very sensitive test for the occurrence of transition points. Direct determination of a not only demonstrates the influence of impurities and of the previous treatment of the metal, but also exhibits anomalous variations in the neighbourhood of the transition point. H. F. Gillbe.

Heat capacities of acetaldehyde and paraldehyde and the heat of transformation of acetaldehyde into paraldehyde. D. LeB. Cooper (Proc. Nova Scotia Inst. Sci., 1927, **17**, 82—90).—The mean specific heats of acetaldehyde and paraldehyde, between 17° and temperatures ranging from −182·5° to −47·0° in the first case, and from −78·5° to 100° in the second, have been determined. From the curves obtained by plotting heat capacity against temperature, the latent heat of fusion of paraldehyde is found to be 25·2 g.-cal. per g. and of acetaldehyde 17·6 g.-cal. per g. The heat of polymerisation of acetaldehyde into paraldehyde, catalysed by sulphuric acid, is given as 20,495 g.-cal., which is 4850 g.-cal. less than that calculated from the heats of combustion. The density–composition curve of mixtures of acetaldehyde and paraldehyde is plotted, and also the heat capacity curve between −182·5° and 100° for the "pyrex" glass used in the experiments. A curve of the existing data for the variation of the equilibrium composition of mixtures of acetaldehyde and paraldehyde with temperature is given. M. S. Burr.

Change of properties of substances on drying. H. B. Baker (J.C.S., 1927, 2902—2903).—The view of Balarev (cf. A., 1927, 613) that the rise in b. p. of substances dried over phosphorus pentoxide may be due to the presence of phosphoric acid or of its esters is shown to be untenable. O. J. Walker.

Transition point of zinc at 175°. G. I. Petrenko (Z. anorg. Chem., 1927, **167**, 411—412; cf. A., 1927, 615).—The existence of a transition point of zinc at 175° has now been confirmed by microscopical examination. R. Cuthill.

Vapour pressures of methylene chloride. J. H. Perry (J. Physical Chem., 1927, **31**, 1737—1741; cf. Rex, A., 1906, ii, 342).—The vapour pressures of purified methylene chloride have been measured over the temperature range 186·1—311·5° Abs., giving a pressure range from less than 1 to 715·8 mm. The extrapolated value of the normal b. p. is 40·67° and the latent heat of vaporisation, calculated from the modified Clapeyron equation, is 7020 g.-cal./g.-mol. at this temperature. Trouton's constant is 22·4 and the ratio of the temperatures Abs. corresponding with vapour pressures of 760 mm. and 200 mm. is 1·114. The value of T_c calculated from the relation given by Prud'homme (A., 1921, ii, 376) is 215·7°, which may be compared with Nadejdine's (J. Russ. Phys. Chem. Soc., 1882, **14**, 157) experimental value of 245·1°. L. S. Theobald.

Physical properties of vinyl chloride. L. I. Dana, J. N. Burdick, and A. C. Jenkins (J. Amer. Chem. Soc., 1927, **49**, 2801—2806).—The vapour pressure of vinyl chloride, f. p. −159·7°, b. p. −13·9°, is given to within 0·3% by $\log p(\text{atm.})=0{\cdot}8420-1150{\cdot}9/T+1{\cdot}75\log T-2{\cdot}415\times10^{-3}T$ between 245° and 333° Abs. The density (g./c.c.) of the liquid between −13° and 60° is $0{\cdot}9471-1{\cdot}746\times10^{-3}t-3{\cdot}24\times10^{-6}t^2$, where t is in °C. The critical pressure is estimated to be 52·2 atm. and the critical temperature 142°. Probable values of the vapour density and latent heat of evaporation are tabulated. S. K. Tweedy.

Influence of grain size on the dissociation pressure of solids. M. Centnerszwer and J. Krustinsons (Z. physikal. Chem., 1927, **130**, 187—192).—The influence of grain size of crystals on the dissociation pressure has been examined for silver carbonate and mercuric oxide, the dissociation pressures being measured by the improved dynamic method previously described (A., 1927, 21). The pressure for the yellow oxide of mercury is higher than that for the red (cf. Schoch, A., 1903, ii, 428), and a darker-coloured yellow oxide, prepared from the red by grinding, gave an intermediate value. The effect of grain size of the crystals on the temperature of dissociation is expressed by the equation $dT/dr=-2\sigma MT/\lambda dr^2$, where r is the radius of the particle and λ the heat of dissociation. The surface tension at the gas–solid boundary is also calculated from the data obtained. L. S. Theobald.

Constancy of pressure during isothermal condensation or vaporisation as a criterion of purity.

E. W. Washburn (Z. physikal. Chem., 1927, **130**, 592—600).—Constancy of pressure during the isothermal evaporation of a liquid is not a general criterion of purity. For cases in which the principle is applicable, equations are derived for calculating the quantity of impurity present, provided that it consists of only one substance and that certain data regarding it are known. H. F. Gillbe.

Entropy at infinite pressure and the equation of state of solids. G. N. Lewis (Z. physikal. Chem., 1927, **130**, 532—538).—An attempt is made to find a theoretical method of extrapolating data regarding interatomic forces at high pressures to much greater pressures. By assuming that at all temperatures the entropy of a pure solid is zero at infinite pressure, the following partly empirical equations are derived: $S_0=\alpha/n\Pi^n$, $(\delta V/\delta T)_{p=0}=\alpha/\Pi^{1+n}$, where Π is the internal pressure of a substance at zero external pressure and α and n are constants. Good agreement is found between these equations and Bridgman's values of $(\delta V/\delta P)_T$ for lithium, sodium, and potassium. H. F. Gillbe.

Internal energy, maximum work, and free energy of the elements. R. D. Kleeman (J. Physical Chem., 1927, **31**, 1669—1673).—The values of the internal energies, referred to a temperature of 298° Abs. and to the volumes possessed at 0° Abs., have been obtained graphically for certain elements, and show a periodicity similar to the entropies as calculated by Lewis and Gibson (A., 1918, ii, 29). The maximum work has been calculated using the same values for the entropies, and gives results which are numerically similar to those obtained for the internal energies. The change which a complex substance may undergo at 0° Abs. is shown to have an important bearing on the calculation of the internal energy, and the case of white and grey tin is discussed in this connexion. L. S. Theobald.

Surface tension of rock salt. G. N. Antonov (Phil. Mag., 1927, [vii], **4**, 792—800).—A modification of the method for the determination of the surface tensions of solids described previously (A., 1926, 671) has been employed for the determination of the surface tension of rock salt. The value 315 dynes/cm. has been obtained. In support of the method, it is claimed that it is in no way dependent on the molecular structure of the material under examination. A. E. Mitchell.

Surface tension of liquid carbon dioxide. E. L. Quinn (J. Amer. Chem. Soc., 1927, **49**, 2704—2711).—The surface tension of liquid carbon dioxide, which was measured between −52·2° and 25° by the capillary-rise method, is given by $0·0653(31·35-t)^{1·24}$ dynes/cm., except at the lowest temperatures. The internal pressure is calculated to be about the same as that of toluene, chloroform, and carbon tetrachloride. The density of saturated carbon dioxide vapour between 0° and 25° is given by d(g./c.c.)$=1·936p^n/(273+t)$, where $n=0·737+0·0048t$, and p is in atm. S. K. Tweedy.

Viscosity of metals. Bismuth. G. Subrahmaniam (Nature, 1927, **120**, 770).—The coefficient of viscosity of bismuth at 23·7° is computed from known data to be $13·71\times10^8$ poises. A. A. Eldridge.

Sutherland's viscosity constant and its relation to the molecular polarisation. F. G. Keyes (Z. physikal. Chem., 1927, **130**, 709—714).—For a large number of gases Sutherland's constant C increases progressively with the Lorenz–Lorentz polarisation constant P_0. The majority of gases exhibit a linear relationship between $T^{\frac{1}{2}}/\eta$ and T^{-1}, T being the temperature, as required by Sutherland's formula. Helium, except possibly at high temperatures, forms an exception. H. F. Gillbe.

Internal friction of mercury. G. Tammann and and J. Hinnüber (Z. anorg. Chem., 1927, **167**, 230—236).—Determinations of the viscosity of mercury by experiments on the rate of flow through capillary tubes of glass appear to be vitiated by the mercury slipping over the surface of the glass. Using copper capillaries, the true value of the viscosity is found to be 0·04931±78 g./cm. sec. at 13·5°, with a temperature coefficient of −0·0012±2 per 1°. The viscosity at 10° is increased by 12·4% by 0·114% of gold. R. Cuthill.

Dielectric constants of binary mixtures. Application of the method of partial molal quantities. J. W. Williams and J. H. Mathews (Z. physikal. Chem., 1927, **130**, 277—285).—When a liquid is placed between parallel plates, 1 cm. apart, of dimensions such as to contain between them 1 g.-mol. of liquid, the dielectric capacity is defined as the molal inductive capacity. This equals $M(\varepsilon-1)/d$, where M is the mol. wt. of the liquid. The application of this concept to dielectric constant data is discussed, and the association factor for ethyl alcohol has been calculated from the known data for the system ethyl ether–ethyl alcohol. L. S. Theobald.

Solid solutions between compounds of elements of different valency. G. Bruni and A. Ferrari (Z. physikal. Chem., 1927, **130**, 488—494).—The grating constants of ferrous, zinc, manganous, and cadmium chlorides have been determined. The ratio c/a is a function of the radius of the metal ion which lies on a smooth curve for magnesium, ferrous, manganous, and cadmium chlorides, whilst that for zinc chloride lies somewhat below the curve. These results are discussed with reference to the author's work on the mixed crystals formed by lithium and magnesium chlorides (cf. A., 1926, 236). R. W. Lunt.

Viscosities of chromic anhydride solutions. J. R. Partington and S. K. Tweedy (J.C.S., 1927, 2900—2902).—The viscosities of chromic anhydride solutions between 0° and 40° are recorded. The chromic anhydride (cf. A., 1926, 697) has m. p. 193° and exhibits no supercooling. The absolute viscosities are calculated from Leroux's values for the absolute viscosity of water, η, which can be represented between 10·9° and 30° by the expression $[0·633161/(T-241·307)]-0·00207155$, where T is the absolute temperature. O. J. Walker.

Densities of co-existing liquid and gaseous carbon dioxide and solubility of water in liquid carbon dioxide. H. H. Lowry and W. R. Erickson (J. Amer. Chem. Soc., 1927, **49**, 2729—2734).—The densities of the isobaric phases at t° C. are given by $d_l=0{\cdot}4683+0{\cdot}001442(31-t)+0{\cdot}1318(31-t)^{\frac{1}{3}}$ and $d_g=0{\cdot}4683+0{\cdot}001442(31-t)-0{\cdot}1318(31-t)^{\frac{1}{3}}$, where 0·4683 is the critical density derived from the law of rectilinear diameters. Within the limits of error, the presence of water vapour does not affect the density of saturated carbon dioxide vapour, so that the solubility of water in the liquid is probably less than 0·05% by weight over the range −5·8° to 22·9°.

S. K. Tweedy.

Solubility of barium *n*-butyrate. H. J. Wing (J. Amer. Chem. Soc., 1927, 49, 2859—2861).—The solubility of barium *n*-butyrate is 37·0 g. in 100 g. water at 0·06°; it decreases to a minimum of about 34·8 g. at about 30°, and then increases to 48·1 g. at 94·96°. The anhydrous salt is in equilibrium with the solution throughout.

F. G. Willson.

Solubility of the barium salts of α-sulphocarboxylic acids. H. J. Backer (Z. physikal. Chem., 1927, 130, 177—183).—Solubility data at 25° are given for the barium salts of the α-sulpho-aliphatic acids and of their halogenated derivatives. These salts are less soluble in water than are the corresponding salts of the fatty acids, and the smaller solubility appears to be connected with the formation of a stable, six-membered ring structure in the barium salt. The introduction of a methyl group or of a halogen increases the solubility of the barium salt, but the introduction of a halogen in the barium α-sulphopropionate lowers the solubility. The bromo-compounds are more soluble than the chloro-derivatives.

L. S. Theobald.

Partition of lactic acid between water and ether and between water and amyl alcohol. W. U. Behrens (Biochem. Z., 1927, 189, 348—349).—A reply to Dietzel and Rosenbaum (A., 1927, 820).

P. W. Clutterbuck.

Condensation of vapours of certain substances at temperatures below their m. p. N. V. Tancov and T. Chodalevitsch (J. Russ. Phys. Chem. Soc., 1927, 59, 631—638).—The vapours of camphor, borneol, and *iso*borneol were cooled in a specially devised apparatus by means of a stream of cold air. Care was taken to avoid contact of the vapours with any crystalline substance or dust. It is found that the supersaturated vapours of all these substances condense to liquids when cooled below their m. p.

A. Ratcliffe.

Velocity of dissolution of solid substances. W. Jacek and Z. Lehr-Spławińska (Rocz. Chem., 1927, 7, 309—333).—Spheres cut out of crystals of sodium chloride and uniformly agitated in water dissolve uniformly, no deformation of the spherical shape being noticeable even after prolonged immersion. The following formula is deduced: $-dr/dt=k_1(c+r^3)$, where r is the radius of the sphere at time t, c the difference between the cubes of the original radius of the sphere and of the radius of a sphere large enough to saturate the volume of water used, and $k_1=\frac{4}{3}\pi k$, where k is the velocity coefficient. For irregularly-shaped bodies, the formula: $-dr/dt=(P/4\pi r^2).k_1(c+r^3)$ where P is the surface area of the body in question, is found to hold. The value of k is given by $k=\rho\times$ unit surface $\div\frac{4}{3}\pi a_1^3$, where ρ is the thickness of the layer of salt dissolved in unit time from the surface of the sphere; k depends on the temperature and on the velocity of translation of the sphere in the solvent, but is independent of its radius and of the volume of solvent used.

R. Truszkowski.

Crystal crusts. H. Erlenmeyer (Helv. Chim. Acta, 1927, 10, 896—900; cf. Washburn, A., 1927, 931).—Creeping occurs mainly with solutions of simple salts, crystallisation commencing at the periphery of the liquid surface. Double salts do not, in general, exhibit creeping and crystallisation usually commences at the bottom of the containing vessel. It is suggested that in solutions of simple salts undissociated molecules predominate at the surface and that on slow evaporation crystallisation begins in the peripheral, capillary film. Capillary layers between the crystals and in the space between the crystals and the walls of the container are responsible for the propagation of the crystal crust. With solutions of double salts, it is assumed that the undissociated molecules of the simple constituent salts are not present at the surface in the requisite proportions, and that on evaporation the solubility of the double salt is not exceeded at the periphery, but in the main body of the solution. Quantitative measurements of the creeping of solutions of a number of salts have been made and the data tabulated.

J. S. Carter.

Causes of solubility: surface forces in a system constituting a pair of partly miscible liquids. R. M. Woodman (J. Physical Chem., 1927, 31, 1742—1745).—Measurements have been made, at 25°, of the surface tensions between air and the separate layers of various equilibrium mixtures of the system water–acetic acid–toluene, together with measurements of the interfacial tension between the layers themselves. The tensions of the aqueous layers, which decrease rapidly as the critical point is approached, are, up to a point, greater than those of the toluene layers, which decrease but little, the two tensions tending to coincide as the critical point is reached. The system obeys the Antonow–Reynolds rule (J.C.S., 1921, 119, 466) that the interfacial tension between the mutually saturated phases is equal to the difference in their surface tensions. Coincidence in the values of the latter is, with a zero interfacial tension, not sufficient to cause complete miscibility; other properties must coincide at the same time, and the rates of change of all three tensions with concentration must be zero.

L. S. Theobald.

Work of adhesion between solid and liquid phases. F. E. Bartell and H. J. Osterhof (Z. physikal. Chem., 1927, 130, 715—723).—A method is described for measuring contact angles at solid–liquid interfaces and for determining the adhesion constant K even when the contact angle is zero. From these data it is possible to evaluate the adhesion tension and the work of adhesion at the interface. Values are given for these quantities for a number of liquids in contact with carbon black and with silica.

H. F. Gillbe.

Adsorption of gases by solids with special reference to the adsorption of carbon dioxide by charcoal. H. H. Lowry and P. S. Olmstead (J. Physical Chem., 1927, 31, 1601—1626).—Theoretical.

A physical interpretation of the theory of adsorption, based on the assumption that there is a force of attraction represented by a potential gradient between dissimilar molecules. The theory when tested by the data of Lowry and Morgan (A., 1925, ii, 1053) and other investigators, for the adsorption of carbon dioxide by charcoal, is satisfactory.

L. S. THEOBALD.

Adsorption of acids by coconut charcoal and acetylene carbon. D. NAMASIVAYAM (J. Indian Chem. Soc., 1927, 4, 449—458).—The adsorption of formic, acetic, propionic, butyric, valeric, chloroacetic, dichloroacetic, trichloroacetic, bromoacetic, dibromoacetic, glycollic, *iso*butyric, *iso*valeric, oxalic, hydrochloric, hydrobromic, nitric, sulphuric, and phosphoric acids by coconut charcoal shows that there is no simple relation between the degree of adsorption and the ionisation constants of the acids. For the range of dilution studied (0·2—0·05*M*), the adsorption of most of the acids follows the equation $m=\alpha C^{1/k}$. The values of k for formic acid and its homologues are nearly equal, and the values of α for hydrochloric, hydrobromic, and nitric acids are also nearly equal. Oxalic acid is not adsorbed so much as acetic acid (cf. Fromageot and Wurmser, A., 1925, ii, 384). With solutions of acetic and oxalic acids, and acetylene carbon, it is found that the solvent is preferentially adsorbed. H. BURTON.

Experimental contribution to the theory of equation of state for adsorbed substances. H. L. ROY (J. Indian Chem. Soc., 1927, 4, 307—319). —The surface tensions of aqueous solutions of acetic, propionic, butyric, valeric, hexoic, heptoic, octoic, and nonoic acids, determined by Drucker (A., 1905, ii, 680), Rehbinder (A., 1924, ii, 662), Szyszkowski (A., 1908, ii, 1018), and the author, using a modified form of Sugden's method, are compared with values calculated from the equations $\pi=RTc/k+\beta c$ and $\pi=RT/2\beta\times ln(2\beta c/k+1)$, where β is twice the surface occupied by 1 g.-mol. of the dissolved substance. The calculated and observed values agree up to moderate concentrations. Molecular cross-sections (f), calculated for the dilute solutions from $f=\beta/2N$, are approximately independent of concentration, and do not increase with increasing mol. wt. Similar measurements and calculations have been made for solutions of methyl, *s*-dimethyl-, ethyl-, and *s*-diethyl-carbamides, and phenol. The results confirm those obtained for the acids. H. BURTON.

Adsorption by polar precipitates. IV. Further experiments with silver salts. J. N. MUKHERJEE, J. K. BASU, and A. MUKHERJEE (J. Indian Chem. Soc., 1927, 4, 459—466; cf. Beekley and Taylor, A., 1925, ii, 855).—Silver chloride, bromide, and iodide have negative charges when in contact with water, but become positively charged after being in contact with dilute silver salts. For silver bromide and iodide, the order of adsorption of anions is benzoate > nitrite > acetate > nitrate, throughout the range of concentrations studied (0·001—0·00005*N*). Silver bromate is adsorbed more at lower dilutions. The above series corresponds with that in which the salts are arranged in the order of increasing solubility. Using sodium salts, the order of adsorption is thiocyanate > arsenite > salicylate > acetate > bromide, which again is the same as that given by the increasing solubility, the bromide being an exception. H. BURTON.

Adsorption and diffusion by metals of electrolytically evolved hydrogen and the influence of the electrolyte. A. COEHN and H. BAUMGARTEN (Z. physikal. Chem., 1927, 130, 545—565).—The charge carried by the gas bubbles in solutions is of great influence on the adsorption and diffusion of hydrogen through palladium, palladium–silver alloys, and iron. The potential changes caused by the diffusion of hydrogen through these metals have been measured. The extent to which the adsorption and diffusion are dependent on the nature and concentration of the electrolyte from which the gas is evolved indicates whether the adsorbed hydrogen is nascent or in the ordinary gaseous state. With platinum the charge on the bubbles of gas has no influence on the diffusion, the reverse being true for the metals mentioned above and for tantalum; gaseous hydrogen is thus not adsorbed by platinum at the ordinary temperature.

H. F. GILLBE.

Surface tension of aqueous solutions of acids. L. ABONNENC (Compt. rend., 1927, 185, 948—950).—Measurements by the author's method (Ann. Physique, 1925, [x], 3, 184) of the surface tension of aqueous solutions of mono- and poly-basic strong acids at 21° indicate that the hydrogen ions (and possibly the hydroxyl ions) are the active constituents which lower the surface tension of water. This is in agreement with the selective adsorption exhibited by these ions, and is confirmed by the slopes of the curves $m=f(c)$, where m is the relative change in surface tension and c the concentration. J. GRANT.

Effect of unimolecular films on the evaporation of ether solutions. I. LANGMUIR and D. B. LANGMUIR (J. Physical Chem., 1927, 31, 1719—1731; cf. Rideal, A., 1926, 119).—The effect of unimolecular films of stearic and oleic acids, of cetyl palmitate, and cetyl and myricyl alcohols on the rate of evaporation of saturated solutions of ethyl ether in water has been measured. The rate of evaporation of ether is reduced to less than one tenth of its value when no film is present. It is of advantage to use the reciprocal of the usual quantity measured in g./cm.^{2} per sec., and to define it as the evaporation resistance, R, measured in cm.^{2} sec./g. Calculations based on Rideal's data for water (*loc. cit.*) then show that a unimolecular film of oleic acid produces a resistance of 800 units at 25°, compared with 3 units when no film is present. Cetyl alcohol opposes a resistance of 6×10^4 units to the evaporation of water. In the case of ether, the effect of the film is due, not to its resistance, but to the cessation of the surface currents which it causes. The evaporation resistance, R, equals h/CD, where h is the thickness of any film or layer through which diffusion occurs, D is the diffusion coefficient, and C is the concentration of the diffusing substance. The concentration of water in the film of cetyl alcohol is then 10^{-8} g./cm.^{3} A method is proposed for calculating the resistance due to the underlying liquid layer for any solution.

L. S. THEOBALD.

Physical chemistry of colour lake formation. II. Adsorption of typical dyes by basic mordants. H. B. Weiser and E. E. Porter (J. Physical Chem., 1927, **31**, 1704—1715; cf. A., 1927, 1021; Marker and Gordon, B., 1924, 1010).—The adsorption of orange-II and metanil-yellow by the hydrous oxides of chromium and aluminium, and of methylene-blue by those of iron and chromium has been measured at various hydrogen-ion concentrations. In every case, lake formation consists of adsorption of the coloured ion by the hydrous oxide. There is no evidence of the formation of definite compounds at any p_H value. Lake formation is a typical adsorption phenomenon, dependent on the physical character of the mordant, the concentration of the dye, and the hydrogen-ion concentration of the bath. The conclusion of Marker and Gordon (*loc. cit.*) that at low p_H values ferric oxide and alumina form salts with orange-II is disproved. A high concentration of sulphuric acid prevents adsorption of the dye and precipitates the corresponding free acid, and the alleged compounds are mixtures of mordant and this acid. The effect of variation in hydrogen-ion concentration on the adsorption of the anion of the dye, in the case of acid dyes, is similar to the adsorption of sulphate or oxalate (A., 1927, 1021), provided that the dye remains soluble.

Precipitation of the dye in the presence of a mordant and adsorption by the mordant must be distinguished. With metanil-yellow, adsorption is normal up to a concentration of 0·001*N*-hydrochloric acid. Beyond this concentration, however, precipitation of the dye is proportional to the quantity of acid added, and there is probably adsorption as well as precipitation from the more acid mixtures.

Methylene-blue is adsorbed only when the dye bath is sufficiently alkaline to induce negative peptisation of the mordant, and the amount adsorbed measures the charge on the particles due to the adsorption of hydroxyl ions. L. S. Theobald.

Importance of ζ-potential in the electro-osmotic transport of water through collodion membranes. Theory of anomalous osmosis. P. J. Jurišić (Biochem. Z., 1927, **189**, 294—301).—The electro-osmotic transport of fluid through a collodion membrane takes place from regions of high to those of low electrokinetic (ζ-) potential, and there is no direct relationship between velocity of transport and membrane potential. P. W. Clutterbuck.

Measurement of osmotic pressures. J. C. W. Frazer and W. A. Patrick (Z. physikal. Chem., 1927, **130**, 691—698).—A method has been evolved for measuring the osmotic pressure of any solution of a non-volatile solute. The solvent is submitted to a negative pressure until its vapour pressure becomes identical with that of the solution, with which it is in thermal equilibrium; this tension is obtained by allowing the solvent to evaporate through a porous disc made by sintering a mixture of powdered "pyrex" glass and clay. Preliminary measurements with 0·00836—0·00047*M*-solutions of potassium chloride indicate that the results given by this method are in fair agreement with the requirements of the Debye–Hückel theory. H. F. Gillbe.

Osmotic pressures of ideal solutions. W. D. Bancroft and H. L. Davis (Z. physikal. Chem., 1927, **130**, 626—630).—Equations for the osmotic pressure of ideal solutions are discussed. Raoult's law is a special case of the equation $PV_s = RTN/n \,.\, \log p/p_1$. H. F. Gillbe.

Soret effect in dilute solutions. H. R. Bruins (Z. physikal. Chem., 1927, **130**, 601—606).—For very dilute solutions of mannitol, the Soret coefficient does not approach zero as the dilution increases, but assumes a constant value which is independent of the concentration. H. F. Gillbe.

Optical properties of sulphonecyanine-5R in different saline solutions. F. Vlès and (Mlle.) M. Gex (Compt. rend., 1927, **185**, 946—948).—The earlier experiments (A., 1927, 1023) have been extended to solutions of some of the chlorides and sulphates of the alkali and alkaline-earth metals. The curves for the function $\varphi = f(px)$, where px is the colog. of the molecular concentration of the salt, are of the same type as for solutions of potassium chloride, but vary in length and are displaced along the px axis, the position of the mid-point of the indicator range being specific for each salt. Irregularities at the ends of the curves indicate precipitation of the indicator or, in the case of very dilute solutions, a second equilibrium. The range of the indicator probably depends on the activity of the salt. J. Grant.

Dielectric constants of solutions of electrolytes. IV. Investigation of acids, salts, and bases in water. V. Measurements with sucrose, carbamide, benzoic and sulphanilic acids, betaine, and alanine in aqueous solution. VI. [With H. Ulich.] **Test of the experimental basis of the method of measurement.** P. Walden and O. Werner (Z. physikal. Chem., 1927, **129**, 389—404, 405—416, 417—426; cf. A., 1927, 307).—IV. The method employed previously has been improved, and results have been obtained for a number of bases and salts in aqueous solution.

V. New measurements with sucrose and with carbamide are in good agreement with Harrington's results, but Fürth's curves are not confirmed, the discrepancies being ascribed to slow hydrolysis. Results for sulphanilic and benzoic acids do not confirm Blüh's figures. Betaine and alanine produce an increase in the dielectric constant of the solvent which is in agreement with Pfeiffer's theory.

VI. A critical discussion of the experimental method and apparatus. H. F. Gillbe.

Extinction coefficients of mixtures of uranyl nitrate and organic acids in the ultra-violet as experimental evidence in favour of the formation of unstable intermediate compounds. J. C. Ghosh and B. N. Mitter (J. Indian Chem. Soc., 1927, **4**, 353—366).—The extinction coefficients of mixtures of uranyl nitrate and varying concentrations of formic, acetic, propionic, oxalic, malonic, succinic, glycollic, lactic, tartaric, and mandelic acids have been measured for different wave-lengths. The values obtained can be explained if it is assumed that 1 mol. of uranyl nitrate and 1 mol. of the acid form an unstable, intermediate complex, possessing a definite molecular extinction coefficient. The dissociation constant of the intermediate complex diminishes with increase in the mol. wt. in homologous series; it increases about 12 times when the hydrogen atom in a methyl group is replaced by a carboxyl group; it increases 2·5 times when a hydroxyl group is substituted for a hydrogen atom in a monobasic acid.

H. BURTON.

F. p. of aqueous solutions of hydrochloric acid. H. M. CHADWELL (J. Amer. Chem. Soc., 1927, 49, 2795—2801).—Previously recorded results are extended to more concentrated regions (cf. Hovorka and Rodebush, A., 1925, ii, 772), the temperature being measured by a platinum thermometer. Assuming the activity coefficient 0·819 for 0·07*M*-acid (Scatchard, A., 1925, ii, 397), the coefficients up to 1*M* are in satisfactory agreement with the results of Scatchard and of Lewis and Randall.

S. K. TWEEDY.

Effect of electrolytes on the viscosity of solutions of sodium palmitate. J. W. MCBAIN, H. J. WILLAVOYS, and H. HEIGHINGTON (J.C.S., 1927, 2689—2699).—By the falling-sphere method the changes in viscosity of sodium palmitate solutions, of concentrations 0·75, 1·0, and $1 \cdot 5 N_w$, on the addition of varying quantities of electrolytes have been investigated. With increasing concentration of electrolyte, the viscosity rises rapidly to a maximum and then falls again until the salting-out concentration is reached. The maximum viscosity increases with the concentration of the palmitate, but the amount of salt required diminishes. The rise in viscosity is contrary to the behaviour to be expected from the Donnan equilibrium. The curves are similar in form to those obtained by Loeb for amphoteric colloids, but show a much greater increase in viscosity and have a different significance. The rise in viscosity is explained on the basis of McBain's general hypothesis of aggregation. The initial aggregation, due to dehydration by reduction of vapour pressure, probably takes place in such a way as to enclose and immobilise a large proportion of the liquid. Increased viscosity may also be due to peculiar surface effects resulting from the extension of chains of oriented molecules inwards from the surface of the aggregate. An explanation of the subsequent fall in viscosity is suggested on the basis of a combination of the principles of dehydration by lowering of vapour pressure, of orientation of like molecules, and of the principle underlying the Donnan equilibrium. The dependence of the phenomenon on the nature of the electrolyte is also discussed.

M. S. BURR.

Ultramicroscopic examination of starch sols. M. SAMEC (Arh. Hemiju, 1927, 1, 243—244).—Solutions of starch examined under an ultramicroscope exhibit thread-like aggregates of erythro-starch and granular aggregates of amylo-starch. Heating diminishes the Brownian movement of the particles of starch sols, thus accelerating aggregation. Peptisation is accompanied by diminution in the size of the ultramicrons, the number of which in unpeptised starch sols is therefore less than might be expected from osmotic pressure measurements.

R. TRUSZKOWSKI.

Dependence of viscosity of starch suspensions on the velocity [of flow]. R. KÖHLER (Kolloid-Z., 1927, 43, 187—190).—A modification of the simple Ostwald viscosimeter is described in which low rates of flow are obtained even with a wide capillary tube. With this apparatus, the characteristic curves obtained by Hatschek with the Couette apparatus (cf. A., 1926, 1097) showing the relationship between viscosity and shear gradient are reproduced. Suspensions of starch (10, 15, 20, and 25% by vol.) in a mixture of carbon tetrachloride and paraffin were used. The viscosity, η, and the pressure of flow, p, are connected by the expression of Waele and Ostwald, $\eta \cdot p^{n-1}=k$, where n is always greater than 1.

O. J. WALKER.

Number of phases in colloidal systems. P. BARY (Rev. gén. Colloïd., 1927, 45, 617—623).—Theoretical. The correct definition of the term "phase" is discussed, and new arguments are brought to bear on the proposal, made previously ("Les Colloïdes," 1921, 418), that when two phases are in contact and at equilibrium, the system must be characterised by a positive interfacial tension. It follows from this that suspensions and gels must be considered as diphasic systems, whilst solutions and jellies contain only one phase. A suspension of gold, in the presence of a protective colloid, consists of two phases, one being the solution of the protective colloid, the other the gold.

L. L. BIRCUMSHAW.

Variation of the charge of colloidal particles. II. Effect of dilution and of non-electrolytes on the charge and its variation with concentration of electrolytes. J. N. MUKHERJEE, S. G. CHAUDHURY, and S. P. R. CHOUDHURI (J. Indian Chem. Soc., 1927, 4, 493—514; cf. A., 1926, 352).—Migration velocity measurements, at 35°, have been made with arsenious sulphide, gold, and copper ferrocyanide sols. Dilution with water causes a large decrease in the rate of migration (cm. sec./volt × 10^5), falling from 60 to 12 for arsenious sulphide on twenty-fold dilution. The initial fall is small when compared with the initial fall for gold and copper ferrocyanide. The effect of ethyl alcohol on colloidal arsenious sulphide containing varying amounts of hydrochloric acid is to diminish the rate of migration. Hydrochloric acid and potassium chloride cause a steady diminution in the rate of migration, sodium benzoate shows two maxima and then a decrease, whilst sodium citrate and potassium ferrocyanide show a decrease followed by an increase. The initial variations with the last three electrolytes are complex, probably because of interaction between the anions in the surface of the sol and those of the added electrolyte or of the hydroxyl ions formed by hydrolysis. With sodium and lithium chlorides there is an increase in the negative charge, at low concentrations, which is probably due to adsorption of chloride ions. The variation produced in the charge on colloidal arsenious sulphide on the addition of nine mixtures of electrolytes has been studied, and the results are discussed. There is no simple relationship between the charge and the coagulating concentration.

H. BURTON.

Modification of the electric sign of colloids at will. A. Boutaric (Rev. gén. Colloïd., 1927, 44, 585—591; cf. A., 1927, 621; Boutaric and Dupin, *ibid.*, 309).—When positive colloids are treated with increasing quantities of electrolytes with multivalent anions, or negative colloids with increasing quantities of electrolytes with multivalent cations, two zones of flocculation are observed, with an intermediate zone of non-flocculation. This phenomenon is illustrated by experiments with gamboge and aluminium chloride, and with ferric hydroxide and sodium phosphate. The signs of the positive and negative colloids are reversed by the action of electrolytes with multivalent anions and cations, respectively, when the electrolyte concentration corresponds with that of the non-flocculating zone. By the successive addition of the two types of electrolytes, a series of alternately positive and negative colloids may be obtained.

L. L. Bircumshaw.

Law of mass action and colloids. H. H. Weber (Biochem. Z., 1927, 189, 381—406).—The curve expressing the union of hydrogen and hydroxyl ions with multivalent acids and bases is interpreted as a "residual normality" (proportion of undissociated to total normality) curve. The residual normality curve is described as a function of the hydrogen-ion concentration and of the "true" (not mean) dissociation constants of the single ions determined from electrotitration curves. The effects of changes of ionic activity and of secondary changes of ionic concentrations of multivalent electrolytes by the formation of undissociated salts on the residual normality curve are analysed in relation to the mass law. The rule of Michaelis that the formation of undissociated salts by an ampholyte does not affect the isoelectric point is, in its general form, incorrect. A formula is given for determining the isoelectric point which shows the effect of such salt formation on the isoelectric point and permits its calculation from various dissociation constants. The frequently observed shifting of the isoelectric point of protein and protein systems (cells) by addition of neutral salts is thus explained in terms of the law of mass action.

P. W. Clutterbuck.

Influence of proteins on solubility of calcium phosphate. J. Csapo (J. Biol. Chem., 1927, 75, 509—515).—Solutions of primary calcium phosphate were mixed with varying amounts of blood-serum, adjusted to different reactions by addition of sodium hydroxide, and, after keeping at 0° for 16 hrs., were centrifuged, the calcium and phosphorus content of the supernatant fluid being determined. The results indicate a decrease in the solubility of calcium phosphate from p_H 6·0 to p_H 6·7, followed by increasing solubility up to p_H 7·3; thereafter the solubility decreases with increasing alkalinity, the rate of decrease being lower the greater the amount of serum present. For $p_H > 6·7$, the solutions are turbid owing to the presence of part of the calcium phosphate in stable suspension. The presence of larger amounts of serum shifts the minimum and maximum of the solubility curve towards the alkaline side, the reverse being true in the presence of excess of phosphate.

C. R. Harington.

Solubility, swelling, and adsorption of cellulose in alkali. W. von Neuenstein (Kolloid.-Z., 1927, 43, 241—249).—The amount of cellulose dissolved in alkali depends on the amount of cellulose taken (cf. von Buzágh, this vol., 17), and it is probable that both adsorption and peptisation processes take place. The degree of swelling of cellulose in water and alkali is similarly affected, and it is suggested that the content of electrolytes or of decomposition products in the cellulose may have an influence on the swelling. O. J. Walker.

Action of alkalis on clay. H. B. Oakley (J.C.S., 1927, 2819—2831).—Suspensions of purified clay were treated with alkali, the clay was removed by coagulation, the p_H of the clear liquid measured, and the total alkali in solution determined by titration. Equivalent quantities of bases were thus found to be taken up at p_H values below about 9. In more alkaline solutions the amounts removed are in the increasing order lithium, sodium, potassium, barium, and calcium. The amounts of sodium and potassium taken up are fairly constant above p_H 11, but barium and calcium show no such limit. The order is the same as that found for amorphous silica (Joseph and Oakley, A., 1926, 132). The amounts of base taken up by both silica and clay are increased by the presence of the neutral salts of the metals concerned. The proportion of neutralised sodium hydroxide which forms soluble compounds is negligible until the p_H is above 9, when it increases rapidly with the alkalinity. The general behaviour of the clay suggests that it is an insoluble or a colloidal weak acid, with a dissociation constant of approximately 10^{-8}, in direct equilibrium with bases in solution, the salts formed being equally insoluble. With alkali more concentrated than p_H 9, however, the clay begins to break down, giving silicates and aluminates which may be soluble, *e.g.*, sodium, or insoluble, *e.g.*, calcium. The viscosity and specific volume of suspensions of clay show pronounced maxima between p_H 8 and 10 with sodium hydroxide, and the viscosity maximum is enormously increased when the clay is coagulated by sodium chloride. Sodium carbonate does not produce the same effect. This behaviour is explained by supposing that, at certain concentrations, sodium hydroxide forms a comparatively non-viscous sol with clay. The addition of sodium chloride produces a very gelatinous sol which, at still higher concentrations, is dissolved by the hydroxide. Comparisons with reference to base absorption and imbibitional water are made between Gezira and Mongalla clays, kaolin, bentonite, ball clay, amorphous silica, and synthetic alumino-silicate. The last-mentioned, although comparatively coarse and only slightly clay-like to the touch, shows considerable analogy with clay.

M. S. Burr.

Gibbs on emulsification. W. D. Bancroft and C. W. Tucker (J. Physical Chem., 1927, 31, 1681—1692).—The modern theory of emulsification was given implicitly by Gibbs, who recognised definitely that a film has two surfaces and therefore two surface tensions, which are not necessarily equal, if in contact with different phases. In all emulsions the dispersed liquid is on the side of the film having the higher surface tension, and an experimental technique has now been developed to show that the surface tension of an emulsifying film is higher on the side of the emulsified liquid. Certain qualitative results are given. L. S. Theobald.

Theory of peptisation. II. A. von Buzágh (Kolloid-Z., 1927, **43**, 215—220; cf. A., 1927, 310).—Variations in the concentration of the colloidal solution with the proportion of solid phase are found in the peptisation of palmitic acid by alkali hydroxides and of sulphur gels. The time must be regarded as a variable in peptisation processes, since there may be either ageing of the sol or a slow change in the composition and state of the solid phase. In the peptisation of ferric hydroxide gel the concentration of the sol decreases with time if a large amount of the solid phase is present. The composition of the latter may change also owing to hydrolytic processes.

O. J. Walker.

Theory of peptisation. III. Peptisation by means of hydrophilic sols. A. von Buzágh (Kolloid-Z., 1927, **43**, 220—224).—When sols are used as peptising agents the curve connecting quantity of colloid dissolved and amount of solid taken exhibits a maximum as in the case of peptisation by electrolytes (cf. preceding abstract). The systems investigated were the peptisation of charcoal and of ferric hydroxide by various soap solutions, of kaolin by humic acid, and of aluminium hydroxide by alkaline alizarin solutions. O. J. Walker.

Denaturation of proteins. W. C. M. Lewis (Z. physikal. Chem., 1927, **130**, 345—352).—Recent views on the nature of denaturation and subsequent flocculation are considered, with special reference to the work of P. S. Lewis (A., 1926, 1204; 1927, 270). It is suggested that whilst flocculation involves the amino- and carboxyl groups of contiguous protein units, the process of denaturation cannot depend on the hydrolysis of the polypeptide linking and is not directly connected with the amino- and carboxyl groups of the protein. Various possibilities in regard to this process are considered, the hydrolysis of a grouping analogous to an ethylene oxide linking being favoured. It is suggested that the process involves the spatial separation (possibly by hydroxyl groups) of the carboxyl and amino-groups belonging to one and the same protein unit, which is thus opened up in a mechanical sense. The mutual affinities of the carboxyl and amino-groups in the same unit are now decreased, with increasing possibility of union with neighbouring units, and so of flocculation.

L. L. Bircumshaw.

Gelatinisation of lyophilic sols and the structure of lyophilic gels. H. G. B. de Jong (Z. physikal. Chem., 1927, **130**, 205—216).—Gelatinisation of agar sols has all the characteristics of a flocculation, but, in spite of this, the electric charge and the hydration of the particles remain almost unchanged. This can only be the case if, at the moment of gelatinisation, these two factors are not distributed uniformly over the particles, which must have unprotected as well as strongly protected regions. Gelatinisation results through these unprotected regions while the electric charge and the hydration remain free to line the inner sides of the spaces formed in the resulting spongy aggregates. Assuming this to be the nature of gel structure, syneresis during the change to a permanent deformation is to be expected, and this has been shown to be the case by submitting threads of a gel of viscose to a stress, when a decrease in volume is obtained. It is further shown that after a permanent deformation an originally isotropic gel shows an anisotropic swelling on suitable immersion, the change in dimension in the direction of the stress being always less than that in the transverse direction. This is reversed for a compression. The significance of the forces of adhesion at the points of contact and of the charge and hydration at the remaining free places is discussed in relation to the swelling equilibrium and to gelatinisation. L. S. Theobald.

Action of benzenesulphonic and naphthalenesulphonic acids on gelatin. C. Marie and A. Buffat (Z. physikal. Chem., 1927, **130**, 233—236).—Benzenesulphonic acid dissolves gelatin rapidly, but naphthalenesulphonic acid precipitates it from solution in water. The sodium, potassium, and copper salts behave like the respective acids.

L. S. Theobald.

Pectin jellies. (Miss) G. Spencer (Fourth Colloid Symposium Monograph, 1926, 302—303).—Pectin jellies may be acid or alkaline; the pectin is always positively charged. Excess of sugar crystallises out, and aids hydrolysis of the pectin.

Chemical Abstracts.

Organophilic colloids. G. S. Whitby (Fourth Colloid Symposium Monograph, 1926, 203—223).—In any homologous series of compounds containing an active group (OH, CN, CHO, CO), imbibition by rubber increases as the series is ascended; the reverse is the case for cellulose nitrate and acetate. The behaviour of numerous solvents is described. The properties of colloids are discussed.

Chemical Abstracts.

Cataphoresis, electrical charge, critical potential, and stability of colloids. H. R. Kruyt, A. C. W. Roodvoets, and P. C. van der Willigen (Fourth Colloid Symposium Monograph, 1926, 304—310).—Experiments with an arsenic trisulphide sol show that the rate of cataphoresis increases with addition of potassium chloride at all concentrations. There is no reason to reject the theory of critical potentials. Chemical Abstracts.

Influence of capillary activity on cataphoresis and coagulation. H. Freundlich and G. V. Slottman (Z. physikal. Chem., 1927, **129**, 305—320).—The cataphoretic transference velocity of arsenious sulphide sols has been measured in presence of ammonium and mono-, di-, tri-, and tetra-ethylammonium chlorides at various concentrations; the concentrations necessary for coagulation have also been determined. Comparison of the concentrations required to bring about equal lowering of the charge on the particles shows good agreement with Traube's rule; the Traube coefficient is about 1·8, *i.e.*, the square root of the more usually observed value. Similar results are found for methyl-, trimethyl-, propyl-, and tripropylammonium chlorides. The tetra-alkylammonium salts are peculiar in that the coagulating influence is less than would be expected as a result of introducing another methyl group into the next lower homologue, but is much greater than that of the corresponding trialkylammonium salt. Similar measurements have been made of the transference velocity and coagulating concentration of ferric hydroxide sols, prepared by oxidising iron pentacarbonyl with hydrogen peroxide, in presence of sodium benzenesulphonate, *p*-toluenesulphonate, and *p*-ethylbenzenesulphonate. The Traube coefficient is in these cases about 3.

The capillary activity of a substance is a deciding factor in its cataphoretic and coagulative influence.

H. F. GILLBE.

Cataphoresis and [electric] charge. H. R. KRUYT and P. C. VAN DER WILLIGEN (Z. physikal. Chem., 1927, **130**, 170—176).—The velocity of cataphoresis of sols of arsenious and mercury sulphides is increased by the addition of univalent cations and lowered by that of multivalent cations, effects which continue nearly to the precipitation concentration. The results are discussed in relation to Powis' theory of critical potential (A., 1916, ii, 521), which they do not necessarily contradict. L. S. THEOBALD.

Association in liquids. [EARL OF] BERKELEY (Nature, 1927, **120**, 840—841).—A device which might be applied to the investigation of association in liquids is described. If a liquid is contained in a tubular cell closed at the top by a semi-platinised plate and at the bottom by a mirror, the cell being mounted as a centrifuge, the system of interference rings centred about the vertical axis will, on rotation of the cell, move across the field of view. A knowledge of the number of rings and the rate at which they pass would give insight into the changes in the " optical density " of the liquid.

A. A. ELDRIDGE.

Equilibrium between the methoxide and hydroxyl ions in mixtures of methyl alcohol and water. I. (FRL.) A. UNMACK (Z. physikal. Chem., 1927, **129**, 349—369).—From conductivity, solubility, and reaction velocity measurements the equilibrium constant K' of the reaction $OH'+MeOH \rightleftharpoons OMe'+H_2O$ has been calculated from the equation $K'=[OH']a_1/[OMe']a_2$, in which a_1, the activity of the methyl alcohol, and a_2, the activity of the water, are obtained from vapour-pressure measurements. From the conductivity determinations $K'=0{\cdot}35$, and from solubility measurements, 0·20, the concentrations being in mol./litre. The constant is somewhat dependent on the ionic concentration and on the ratio of the concentrations of methyl alcohol and water. H. F. GILLBE.

Acid dissociation of aquo-ions. J. N. BRÖNSTED and C. V. KING (Z. physikal. Chem., 1927, **130**, 699—708).—The acidity of a positive aquo-ion such as the hexa-aquochromic ion is governed by a dissociation of the type $[Cr(H_2O)_6]^{+++} \rightleftharpoons \left[\begin{matrix} OH \\ Cr(H_2O)_5 \end{matrix}\right]^{++} + H^+$. The variation with concentration of the acid–base dissociation constant K_c is in agreement with the theoretical equation $\log K_c = \log K_a - z_0\sqrt{\mu} - B\mu$, where μ is the ionic strength, K_a the acid dissociation constant, and z the valency of the ion. K_c for the hexa-aquochromic ion, determined by measurement of the velocity of hydrolysis of ethyl diazoacetate in presence of hexa-aquochromic picrate and perchlorate, at 15° and infinite dilution, is $1{\cdot}26\times10^{-4}$.

H. F. GILLBE.

Activity of weak acids in aqueous sulphate solutions. M. RANDALL and C. F. FAILEY (J. Amer. Chem. Soc., 1927, **49**, 2678—2681).—From measurements of the distribution of mono- and di-chloroacetic acids between magnesium sulphate solutions and di-*n*-butyl ether at 25°, the " activity coefficient " of each acid, defined as the ratio of the molality in pure water to that in a salt solution of a given activity, is shown to diminish by an amount which is larger the greater the dissociation constant of the acid. This agrees with the assumption that the stronger acid forms the larger amount of hydrogen sulphate ion. Potassium sulphate lowers the " activity coefficient " to a greater extent than magnesium sulphate (cf. Randall and Langford, A., 1927, 729).

S. K. TWEEDY.

Hydrogen-ion concentration of saturated solutions of calcium carbonate and hydrogen carbonate in water. J. W. WILLIAMS and J. A. CHUCKA (J. Amer. Med. Assoc., 1927, **89**, 445—446).—The p_H value at 25° of calcium carbonate suspensions, determined with the hydrogen electrode, was 8·64—8·86 (average 8·78); that of calcium hydrogen carbonate solution, determined with the quinhydrone electrode, was 5·98 in presence of excess of carbon dioxide, and 6·19 otherwise.

CHEMICAL ABSTRACTS.

Application of Ghosh's theory to complex compounds. A. GRÜNBERG (Ann. inst. platine [Russia], 1926, **4**, 276—298).—Conductivity measurements for many complex cobalt and platinum salts are in accord with Ghosh's theory, but the compounds $[Pt(NH_3)_4Cl_2](NO_3)_2$, $[Co(NH_3)_5NO_2]Br_2$, and $[Co(NH_3)_5NO_2](NO_2)_2$ give high values on account of hydrolysis. Sources of variation are discussed.

CHEMICAL ABSTRACTS.

Mol. wt. determination of saturated vapours from pure liquids and mixtures by the method of displacement by a current of air. M. S. VREVSKI (J. Russ. Phys. Chem. Soc., 1927, **59**, 593—597).—A method for determination of mol. wt. of saturated or dissociated vapours has been devised in which a current of air is passed through the volatile liquid instead of the vapours displacing air as in Victor Meyer's method. A. RATCLIFFE.

Dissociation of acetic acid vapour and the equilibrium between a solution of acetic acid and its vapour. M. S. VREVSKI, K. MISCHTSCHENKO, and B. MUROMCEV (J. Russ. Phys. Chem. Soc., 1927, **59**, 598—607).—The pressure and density of the saturated vapour of acetic acid obtained by the method of displacement by a current of air agree with the equation of Gibbs at temperatures between 30° and 90°. This also applies to acetic acid solutions. The partial pressures of (AcOH) and $(AcOH)_2$ in the vapour have been calculated. A. RATCLIFFE.

Dissociation of the vapour of formic acid and the equilibrium between a solution of formic acid and its vapour. M. S. VREVSKI and A.

Glagoleva (J. Russ. Phys. Chem. Soc., 1927, **59**, 608—616).—The saturated vapour of formic acid at temperatures between 25° and 80° and the vapour of formic acid solutions at 60° and 80° are found to obey Gibbs' law. The number of associated molecules in the vapour of a formic acid solution of a given concentration decreases with rise of temperature, but the percentage of water in the vapour phase is increased. A. Ratcliffe.

Equilibrium between solutions of formic acid in benzene and the vapour phase. M. S. Vrevski, N. Held, and G. Schukarev (J. Russ. Phys. Chem. Soc., **59**, 1927, 617—630).—By studying the composition of the vapour and vapour pressures of a solution of formic acid in benzene at temperatures below 73·2° at which two layers exist, it is shown that this system belongs to group IV according to the two-layer system classification of Rosenbum and Büchner ("Die Heterogenen Gleichgewichte," 1918). Further, at 71° the system changes from group IV to group III. The densities and partial pressures at 59·96° and 25° are in agreement with Gibbs' law. The proportion of double molecules in the vapour increases rapidly with rise of temperature.

A. Ratcliffe.

Distribution of a base (sodium hydroxide) between two acids (nitric and hydrochloric) in saturated aqueous solutions. V. I. Nikolaev (J. Russ. Phys. Chem. Soc., 1927, **59**, 677—684).—Analyses of solutions saturated with respect to sodium nitrate and sodium chloride at temperatures between 15° and 210° show that with rise of temperature or with an excess of the base or the free acids in solution nitric acid takes up in every case more of the base than hydrochloric acid. It is possible that heats of dissolution of the base, acids, and products of the reaction as well as the presence of water have an influence on the distribution of the base between the acids in a saturated solution. A. Ratcliffe.

Molecular volume of water in metal salt hydrates. E. Moles and M. Crespi (Z. physikal. Chem., 1927, **130**, 337—344; cf. Moles, A., 1926, 336).—A determination of the molecular volumes of the hydrates of manganous, ferrous, cobalt, nickel, copper, and zinc sulphates shows that the volume of the first water molecule lies between 10 and 11, whilst that of the remaining molecules is about 14·6. Nickel sulphate monohydrate forms an exception, the molecular volume being abnormally high. The results are in accord with the Werner co-ordination theory, but they lead to the conclusion that the first, not the seventh, water molecule is united with the anion. The molecular volumes of the following hexa-aquochromic salts have also been determined: potassium chrome alum, violet chromic sulphate, violet chromic tetrasulphate, violet chromic chloride, and violet chromic chlorosulphate. The same relations are found to hold as for the sulphates of bivalent metals. The hexa-aquosulphates are formulated as follows: $[Cr(H_2O)_6]_2(SO_4 \cdot H_2O)_3,2H_2O$, $K[Cr(H_2O)_6](SO_4 \cdot H_2O,SO_4),5H_2O$, and $H[Cr(H_2O)_6](SO_4 \cdot H_2O)_2$. The values 52 and 51·6, calculated for the molecular volume of the mono-aquosulphate anion from data for the two series of sulphates, are in good agreement with the value 54 calculated for H_2SO_4,H_2O at 0° Abs.

L. L. Bircumshaw.

System ethyl alcohol–carbon tetrachloride. S. F. Calhoun and T. C. Poulter (Proc. Iowa Acad. Sci., 1926, **33**, 169).—The total and partial vapour pressures of the system ethyl alcohol–carbon tetrachloride were determined at 25° and 60°. An apparatus for the determination of vapour pressures of substances which do not readily react with mercury was designed. Chemical Abstracts.

System magnesium sulphate–water from 68° to 240°. H. L. Robson (J. Amer. Chem. Soc., 1927, **49**, 2772—2783).—The solubility of magnesium sulphate monohydrate, determined in a special solubility bomb, decreases rapidly as the temperature rises to 200°, and then slowly up to at least 238°. Étard's measurements probably fall on the supersaturation curve (A., 1894, ii, 442). The solubilities of the hexa-, penta-, and tetra-hydrates were measured at 85°, 95°, and 100°; optical and crystallographic properties of all the hydrates are recorded and the methods of preparation are discussed. It is suggested that the rate at which a salt approaches equilibrium with its aqueous solution is related to its degree of crystallographic perfection. S. K. Tweedy.

Boundaries of the heterogeneous region of cadmium amalgams. A. L. T. Moesveld and W. A. T. de Meester (Z. physikal. Chem., 1927, **130**, 146—153).—The liquidus curve for the cadmium amalgams has been determined by measurements of the *E.M.F.* of homogeneous liquid amalgams at six temperatures in the range 0—41°. The change in composition (concentration) of the liquid with temperature can be represented by the equation $C = 2{\cdot}855 + 0{\cdot}0954t + 0{\cdot}00128t^2$. The solidus curve could not be determined in a similar manner. Exact data for the latter are unknown, and former determinations, which are only approximate, may be uncertain on account of the slowness with which equilibrium is established in solid amalgams. A 10% amalgam is recommended for use in the Weston cell.

L. S. Theobald.

Thermal dissociation of strontium carbonate. E. O. Jones and M. L. Becker (J.C.S., 1927, 2669—2676).—Two different forms of apparatus are described for the measurement of dissociation pressures. Between 650° and 1100°, the observed values for strontium carbonate lie on a curve of the same form as that found by others for calcium and barium carbonates, viz., $\log p_1 - \log p_2 = -K(1/T_1 - 1/T_2)$, K for strontium being taken as $1{\cdot}05 \times 10^4$ and the dissociation tension at 928° as 10 mm. The curve lies wholly between those of the other two carbonates. The temperature at which the dissociation pressure is 1 atm. is, by extrapolation, 1258°, approximately 100° higher than those given by Brill (A., 1905, ii, 522) and Hedvall (A., 1917, ii, 208). Except for the extrapolated values at high temperatures, the authors' results are not in good agreement with those of Pott (Diss., Freiburg, 1905). Confirmation of the validity of the curve, especially at low temperatures, has been obtained, however, by using the carbonate to control the carbon dioxide tension in a study of the

C–CO–CO_2 equilibrium. The equilibrium constants thus determined for the system at different temperatures lie closely on Tigerschiöld's curve (Jernkontoret's Annaler, 1923, 67). No evidence of the existence of a basic carbonate has been obtained. M. S. BURR.

Cause of formation of hair copper in copper mattes. (System : iron–copper–sulphur.) P. P. FEDOTÉEV [with D. N. NEDRIGAILOV] (Z. anorg. Chem., 1927, **167**, 329—340; cf. Tiedemann, B., 1926, 710).—The constitution of the system ferrous sulphide–cuprous sulphide has been investigated by thermal analysis and by microscopical examination, which latter leads to the conclusion that the two sulphides are only partly miscible in the solid state. The formation of hair copper in the system probably depends on the equilibrium $Cu_2S \rightleftharpoons Cu + CuS$, set up in solid solution. R. CUTHILL.

Phase diagram of sodium nitrate. N. S. KURNAKOV and V. J. NICKOLAJEV (Z. physikal. Chem., 1927, **130**, 193—204).—The ternary system Na_2O–N_2O_5–H_2O has been investigated by measurements of solubility and of the density of the saturated solutions at 25° and 65°. L. S. THEOBALD.

Equilibrium in the system $CuSO_4$–Na_2SO_4–H_2O at 0°, 25°, and 37·5°. R. M. CAVEN and W. JOHNSTON (J.C.S., 1927, 2902).—An error in a previous paper (cf. A., 1927, 1142) is corrected. O. J. WALKER.

System potassium carbonate–sodium carbonate–water at 40° ; trihydrate of sodium carbonate. J. W. BAIN (J. Amer. Chem. Soc., 1927, **49**, 2734—2738).—The existence of sodium carbonate trihydrate is demonstrated; it is converted into monohydrate with evolution of heat at 39·8°. The recorded data for the solubility of sodium carbonate at 40°, and for some unknown temperature range above this, refer to solutions in equilibrium with the metastable monohydrate and require revision (cf. Bain, A., 1925, ii, 577; Hill and Miller, A., 1927, 418). S. K. TWEEDY.

System mercuric iodide–potassium iodide–water. (MLLE.) M. PERNOT (Compt. rend., 1927, **185**, 950—953).—Measurements at 20°, 34°, and 80° by the method of Schreinemakers indicate the existence of the compound HgI_2,KI,H_2O. The compounds described by other workers may be mixtures of the above with potassium iodide. J. GRANT.

System $FeCl_2$–$NiCl_2$–H_2O at 25°. Y. OSAKA and T. YAGINUMA (Z. physikal. Chem., 1927, **130**, 480—481).—Two series of solid solutions are formed. Ferrous chloride (with $4H_2O$) is saturated when 10·6% of the metal is replaced by nickel, and nickel chloride (with $6H_2O$) is saturated when 65·6% of the metal is replaced by iron. The liquid phase in equilibrium with the two saturated solid solutions has the composition $FeCl_2$ 21·60, $NiCl_2$ 19·36, H_2O 59·04%. R. W. LUNT.

Ternary system manganous phosphate–phosphoric acid–water, and the manganodiphosphoric acids. G. GRUBE and M. STAESCHE (Z. physikal. Chem., 1927, **130**, 572—583).—Transport measurements indicate that solutions of manganous phosphate in concentrated phosphoric acid contain a complex manganese anion. The formula of the acid, as determined by observation of the isotherms of the system $Mn_3(PO_4)_2$–H_3PO_4–H_2O at 25° and 55°, is $H_4Mn(PO_4)_2,3H_2O$. Tripotassium hydrogen manganodiphosphate pentahydrate and sodium dihydrogen manganodiphosphate tetrahydrate are stable red crystalline salts. The free acid forms almost colourless crystals which on dissolution in water gradually precipitate the sparingly soluble manganous phosphate, $Mn_3(PO_4)_2,2H_2O$. Over concentrated sulphuric acid the trihydrate of the acid loses two molecules of water. The only stable compounds existing between 25° and 55° in presence of phosphoric acid at various concentrations are anhydrous manganous phosphate and manganous hydrogen phosphate, and $H_4Mn(PO_4)_2,3H_2O$. H. F. GILLBE.

Reciprocal system : water, sodium chloride, magnesium sulphate, magnesium chloride, sodium sulphate. A. KÜPPER (Caliche, 1927, 8, 467—487).—The isotherms of this system from 0° to 83° are described and figured, and solubility tables are given from 0° to 100° for each of the salts. CHEMICAL ABSTRACTS.

Quaternary system : water, sodium nitrate, sodium chloride, sodium sulphate, between 100° and 0°. A. CHRETIEN (Caliche, 1926, 8, 390—408).—Graphs and tables are given. At 68·5° the solution is saturated with respect to chloride, nitrate, anhydrous sulphate, and darapskite, $Na_2SO_4,NaNO_3,H_2O$. Darapskite is not formed above 68·5° when the solution is saturated with sodium chloride. Above 78·5° the sulphate is anhydrous, and below 7·2° is present as decahydrate in contact with solutions saturated also with nitrate and chloride only. At 16° there are four solid phases: chloride, darapskite, anhydrous sulphate, and sulphate decahydrate. CHEMICAL ABSTRACTS.

System $FeCl_3$–$AlCl_3$–H_2O at 25°. G. MALQUORI (Gazzetta, 1927, **57**, 665—665).—Neither double salts nor mixed crystals are formed. R. W. LUNT.

System $AlCl_3$–KCl–HCl–H_2O at 25°. G. MALQUORI (Gazzetta, 1927, **57**, 661—662).—Neither additive compounds nor mixed crystals are formed; the fractional crystallisation of aluminium and potassium chlorides is readily carried out in the presence of 10% of hydrogen chloride. R. W. LUNT.

System $Al(NO_3)_3$–KNO_3–$Fe(NO_3)_3$–H_2O at 25°. G. MALQUORI (Gazzetta, 1927, **57**, 663—664).—This system shows neither double salt nor mixed crystal formation. R. W. LUNT.

High-temperature equilibrium between thorium oxide and carbon. C. H. PRESCOTT, jun., and W. B. HINCKE (J. Amer. Chem. Soc., 1927, **49**, 2744—2753).—The equilibrium $ThO_2 + 4C$ (graphite) $= ThC_2 + 2CO$ was investigated between 2000° and 2500° Abs. in a graphite furnace. The equilibrium pressures are given by $\log_{10}p$ (atm.)$=8·069—19,325/T$, from which $\Delta F=176,970-73·89T$ and $\Delta H=176,970$ g.-cal./mol. at 1 atm. The heat of formation of thorum carbide is $\Delta H=-78,930$ g.-cal./mol.; its m. p. is very close to 2773° Abs. S. K. TWEEDY.

High-temperature equilibrium between aluminium oxide and carbon. C. H. Prescott, jun., and W. B. Hincke (J. Amer. Chem. Soc., 1927, **49**, 2753—2759).—The equilibrium pressures for the reaction $2Al_2O_3+9C=Al_4C_3+6CO$ between 2000° and 2300° Abs. are given by : $\log_{10}p$ (atm.) $=8\cdot21-18{,}480/T$, whence $\Delta F=507{,}760-225\cdot6T$ and $\Delta H=507{,}760$ g.-cal./mol. at 1 atm. ; the heat of formation and free energy of formation of aluminium carbide at 25° are $-60{,}260$ g.-cal. and $-53{,}240$ g.-cal., respectively. Berthelot obtained $-220{,}830$ g.-cal. for the former figure. S. K. Tweedy.

Saturation of sugar–lime solutions. II. A. H. W. Aten, P. J. H. van Ginneken, and E. Verwey (Z. physikal. Chem., 1927, **130**, 365—377; cf. A., 1912, i, 9).—Experiments on the saturation of sugar–lime solutions by carbon dioxide are recorded. The influence of time, temperature, and the composition of the original solution has been investigated, and curves are given showing the relation of R to N under different conditions, R being the degree of saturation of the solution (or the ratio of the absorbed carbon dioxide to the normality of the original solution), and N the ratio of the normality of the filtrate to that of the original solution. From dilute solutions (up to about 0·7 mol. of sugar $+N$CaO) a basic precipitate separates when R is $>0\cdot5$, which can be represented by the formula $3CaO,2C_{12}H_{22}O_{11},xCaCO_3$. The value of x increases with R, and for precipitates formed at the ordinary temperature is greater than 8. The precipitate changes slowly (more rapidly on shaking) with the formation of a hydrate of calcium carbonate, $CaCO_3,6H_2O$. From stronger sugar–lime solutions, *e.g.*, 0·7 mol. of sugar $+1\cdot7N$CaO, a second strongly basic precipitate is formed when $R=0\cdot1$—$0\cdot3$. The composition of this varies from $6CaO,3C_{12}H_{22}O_{11},CO_2$ to $6CaO,3C_{12}H_{22}O_{11},2CO_2$. The separation of each precipitate is a reversible process, that from more concentrated solutions passing into solution on warming and reappearing on cooling, whilst that from more dilute solutions is less soluble at higher temperatures than at the ordinary temperature. The conductivity of the saturated solution undergoes a marked decrease with time, and from a consideration of the data it appears that the solution contains complexes of the composition $xCaCO_3,yCa(OH)_2,zC_{12}H_{22}O_{11}$, where $x/y=0\cdot5$—2. The experimental results are discussed, with special reference to the probable influence of the sugar on the formation and composition of the precipitates. L. L. Bircumshaw.

Hydrolysis of compounds which may occur in Portland cement. W. Lerch and R. H. Bogue (J. Physical Chem., 1927, **31**, 1627—1646).—The hydrolysis of the compounds $3CaO,SiO_2$, $3CaO,Al_2O_3$, β-$2CaO,SiO_2$, $5CaO,3Al_2O_3$, γ-$2CaO,SiO_2$, and $2CaO,Fe_2O_3$ in the pure state has been investigated at the ordinary temperature but without reference to the conditions which obtain in cement mortars and concretes. In each case, the compound is hydrolysed and an equilibrium is reached. The order in which the compounds give up lime, in decreasing amount, is that given above, and the times required for equilibrium to be reached are, aluminates, 1 day, tricalcium silicate, 8 days, and the remaining compounds, 12 days. The hydroxyl-ion concentrations necessary to prevent hydrolysis are, respectively, in terms of p_H, —, 12·3, 13·7, 11·7, —, and 13·0 for the compounds in the above order. When the soluble products are removed from the system, the silicates, aluminates, and ferrite hydrolyse eventually to hydrous silica, hydrous alumina, and hydrous ferric oxide, respectively. When the soluble products are not removed, hydrolysis proceeds with the formation of calcium hydroxide and a silicate, aluminate, or ferrite, which is less basic, the composition of this component being dependent on the concentration of hydroxyl ion and the amount of available water.
L. S. Theobald.

Equilibria in systems in which phases are separated by a semipermeable membrane. XXIII. F. A. H. Schreinemakers (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 635—642).—A further discussion of the influence of temperature and pressure on osmotic equilibria (see A., 1927, 1142).

Reaction regions. XVI. $(NH_4)_2Cr_2O_7$–K_2SO_4–KCl and $(NH_4)_2Cr_2O_7$–Fe–S. W. P. Jorissen and G. M. A. Kayser (Z. physikal. Chem., 1927, **130**, 482—487).—Data are given, and expressed graphically, for the limits of composition within which reaction takes place when induced by a burning magnesium ribbon in the above systems.
R. W. Lunt.

Heat of mixing of metals. M. Kawakami (Z. anorg. Chem., 1927, **167**, 345—363).—The heat of mixing of a number of pairs of the following metals in the molten state and in various proportions has been measured : mercury, potassium, sodium, tin, cadmium, bismuth, zinc, lead, and antimony. Where no compound formation occurs, the heat of mixing is, in general, negative, but in cases where compounds are known to be formed the heat effect is positive. It therefore appears probable that intermetallic compounds which can exist in the solid state do not dissociate on fusion. R. Cuthill.

Temperature effects of mixing non-aqueous liquids. W. M. Madgin, J. B. Peel, and H. V. A. Briscoe (J.C.S., 1927, 2873—2877).—A consideration of the data previously obtained (A., 1927, 521), relating to the thermal effects occurring on mixing a number of pairs of non-aqueous liquids, makes it evident that these changes are not related to the polarity of the liquids as indicated by their dielectric constants. The effect of variation of initial temperature on the temperature change on mixing has been determined for a series of twelve mixtures in which the temperature change varies from a large positive to a large negative value. The variation of the change with the initial temperature is always in the same direction, *i.e.*, it becomes more positive or less negative the lower the initial temperature. The effect may be explained by assuming that the two liquids contain associated molecules which dissociate on mixing and combine with one another to form compound molecules, the first process being endothermic. Alteration of the initial temperature changes the thermal effect of the reactions, and also the positions of equilibria. M. S. Burr.

Heat of dissolution of potassium nitrate in water. W. A. Roth (Z. physikal. Chem., 1927, **130**, 539—544).—Measurements of the solubility of potassium nitrate in water confirm the evidence for the existence of two modifications given by crystallographic and thermal data. The heat of dissolution in 350 mols. of water at 20·5° is −8·518, and in 460 mols., −8·367 kg.-cal. These values do not alter with time. Intermediate values gradually change with time, owing probably to the presence of two modifications. The heat of transition from one form to the other is 0·15 kg.-cal. H. F. Gillbe.

Heat of formation of zinc oxide. G. S. Parks, C. E. Hablutzel, and L. E. Webster (J. Amer. Chem. Soc., 1927, 49, 2792—2795).—The molal heat of dissolution of zinc oxide in 2·633*N*-hydrochloric acid is −15,263 g.-cal. (15°) at 20°. Combination of this result with the heat of dissolution of zinc in acid of the same concentration (Richards and Burgess, A., 1910, ii, 391) gives 83,240 ± 200 g.-cal. for the heat of formation of zinc oxide at 20°. S. K. Tweedy.

Calculation of heats of combustion. J. E. Snyder (J. Amer. Chem. Soc., 1927, 49, 2806—2807; cf. Kharasch and Sher, A., 1925, ii, 636).—The heat of combustion, in kg.-cal./mol. at constant pressure, of aromatic compounds containing carbon and hydrogen with or without oxygen is given by $26{\cdot}05\lambda+24{\cdot}85\mu+y$, where μ and λ represent the number of μ and λ electrons in the compound (Pauling, A., 1926, 662) and y is a term represented by 13 for each ethylenic linking and 22·7, 19·5, 13, 13, 6·5, 3·2, and 3·2, respectively, for the ether, aldehyde, primary alcohol, ester, secondary alcohol, phenol, and tertiary alcohol groups. The carboxyl and ketone groups do not influence y. The average difference between the calculated and experimental values is 0·37%. S. K. Tweedy.

Calorimetric method for determination of the coefficient of absorption of radium β-rays. D. K. Yovanovitch (Arh. Hemiju, 1927, 1, 206—212).—The heat changes accompanying the absorption by aluminium, copper, or lead of the α- and β-radiation of radium are respectively 129·0 and 13·4 g.-cal./hr.; the coefficient of absorption of β-rays is 51·02. R. Truszkowski.

Transference numbers and degree of solvation of the ions of lithium chloride in certain alcohols. J. N. Pearce and W. G. Eversole (Proc. Iowa Acad. Sci., 1926, **33**, 151—164).—The true and ordinary transference numbers of lithium ions in solutions of lithium chloride in methyl, ethyl, and *n*-propyl alcohols have been determined with camphor as the reference substance. In a given solvent these values and the degree of solvation decrease as the concentration of the salt is increased; for a fixed concentration the degree of solvation decreases as the complexity of the solvent molecule increases. Chemical Abstracts.

Correction of conductivity data for the conductivity of the solvent. W. F. K. Wynne-Jones (J. Physical Chem., 1927, **31**, 1647—1662).—A solvent correction can be applied to conductivity data in water, methyl and ethyl alcohols, on the assumption that the impurity present is carbon dioxide, which is probably to be found even in the most highly purified solvents. The effect on conductivity data in any solvent will be determined by its solubility therein and by the type of compound formed. When the concentration and characteristics of the latter are known, the appropriate correction can be applied by the methods now described. When this is not the case, the correction can be applied if the law followed is known, although this method is less desirable than those mentioned above. In the case of aqueous solutions, the nature of the cell is of greater importance than the conductivity of the water, when strongly acid or alkaline solutions are employed at high dilutions. L. S. Theobald.

Molecular structure in solution. III. Electrical conductivities of aqueous solutions of cobalt chloride and hydrochloric acid. Prediction of crystal structure. O. R. Howell (J.C.S., 1927, 2843—2850).—The electrical conductivities of a series of solutions containing a constant amount of cobalt chloride with increasing concentrations of hydrochloric acid have been determined and compared with those of a similar series for hydrochloric acid alone. By plotting the differences in the values for corresponding solutions against concentration of acid, a curve is obtained which exhibits a pronounced minimum at the same concentration of acid as that which gives a maximum on the viscosity-difference curve previously obtained (A., 1927, 205). Its general form may be accounted for on the theory originally put forward (*loc. cit.*), viz., that, with increasing acid concentration, the hydrated cation, $Co(H_2O)_6^{\cdot\cdot}$, is progressively converted into the anion $CoCl_4''$. The conductivity-difference curve falls sharply to the minimum, whilst the viscosity-difference curve falls slightly before rising to the maximum. This is due to the initial depression of ionisation of cobalt chloride by addition of acid. The conductivity decrease is aided by reduction of ionisation, but the viscosity increase is checked, because of the decrease in the number of viscous $Co(H_2O)_6^{\cdot\cdot}$ ions. For the same reason there are similar resemblances and differences between the curve obtained by plotting concentration of acid against difference of specific resistance, instead of conductivity, and those showing differences of refractive index and density (A., 1927, 1136). The structure of zinc and magnesium orthosilicates, and of cobalt oxide and fluoride, originally predicted from the theory of the colour of cobaltous compounds (A., 1924, ii, 817), has since been confirmed by other methods. M. S. Burr.

Thickness of the Helmholtz double layer. J. F. McClendon (Science, 1927, 66, 200).—The thickness of the double electric layer around colloid particles is considered by Gouy to be of dimensions greater than molecular. The surface of a charged metallic electrode, immersed in a solution of an electrolyte, and the layer of excess ions of opposite sign act as the plates of a condenser, the capacity of which can be measured, whence the thickness of the Helmholtz double layer can be calculated. Using gold electrodes the values for 0·1*N*- and 0·001*N*-

solutions, respectively, were 0·194 and $0{\cdot}325\times10^{-6}$ cm. The former value is in fair agreement with Gouy's value, and the change, as for Gouy's values, is in the direction of increase of thickness with dilution of the electrolyte. A. A. ELDRIDGE.

Theory of the hydrogen electrode. F. LEUTHARDT (Helv. Chim. Acta, 1927, **10**, 888—896).—The importance of considering the solubility of hydrogen in the aqueous medium when making measurements with the hydrogen electrode is emphasised. If γ_0 is the solubility in a standard solution and γ that in the medium under examination, the correction to apply to the observed *E.M.F.* is $\Delta\pi=RT/2F\,.\log_e\gamma_0/\gamma$. Measurements with the cells $H_2|HClc|HClc$, aqueous solution of glycerol$|H_2$ yield values in good agreement with this expression. Further support is afforded by measurements of similar cells, with and without glycerol, in which one electrode was maintained at a constant temperature whilst the temperature of the other was varied. Values of $\Delta\pi$ for solutions of hydrochloric acid, potassium chloride, acetic acid, glycerol, and ethyl alcohol at various concentrations are tabulated. These values are fairly large; *e.g.*, for 1·0, 2·0, and 4·0*N*-solutions of potassium chloride the values of $\Delta\pi$ at 15° are 2·5, 5·4, and 10·3 millivolts, respectively.

J. S. CARTER.

Effect of neutral salts on potential of hydrogen electrode. III. J. PRZEBOROVSKI and M. FLEISSNER [with T. POPOWA] (Z. anorg. Chem., 1927, **167**, 364—368; cf. A., 1924, ii, 87).—The potential of a hydrogen electrode in a solution of hydrogen bromide is increased by the presence of the chlorides or bromides of potassium, sodium, or lithium. In general, the bromides have a greater effect than the corresponding chlorides, the lithium salts have the greatest effect, and the potassium salts the least, the results as a whole pointing to a close connexion between the neutral salt effect and hydration. With addition of increasing amounts of ethyl alcohol to a solution of sulphuric acid, the potential of a hydrogen electrode immersed in the solution first decreases, then passes through a minimum, and finally rises again, and in presence of alcohol the neutral salt effect is less than it is in solutions containing no alcohol. R. CUTHILL.

Apparent potential of dextrose solutions. R. WURMSER (Compt. rend., 1927, **185**, 1038—1041).—Platinum or gold electrodes in a buffered 3% solution of dextrose at 40° attain potentials which are equal for the two metals, but the potential and the rate at which it is developed depend on the nature of the buffer and on the p_H value. The final value (E) is given (with respect to the normal hydrogen electrode), for a 0·1*M*-phosphate buffer mixture, by the relation, $E=0{\cdot}489-0{\cdot}086p_H\pm0{\cdot}002$ volt. At p_H 7·5 $E=-0{\cdot}147$ volt, which is near the value obtained for lævulose (A., 1927, 316). The presence of a dye (methylene-blue, phenosafranine, or Janus-green) lowers or raises the potential according as it is present in the oxidised or reduced state. For $p_H>10$ the limiting potentials are not constant, owing to the partial utilisation in side reactions of the hydrogen liberated. J. GRANT.

Simple type of flowing junction. E. J. ROBERTS and F. FENWICK (J. Amer. Chem. Soc., 1927, **49**, 2787—2791).—The two streams of solution play on opposite sides of a vertical mica strip and flow down wax channels past a small hole in the strip. A constant *P.D.* is attained in a few seconds. The observed *P.D.* between 0·1*M*-hydrochloric acid and 0·1*M*-potassium chloride solutions agrees fairly well with that obtained by MacInnes and Yeh (A., 1922, ii, 252) and is in accord with the value calculated from Lewis and Sargent's equation. S. K. TWEEDY.

Cells with identical unchangeable electrodes. V. KARPEN (Compt. rend., 1927, **185**, 942—944).—The experiments previously described (A., 1927, 1144) have been extended to other types of unattackable electrodes and analogous results obtained. The *E.M.F.* is lower in an atmosphere of hydrogen, but is unaltered in oxygen. Cells with such electrodes (*e.g.*, carbon or platinum) in an aqueous solution of sodium hydroxide and in an immiscible liquid (*e.g.*, amyl alcohol) give potentials of the order of 0·5 volt, the electrode in the aqueous layer being negative.

J. GRANT.

Contact resistance between electrodes and electrolytes. O. SCARPA and E. DENINA (Z. Physikal. Chem., 1927, **130**, 449—471).—Since the sum of all the potentials in a circuit comprising a source of *E.M.F.* and an electrolyte containing two electrodes is zero, the following expression obtains: $V-ir-E^+-E^--e^+-e^--i\rho^+-i\rho^-=0$, where V is the *E.M.F.* of the source, i the current, E^+ and E^- are the *E.M.F.* of polarisation at the electrodes, e^+ and e^- the contact potentials between the electrodes and the electrolyte, and ρ^+ and ρ^- the contact resistance between electrodes and electrolyte. The difficulties associated with the determination of E^+, E^-, e^+, and e^- have been avoided by the use of a double electrode which may be either cathode or anode. From measurements of the resistance of the electrolyte from one member of the double electrode to the other values have been obtained for the apparent contact resistance. These measurements have been carried out by an alternating-current bridge method, a small alternating current passing through the electrolyte between the two members of the double electrode, precautions being taken to ensure that these were at the same potential. Values of the apparent contact resistance per sq. cm. of electrode surface have thus been obtained for a wide range of continuous currents flowing through the electrolyte from the double-membered electrode to the other electrode. The data refer to the following: anodes and cathodes of nickel, copper, retort carbon, lead, gold, silver, soft and electrolytic iron, graphite, and platinised platinum in sodium hydroxide solution and in sulphuric acid solution. It is shown that the contact resistance so determined is a function of the degree of polarisation of the electrodes, of the nature of the electrodes and of the electrolyte, of the current density, of the duration of the polarisation, of the physical state of the electrode surface, and of the temperature. R. W. LUNT.

Effects of uneven distribution of current density over an electrode. E. S. HEDGES (J.C.S., 1927, 2710—2711).—In electrolysis the current tends to concentrate at the edges and corners of a rectangular electrode, and all dependent phenomena follow the same course, *e.g.*, film formation, corrosion, or metallic deposition. Curious effects are observed with easily passivated metals. The inside of an anode may become passive and the outside active, the lower portion of the outside passive and the upper active near the liquid line, or only the corners and edges of an electrode may be passive. The inside of a cobalt electrode sometimes dissolves to give a solution of green cobaltic ions, whilst on the outside a pink cobaltous solution is formed. Periodic phenomena have been observed, but they do not consist of an alternation of the active and passive regions as required by Adler's theory (A., 1912, ii, 891). In fact they do not differ from those observed at higher current densities when the whole surface of the electrode becomes alternately active and passive. In addition, electrodes have been examined which, although differentiated into active and passive zones, do not dissolve periodically. M. S. Burr.

Flame and combustion. W. A. Bone and D. T. A. Townend (Nature, 1927, **120**, 880).—Polemical. A. A. Eldridge.

Ignition of natural gas–air mixtures by heated metal bars. H. F. Coward and P. G. Guest (J. Amer. Chem. Soc., 1927, **49**, 2479—2486).—Wide metal bars ignite mixtures of natural gas (93·2% of methane) and air more readily than narrow bars, and metals of greater catalytic effect must be much hotter than those of smaller catalytic effect. This temperature difference may attain several hundred degrees. For nickel, tungsten, and certain steels the ignition temperature rises regularly with increasing natural gas content, although for platinum the most violently explosive mixtures require the highest temperatures. Iron bars did not give reproducible results. Catalytically active solid surfaces tend to raise the ignition temperature of the mixture; nickel exhibits definite catalytic action as compared with silica. Moderate turbulence brings inflammable gas into the zone of burnt-out mixture and this raises its temperature (possibly to the ignition point) when it is near to, but not on, the heated surface.

S. K. Tweedy.

Thermal decomposition of ozone. E. H. Riesenfeld and W. Bohnholtzer (Z. physikal. Chem., 1927, **130**, 241—276).—The thermal decomposition of ozone in the dark has been investigated using a Warburg differential manometer. The values of the concentration, c, and of the velocity of decomposition, $\Delta c/\Delta t$, in mol. per litre were derived by graphical means. The decomposition of ozone in pure ozone–oxygen mixtures can be resolved into two reactions, one unimolecular and the other bimolecular. At a pressure of 400 mm. and a temperature of 90°, the velocity coefficients k_1 and k_2 of these reactions have the mean values $0{\cdot}488\times10^{-2}$ and 2·30, respectively, and at 99·5°, the values $0{\cdot}673\times10^{-2}$ and 6·34. These are maximal values for the limiting velocity of decomposition, *i.e.*, the decomposition obtained when accelerators of the reaction are excluded. The bimolecular reaction is independent of pressure, but the unimolecular reaction is inversely proportional to the total pressure prevailing at a given time. The temperature coefficient between 90° and 100° for the unimolecular reaction is 1·8 and for the bimolecular reaction 2·94; near 90°, the velocity of decomposition can be expressed by the formula $\Delta c/\Delta t=(1{\cdot}8c\,.\,P^{-1})1{\cdot}8^{(t-90)/10}+(2{\cdot}30c^2)2{\cdot}93^{(t-90)/10}$, where P is the total pressure in mm. of mercury and c is the concentration in mol. per litre. The values for the limiting velocity of decomposition agree with those of previous workers, and since this velocity is independent of the size, shape, and material of the reaction vessel, it is assumed that both reactions are of the homogeneous type. Traces of catalysts have a marked effect, a hundredfold increase being not unusual. Two types of catalysis have been observed, the one, as produced by dust particles, for example, proceeding as a unimolecular reaction, and the other, which is produced by gaseous organic substances, showing a high and uncertain order of reaction, explicable on the assumption that the catalyst is destroyed during the course of the reaction. The addition of carbon dioxide, nitrogen, helium, or argon accelerates the decomposition of ozone. The bimolecular reaction increases whilst the unimolecular reaction, in consequence of the increase in pressure, decreases. Referred to the same pressure of ozonised oxygen, the unimolecular reaction is retarded, but referred to the same total pressure it is accelerated.

L. S. Theobald.

Thermal decomposition of ozone. Computation of velocity coefficients determined by the manometric method. R. O. Griffith and A. McKeown (J. Amer. Chem. Soc., 1927, **49**, 2721—2729).—A reply to the criticism of Wulf and Tolman (A., 1927, 631). Velocity coefficients of the above reaction may be vitiated by incorrect interpretation of the observed pressure differences and by erroneous estimation of the pressure corresponding with total decomposition. Warburg's data (A., 1902, ii, 130) suffer slightly from the first error; Wulf and Tolman's data are vitiated more seriously by the second error, and Jahn's results (A., 1906, ii, 225) suffer very considerably from both errors. S. K. Tweedy.

Velocity of interaction of ions. F. G. Soper (J. Physical Chem., 1927, **31**, 1790—1797; cf. Brönsted and Livingston, A., 1927, 319).—Theoretical. The rate of interaction of ions can be represented by the equation $\log k=c+0{\cdot}66z_Az_Bu^{\frac{1}{2}}$, where k is the classical velocity coefficient, z_A and z_B are the valencies of the ions, and u is the ionic strength. The potential energy possessed by the ions in virtue of their charges is regarded as contributing to the critical increment of the reaction, and is evaluated on the Debye–Hückel theory. The velocity equation has been tested by determining graphically the value of the constant of the last term, using the data of other investigators for the reactions between the following pairs of ions: iodide and persulphate, formate and silver, hydroxyl and dibromosuccinate, iodide and iodate, and ferric and stannous. The average value of the constant is 0·62±0·13. L. S. Theobald.

Effect of shaking on the evolution of gases from supersaturated solutions and its importance for the measurement of the velocity of certain

chemical reactions. K. J. Pedersen (J. Amer. Chem. Soc., 1927, 49, 2681—2689).—The velocity of the unimolecular action of acid with sodium hydrogen carbonate (Faurholt, A., 1925, ii, 295) passes through a maximum as the number of horizontal shaking impulses given to the solution per minute is progressively increased; the length of each impulse also has an effect. The maximum is attributed to a kind of resonance effect on the motion of the liquid in the vessel. A mathematical expression for the velocity of evolution of gas during a reaction is derived and numerical examples illustrating its application are given. The importance of the results in avoiding the supersaturation error in certain reaction-velocity measurements is discussed (cf. Brönsted and King, A., 1925, ii, 1171). S. K. Tweedy.

Determination of the kinetics of excessively rapid reactions by separation of the reactions. E. Abel and R. Siebenschein (Z. physikal. Chem., 1927, **130**, 631—657).—Periodic acid does not react directly with iodides with the formation of free iodine, but is first reduced to iodic acid, which then reacts in the usual way with a further quantity of iodide. The kinetics of the reactions involved are discussed. H. F. Gillbe.

Kinetics of the addition of water to oxy-compounds. New hydrogen-ion catalysis. L. Smith, G. Wode, and T. Widhe (Z. physikal. Chem., 1927, **130**, 154—166).—The catalytic activity of nitric and perchloric acids in the addition of water to epichlorohydrin and to ethylene oxide has been investigated. Catalysis by the hydrogen ion takes place, the nature of the anion being of little importance in the first case. In aqueous solution the elements of hydrochloric acid quickly unite with epichlorohydrin, the reaction being of the third order, but with the other acids addition of water is much slower. Catalytic activity of the hydrogen ion is also shown in the case of trimethylene oxide and sulphuric acid. In all cases the addition of water in neutral solution is extremely slow. L. S. Theobald.

Decomposition of triethylsulphonium bromide in mixed solvents. R. F. Corran (Trans. Faraday Soc., 1927, **23**, 605—614).—The velocity coefficients of the unimolecular decomposition of triethylsulphonium bromide have been determined at 80° and 90° in mixtures of benzyl alcohol with toluene and glycerol, respectively. In general the reaction in organic solvents reaches practical completion, but in the mixtures containing glycerol an equilibrium was obtained and a correction for it applied to the velocity coefficients in these mixtures. The results show that the rate of decomposition is increased by toluene and decreased by glycerol. Both solvents, however, cause a fall in the apparent critical increments of activation as calculated from the temperature coefficients. This indicates anomalous behaviour on the part of the glycerol. The absorption spectra of the salt in various mixtures have been determined for the short infra-red region by the methods of Taylor and Lewis (J.C.S., 1922, **121**, 665), the radiomicrometer being replaced by a thermopile and Moll galvanometer. With the benzyl alcohol–toluene mixtures there is a shift in the position of the band head which is in satisfactory agreement with the alteration in the observed critical increment. For the glycerol mixtures the head of the band shifts towards the shorter wave-lengths, which is opposite to that calculated from the critical increment, but in the direction to be expected from the effect of glycerol on the velocity coefficient. Therefore the band head probably gives the true critical increment. No explanation of the anomaly can be given. Investigations on the velocity of decomposition in practically dust-free propyl alcohol solutions indicate that the dust ordinarily present has no appreciable influence (cf. Rice, A., 1926, 917). M. S. Burr.

Oxidation of organic molecules. II. C. Fromageot (J. Chim. phys., 1927, 24, 623—656; cf. A., 1926, 1124).—Acetaldehyde is slowly oxidised by ceric ions when the former is present in great excess. The oxidation may be attributed to a relatively small number of abnormally reactive molecules, consisting probably of hydrated vinyl alcohol, and the velocity of the reaction is conditioned by the speed of formation of these active molecules. Similar keto–enol tautomerism is indicated by a study of the ultraviolet absorption spectrum of pyruvic acid in aqueous solution at varying concentration and p_H. Ceric ions oxidise the ketone form instantaneously and the enol form more slowly but with the absorption of a larger amount of oxygen. There is no difference in the behaviour of the two forms towards thallic ions, the oxidation being much slower in this case. An approximate calculation of the proportions of the two forms present under various conditions has been made, and it is shown that the oxidation of the ketone form by ceric ions takes place in accordance with the equation $Ac{\cdot}CO_2H+0{\cdot}5O_2 \longrightarrow AcOH+CO_2$. Evidence is given of the formation of an intermediate complex between the ceric ions and the pyruvic acid. G. A. Elliott.

Mutarotation. III. Dextrose equilibria in methyl alcohol and mixtures of methyl alcohol and water. J. C. Andrews and F. P. Worley (J. Physical Chem., 1927, **31**, 1880—1883).—The equilibrium optical rotation of dextrose in methyl alcohol and in mixtures of methyl alcohol and water has been measured. The proportion of α-glucose is increased as water is replaced by methyl alcohol. No change in the optical rotation could be detected after dissolving in methyl alcohol or water mixtures of α- and β-glucose in the calculated proportion for equilibrium. The results are considered not to eliminate the possibility of the formation of an intermediate substance, although none could be detected. L. S. Theobald.

Mutarotation and the reaction of the solution. H. Colin and (Mlle.) A. Chaudun (Bull. Soc. chim., 1927, [iv], **41**, 1461—1465).—The effect of lithium and calcium hydroxides on the rate of mutarotation of dextrose is similar to that of sodium hydroxide (A., 1927, 426) for concentrations below $N/500$. The accelerating influence of methylamine is greater than that of ammonia, and is even greater than would be expected from its conductivity, the active agent being assumed to be the hydroxyl ion. Carbamide at a concentration of 2%, and pyridine in

$0{\cdot}01N$-solution have no effect whatever. The rate of transformation of dextrose is accelerated by all acids, except at very high dilutions, whereas the mutarotation of lævulose is retarded by weak acids at all dilutions, and by strong acids in very dilute solution, but is promoted by concentrated strong acids. R. Cuthill.

Hydrolysis of the peptide (–CO·NH–) linking. A. I. Escolme and W. C. M. Lewis (Trans. Faraday Soc., 1927, 23, 651—660).—The rate of hydrolysis of acetylglycine at 60° and 70°, and of benzoylglycine at 80° and 90°, by hydrochloric acid of different concentrations, has been determined in aqueous solutions, and also in solvents consisting of mixtures of water with glycerol, propyl alcohol, and potassium chloride, respectively. In all cases the reaction is unimolecular. Under all conditions the same critical increment of activation has been obtained for both amino-acids, namely, 22,000 g.-cal. No quantitative statement of the mechanism of the process involved has been found possible, but the results suggest that the activity of the hydrogen ion and of the water are important factors, except where a strong electrolyte, such as potassium chloride, is present, when the activity theory becomes inapplicable. The results also suggest that the activity of the substituted amino-acid, which should logically enter into any "activity" theory of chemical change, cannot differ much from the ordinary volume concentration. With the object of getting further information on this point, solubility determinations of acetylglycine and benzoylglycine in mixtures of water, glycerol, and hydrochloric acid have been made. The addition of glycerol, however, diminishes the solubility of acetylglycine, whilst it increases that of benzoylglycine. M. S. Burr.

Activity theory of reaction velocity. Interaction of *N*-chloroacetanilide and hydrochloric acid. F. G. Soper and D. R. Pryde (J.C.S., 1927, 2761—2770).—The velocity equation for those reactions which involve neutral molecules and are catalysed by acids is discussed. The classical velocity coefficients are not true constants, and the use of an equation of the type $v=kC_{\text{catalyst}}\,C_AC_B$ for determining the effective concentration of the catalyst is not justifiable. Defining the activity a_A of a substance in the usual way, the simplest type of the modified velocity equation is $v=ka_Aa_B$. This equation is supported by measurements of the rate of interaction of *N*-chloroacetanilide with hydrochloric acid. The speed of this transformation, which involves two successive stages (cf. Orton and Jones, Rep. Brit. Assoc., 1910, 85), is approximately equal to that of the first stage, viz., the formation of chlorine. The rate of formation of chlorine was measured in the presence of acetanilide, phenol, and *p*-cresol. Correction of this rate for the speed of hydrolysis of *N*-chloroacetanilide to hypochlorous acid gave that of the direct interaction of the chloroamine and hydrochloric acid. The activity of the chloroamine in presence of hydrochloric acid was deduced from solubility measurements, and the activity of the un-ionised hydrochloric acid was replaced by the activity product of the hydrogen and chlorine ions. The reaction velocity is also shown to be independent of viscosity. O. J. Walker.

Velocity of hydrolysis of phenylsuccinimide derivatives. A. Sanna (Gazzetta, 1927, 57, 761—771).—The velocity of hydrolysis of the following phenylsuccinimides in alcohol by alcoholic sodium hydroxide solution has been determined at 25°: *o*-, *m*-, *p*-nitro-; *o*-, *m*-, *p*-chloro-; *o*-, *m*-, *p*-bromo-; *o*-, *m*-, *p*-iodo-phenylsuccinimide. The data indicate that the reaction is bimolecular. R. W. Lunt.

Chemical reactivity of atoms and groups in organic compounds. J. F. Norris (Z. physikal. Chem., 1927, 130, 662—672).—The velocity coefficients of the reaction between ethyl alcohol and substituted derivatives of benzoyl chloride (at 0°) and of diphenylchloromethane (at 25°) have been measured at about $0{\cdot}1M$-concentration. The influence of substituents is the reverse for the two series of compounds, and is much greater for the alkyl derivatives. The reactivity of the chlorine atom in the acyl compounds is influenced more by the position than by the nature of the substituent; the influence of position decreases in the order ortho, meta, para. Negative groups in all positions increase lability, but the tendency of positive groups to decrease reactivity is masked in the ortho-position. Diphenylchloromethane is considerably more labile than benzoyl chloride; the velocity coefficient for the acyl chloride increases 9 times between 0° and 25°, whereas for the alkyl chloride the constant increases 26 times.

The reactivity of the hydroxyl hydrogen atom in a number of alcohols has been studied by measuring the rate of reaction of the alcohol with *p*-nitrobenzoyl chloride at 25°. For the normal primary alcohol series the reactivity of the hydroxyl hydrogen atom decreases with the first three members, increases with the next three, and finally decreases. For secondary alcohols with the hydroxyl group in position 2 the reactivity decreases with the first three members and then increases. A similar periodicity in cycles of three is produced by the introduction of methyl groups. In a straight carbon chain the position of the hydroxyl group is of very great influence on the reactivity. In the aromatic alcohol series the reactivity alternates as the distance between the phenyl radical and the hydroxyl group increases.

Preliminary measurements have been made of the reactivity of the hydroxyl group in alcohols by study of the reaction between the alcohol and hydrogen bromide. Increase of chain length of both the primary and secondary alcohols causes alternation of the reactivity, which is also influenced considerably by the position of a methyl group as a side-chain. H. F. Gillbe.

Relation between rate of stirring and velocity of reaction in heterogeneous systems. A. Kleinówna (Rocz. Chem., 1927, 7, 159—162).—Polemical, in reply to Bekier and Rodziewicz (A., 1927, 426). R. Truszkowski.

Effect of alkali on oxidation of sodium sulphite with air. S. Miyamoto (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, 7, 40—45).—See A., 1927, 525.

Effect of alkali on oxidation of ferrous hydroxide with air. S. Miyamoto (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, 7, 35—39).—See A., 1927, 425.

Heterogeneous thermal decomposition of ammonia in strong electric fields. R. E. Burk (Proc. Nat. Acad. Sci., 1927, 13, 719—720).—Electric fields up to 150,000 volts per cm. have no effect on the rate of decomposition of ammonia on electrically heated wires. W. E. Downey.

Dissolution velocity of zinc in a current of sulphuric acid. M. Straumanis (Z. physikal. Chem., 1927, 129, 370—388).—The rate of dissolution of the metal has been determined by a method in which the acid is allowed to flow at a constant rate on to a fixed horizontal plate of the metal, collected in a vessel below, and returned by means of a pump to its original position so as to maintain a continuous flow. The quantity of metal dissolved is measured in terms of the volume of hydrogen evolved. The variation of the dissolution velocity of zinc in 0·5*N*-sulphuric acid in presence of cupric, nickel, silver, bismuth, and cobaltous sulphates and auric chloride at various concentrations has been determined. The accelerating influence of these metals is not in the same order as their position in the electropositive series. The velocity during the induction period of the reaction, *i.e.*, before the catalysing metal has deposited on the zinc plate, is a linear function of the time. Change of the velocity of the acid stream has but little influence on the rate of dissolution. The rate of dissolution of zinc and of cadmium in dilute sulphuric or hydrochloric acid in presence of other metallic salts indicates that the whole process may be qualitatively explained on the theory of local currents, if due consideration be attached to the variation of the over-voltage and of the potential of the dissolving metal with the current strength and with the concentration and nature of the acid. H. F. Gillbe.

Corrosion of lead by mineral waters. P. Kaja.—See B., 1927, 911.

Effect of addition of some alkaloids on the rate of dissolution of iron in dilute hydrochloric acid. II. Effect of nicotine, narcotine, and gelatin, and the fall of *E.M.F.* produced in the iron in presence of brucine. M. B. Rane (J. Indian Chem. Soc., 1927, 4, 387—395; cf. A., 1925, ii, 410).—The increase in the rate of dissolution of iron wire in hydrochloric acid is not due to the catalytic influence of the iron salt formed during the reaction, but probably to the capillaries produced in the iron (cf. McCulloch, A., 1925, ii, 879). The inhibiting effect of alkaloids on the evolution of hydrogen has been observed with nicotine and narcotine. Gelatin has a similar effect, but no effect is observed with sucrose, dextrose, aniline hydrochloride, phenol, cresol, nitrobenzene, and phenylenediamine. The *E.M.F.* of iron in contact with *N*-hydrochloric acid and *N*-ferrous sulphate falls when small quantities of brucine are added. H. Burton.

Silver-ion catalysis of persulphate oxidations. I. Salt effect on the velocity of oxidation of ammonia. II. Comparison of the velocity with various reducing agents. C. V. King (J. Amer. Chem. Soc., 1927, 49, 2689—2699).—The influence of hydroxides in the above oxidation reaction observed by Yost (A., 1926, 365) is a perfectly general salt effect conforming to Brönsted's theory (assuming the reaction course deduced by Yost), since the same results are obtained in the presence of added nitrates. The sodium ion has less effect than the potassium ion. The reaction is only pseudo-unimolecular in that range of salt concentration in which change of ionic concentration during the reaction counteracts the consumption of ammonia. The reaction $S_2O_8''+C_2O_4''\longrightarrow 2SO_4''+2CO_2$ in presence of silver ions is very much more rapid than would be expected, and it appears that the nature of the reducing agent may have some influence on the velocity. S. K. Tweedy.

Effect of hydrochloric acid on the oxidation of stannous chloride with air. S. Miyamoto (Bull. Chem. Soc. Japan, 1927, 2, 259—269).—The catalytic effect of hydrochloric acid on the atmospheric oxidation of stannous chloride has been investigated. With hydrochloric acid concentrations of less than about 0·25*N*, the order of the reaction is between first and zero. Above that concentration the velocity is independent of the stannous chloride concentration. The temperature coefficient between 20° and 40° is small. C. W. Gibby.

Application of the interference method to the determination of the surface area of metallic nickel films. F. H. Constable (Nature, 1927, 120, 769—770).—A nickel film, electrolytically deposited on china clay coated with graphite, was activated by oxidation in air and reduction by hydrogen at 520°. The surface area per unit mass was calculated from the slope of the straight line obtained on plotting the conductivity against the equivalent air thickness corresponding with the colour shown by the partly oxidised rod. The results show that the surface of electrolytic nickel is 1·84 times the apparent area, and that the apparent surface may be considerably increased by reduction at 400°. A. A. Eldridge.

Catalysis by nickel of the union of hydrogen and oxygen. D. R. Hughes and R. C. Bevan (Proc. Roy. Soc., 1927, A, 117, 101—108).—Nickel wires were heated in hydrogen and mixtures of hydrogen with oxygen, the current and corresponding fall of potential of the wires being measured. The same current raised the temperature of the wire more when it was in hydrogen than when it was in the mixture, from which it is concluded that the surface of the wire was in a very different condition in the two experiments. The wire was (*a*) previously heated in hydrogen, (*b*) heated in a mixture of hydrogen and oxygen at a temperature well below that of combination, and (*c*) heated in oxygen until it had become visibly oxidised, and in each case subsequently heated in hydrogen at a pressure of 12910×10^{-6} mm. and the resistance determined. For a given current the temperature of the visibly oxidised wire was the same as that of the wire which had been heated in the mixture, whereas the nickel which had not been in contact with oxygen was at a much higher temperature. It is concluded that when nickel is heated in the mixture it becomes completely covered with a layer of oxide, and that a hydrogen molecule leaving the surface removes more energy than one leaving the metal surface at the same temperature.

The coefficient of radiation of the oxidised wires was found to depend on the thickness of the oxidised sheath, in contrast with the average heat removed from the surface by an escaping molecule of hydrogen, which depends only on the nature of the surface. From determinations of the temperature coefficient of resistance of a nickel wire, the "accommodation" coefficient of hydrogen in contact with the respective surfaces was calculated, and found to be 0·25 for nickel, 0·48 for oxidised nickel, at a temperature of 164°. The value for oxygen in contact with oxidised nickel was 0·95. The rate of formation of water on thinly and visibly oxidised wires, respectively, was practically the same. From experiments on the rate at which a reduced wire is oxidised when brought into contact with a standard oxygen–hydrogen mixture at a temperature at which the gases will combine at a measurable rate, it is shown that the reduction of the oxidised wire does not start all over the outer surface of the oxide film, but that either the hydrogen penetrates the film, and the reduction occurs at the junction of the metal and the oxide, or the reduction starts at nuclei. Of the two alternatives, the former seems more probable when the film is thin.

L. L. Bircumshaw.

Colloidal palladium as catalyst at the hydrogen electrode. E. Biilmann and A. Klit (Z. physikal. Chem., 1927, **130**, 566—571).—An investigation has been made of electrodes at which the reaction $H_{gas} \rightleftharpoons H^{\cdot}$ is catalysed by colloidal palladium. At polished platinum and gold electrodes similar potentials are obtained to those at ordinary platinised electrodes under the usual conditions. The extent to which the electrodes become polarised is dependent on the concentration of the colloidal palladium; only with concentrations above 2 mg. of palladium per litre can a well-defined measurable potential be obtained.

H. F. Gillbe.

Catalyst for hydrogenation in the cold, and mechanism of this catalysis. M. Bourguel (Bull. Soc. chim., 1927, [iv], **41**, 1443—1450).—Experiments have been made on the reduction of hydrocarbons in the cold with a catalyst prepared by reducing sodium chloropalladite with hydrazine hydrate in the presence of starch as protective colloid. In the reduction of acetylenes and of acetylenic acids and alcohols, there is an abrupt change in the rate of reduction when the amount of hydrogen taken up is exactly equal to 2 atoms per mol. of the unsaturated compound, and at the same time, and not before, the substance ceases to react with cuprous chloride. In explanation of the results, Armstrong and Hilditch's theory is advocated, a palladium–hydrogen complex being formed first, then adding on the organic substance, and finally decomposing into the metal and reduced compound. As it is observed that in the reduction of a liquid immiscible with water the palladium is removed from its aqueous colloidal solution to form a film at the interface of the two liquids, the formation of an oriented layer of the palladium–hydrogen complex is suggested, the hydrogen atoms being directed towards the organic liquid and attracting molecules of the acetylene type in preference to those of the ethylene type.

R. Cuthill.

Catalytic formation of methane from carbon monoxide and hydrogen. III. Study of various catalysts. K. Chakravarty and J. C. Ghosh (J. Indian Chem. Soc., 1927, **4**, 431—436).—The effects of various catalysts, mostly mixed metallic hydroxides, for the reaction $2CO+2H_2=CH_4+CO_2$ have been studied, and it is found that whilst some of them, *e.g.*, nickel hydroxide on aluminium hydroxide, were active at 300°, they were not steady, and the rate of fall of activity was rapid. The sugar charcoal–nickel catalyst on pumice (A., 1925, ii, 1175) is more active if 50% more nickel is used in its preparation and, in contradistinction to the others used, loses its activity very slowly.

H. Burton.

Oxidation of ammonia in presence of contact catalysts. IV. J. Zawadzki and H. Narkiewicz (Rocz. Chem., 1927, **7**, 369—379).—The catalytic action of platinum gauze on ammonia and oxygen may be represented graphically by a series of closed curves, the co-ordinates of which are the temperature and the velocity of the current of gas mixture. By taking finer gauze and increasing the number of layers through which the gases pass, the optimum point of oxidation to nitric oxide is shifted towards the region of higher temperature and shorter contact, so that yields of more than 90% may be obtained above 1000°.

R. Truszkowski.

[Catalytic] oxidation of ammonia. F. Raschig.—See B., 1927, 906.

[Catalytic] oxidation of ammonia. G. B. Taylor.—See B., 1927, 936.

Decomposition of carbon monoxide by reduced copper below 400°. A. Steopoe (Bul. Chim. Soc. Română Stiin., 1926, **29**, 79—82).—A reduced copper catalyst was prepared by passing a current of carbon monoxide over cupric oxide precipitated on asbestos. The cupric oxide had been dried below 120°, and reduction was carried out at 200°. On continued passage of carbon monoxide over this catalyst carbon dioxide was formed (*a*) by reduction of some residual cuprous oxide, and (*b*) by decomposition of the carbon monoxide. The extent of each reaction was determined by measuring the amount of carbon dioxide produced and the variation in weight of the catalyst. The yield of carbon dioxide due to reaction (*b*) increased from 0·46% at 200° to 1·43% at 350°. Similar results were obtained with a catalyst prepared in the same way from commercial copper sulphate.

A. B. Manning.

Action of acetylene on metals yielding explosive acetylides. J. F. Durand and M. Banos (Bull. Soc. chim., 1927, [iv], **41**, 1294—1299).—When dry acetylene is passed over finely-divided silver, some reaction occurs at 400°, and at 600° a brilliant flame appears, moving against the gas current. During this phenomenon hydrogen is evolved, carbon is deposited on the silver, and silver is deposited on the tube in which the experiment is carried out. With gold, the phenomenon is observed at 480°. Using copper, preheated at 400° in a stream of carbon dioxide, the phenomenon is observed at 480°, the flame appearing and disappearing regularly to 620°, when it disappears. On cooling, the phenomenon reappears at 480°. Similar results are obtained using mercury, the phenomenon appearing at 540°, continuing rhythmically to 680°, and then disappearing. In view of the results using mercury (vapour), it is concluded that the phenomenon is due to chemical catalysis, and not to adsorption on the metal. H. BURTON.

Catalytic oxidation of ethyl alcohol. G. FESTER and G. BERRAZ (Anal. Asoc. Quím. Argentina, 1927, 15, 210—215).—The oxidation of ethyl alcohol by air when passed over heated catalysts has been studied. Vanadium pentoxide, silver vanadate, and copper vanadate deposited on silica, silver vanadate on fuller's earth, and zinc oxide were used as catalysts. Acetaldehyde, acetic acid, and carbon dioxide were determined in the products.

The principal product was always acetaldehyde (up to 23·8% with silver vanadate). The optimum temperature was about 360°. Above this, excessive formation of carbon dioxide took place. The optimum combination of high yield of acetaldehyde and low carbon dioxide formation was obtained with vanadium pentoxide (9—13% and 2—5%, respectively) and zinc oxide (10·7% and 4·8%). R. K. CALLOW.

Catalytic oxidation of gaseous cyanogen to nitric oxide, and the intermediate product. S. ABE and R. HARA (Tech. Repts. Tôhoku Imp. Univ., 1927, 7, 1—23).—Experiments in which gaseous cyanogen was oxidised with air in presence of various catalysts show that the first stable products are nitric oxide and carbon monoxide and that under the most favourable conditions more than 90% of the cyanogen is thus oxidised. With the most efficient catalyst, platinum net, production of nitric oxide begins rather abruptly at about 450—550° and is maximal at about 700—800°. At higher temperatures conversion of cyanogen into free nitrogen commences. At each temperature there appears to be an optimum velocity of gas flow. Maximum yields are obtained with a rapidly-flowing inlet gas containing 4% of cyanogen. Platinised asbestos, ferric oxide, nickel oxide, and copper oxide are also efficient catalysts. With ferric oxide and nickel oxide considerable quantities of carbon are deposited under certain special conditions, *e.g.*, high concentrations of cyanogen. Under certain conditions and with copper oxide as catalyst yellowish-vermilion solid deposits were found in the exit tube of the furnace. On heating, this substance yields a white sublimate and a residue containing copper. In presence of copper oxide, oxidation of cyanogen occurs at temperatures of the order 220—230°.

The walls of the tube eventually became coated with a minute quantity of a white *substance*, $C_3H_2ON_4$, produced by the action of moisture on a transparent yellow *compound*, C_2N_2O, thus: $2C_2N_2O+H_2O=C_3H_2ON_4+CO_2$. The catalytic oxidation of cyanogen is therefore represented by the equations: $2C_2N_2+O_2=2C_2N_2O$; $2C_2N_2O+3O_2=4CO+4NO$.

The isolation of an intermediate compound, together with the discovery that cyanic acid is formed at an intermediate stage in the oxidation of hydrogen cyanide (Hara and Sinozaki, A., 1925, ii, 983), suggests that in the catalytic oxidation of ammonia the first reaction is not the production of nascent or atomic nitrogen, but rather the formation of some intermediate compound containing oxygen. J. S. CARTER.

Catalytic activity and adsorptive power of supported iron, cobalt, nickel, copper, and silver. R. N. PEASE and L. STEWART (J. Amer. Chem. Soc., 1927, 49, 2783—2787).—The above metals deposited on diatomite brick were used as catalysts in the hydrogenation of ethylene. The catalysts were similarly prepared and are therefore comparable. Cobalt and nickel caused instantaneous action at − 20°; iron was moderately active at 0°, copper at 50°, and silver at 100°. A support gives stability where it is needed, but it yields a catalyst of somewhat smaller surface. Supported copper is a poorer catalyst than the unsupported material. This metal can be reduced at comparatively low temperatures, and the use of a support, which obviates reduction at high temperatures and the accompanying sintering and deactivation, is of no particular advantage as it is in the case of the other metals. More hydrogen is adsorbed by nickel and cobalt than by the other metals, and more ethylene by iron. In the presence of silver at 100° the reaction rate is proportional to the hydrogen, and independent of the ethylene, concentration (Pease, A., 1923, ii, 862). In the presence of iron at 0° excess of hydrogen increases the rate, whilst excess of ethylene has little influence. Heats of activation are recorded. The highly active hydrogenation catalysts are those metals which in ionisation produce large numbers of stable complexes in solution. This is probably due to a capacity for electron sharing, and it may be that this associative property of the metal brings the reactants together and renders them both labile, so that a system of lower free energy is produced. S. K. TWEEDY.

Aluminium ovens for catalytic purposes. F. FISCHER and H. TROPSCH.—See B., 1927, 927.

Electrolytic deposits of cadmium for the protection of metals and alloys against corrosion. J. COURNOT and J. BARY.—See B., 1927, 910.

Electromotive behaviour of complex cyanides of manganese and the cyanide, $K_3Mn(CN)_4$. G. GRUBE and W. BRAUSE (Ber., 1927, 60, [*B*], 2273—2278; cf. Bellucci and Corelli, A., 1914, i, 260; Grube, A., 1927, 119; Manchot and Gall., *ibid.*, 220).—Crystalline potassium manganocyanide is conveniently prepared by the action of aqueous potassium cyanide on manganese carbonate at 70—80° in an atmosphere of hydrogen. It is converted by prolonged oxidation in warm solution by air into potassium manganicyanide. The manganous salt is stable in aqueous solution only in the presence of an excess of potassium cyanide; it is quantitatively oxidised by potassium ferricyanide to manganicyanide, the end-point being readily determined potentiometrically. The normal potential of the process $Mn(CN)_6''''+\oplus \rightleftharpoons Mn(CN)_6'''$ is $-0·225\pm0·004$ volt or $-0·223\pm0·004$ volt in 1·54*N*- or 2·3*N*-potassium cyanide solution. The *compound* $K_3Mn(CN)_4$ is prepared by electrolytic reduction of a solution of potassium mangano- and mangani-cyanide in aqueous potassium cyanide at 1—2° in a diaphragm cell from which air is excluded; the anolyte is 1·5*N*-potassium cyanide solution and polished platinum foil electrodes are employed. It is an unstable, colourless compound which, even at a low temperature, readily decomposes water and passes back into the manganocyanide. H. Wren.

Relative stability of nitrous oxide and ammonia in the electric discharge. W. K. Hutchison and C. N. Hinshelwood (Proc. Roy. Soc., 1927, A, **117**, 131—136).—The stabilities of nitrous oxide and of ammonia under electrical excitation were compared by measuring the effect of the same discharge passed simultaneously through the two gases in series, in parallel, and independently through each alone. The increase of pressure in the discharge tubes due to the decompositions was calculated for different initial pressures and with different times and strengths of discharge, using platinum, aluminium, and glass electrodes. When the discharge is feeble, the absolute amount of decomposition is independent of the initial pressure of the gas, but with increasing intensity of discharge the amount of decomposition becomes proportional to the initial pressure. All measurements were made with discharges sufficiently intense to bring the reaction into this " unimolecular " region, and in all cases the ammonia appeared to be 5—7 times as difficult to decompose as the nitrous oxide. The results agree in a general way with what might be expected from the known thermal reactions.

L. L. Bircumshaw.

Electrochemical preparation of Scheele's green. B. P. Bruns.—See B., 1927, 947.

Electrolytic oxidation of *p*-toluic acid in alkaline solution. A. J. Allmand and A. Puttick (Trans. Faraday Soc., 1927, 23, 641—650).—An attempt has been made to increase the efficiency of the electrolytic process for the oxidation of *p*-toluic acid in alkaline solution to terephthalic acid by the superposition of an alternating current on the direct current. With direct current alone the highest current efficiency, 16%, is obtained at a platinum anode with a current density of 4 amp./sq.dm. in 2*N*-potassium hydroxide containing 0·25*N*-potassium *p*-toluate. Discoloured solutions are obtained when the free alkali concentration is decreased, and the yield is lowered when either alkali or salt concentration is increased, or the current density is increased or decreased. With superposed alternating current, whether of frequency 50 or 500, or of high or low current density, no improvement in efficiency is effected, and with currents of low frequency, or with large currents of high frequency, the efficiency is definitely lowered. There are three anodic processes, (i) evolution of unutilised oxygen, (ii) oxidation of *p*-toluic acid to terephthalic acid, (iii) complete oxidation of *p*-toluic acid with formation of carbon monoxide and carbon dioxide. The action of the alternating current is to favour (i) and (iii) more than (ii). Anode potential measurements have been made, and it is impossible to trace any connexion between these and the different terephthalic acid yields.

M. S. Burr.

Electrolytic reduction and reactions in the glow discharge at the liquid-gas interface. A. Klemenc (Z. physikal. Chem., 1927, **130**, 378—389).—The behaviour on electrolysis, using a Wehnelt gas electrode, of dilute and more concentrated sulphuric acid, of ferrous or ferric sulphate solution in sulphuric acid, and of potassium nitrate in potassium or sodium hydroxide solution has been examined with the object of determining whether or not the electrolytic processes at a hydrogen electrode are dependent on the presence of a solid electrode. The results with sulphuric acid confirm those previously found by Haber and Klemenc (A., 1915, ii, 212). A reduction of the ferric sulphate occurs, but it is not possible to decide whether the ferric ion is reduced by the slow electrons discharged from the gas cathode, or according to the equation $Fe^{\cdot\cdot\cdot}+H \longrightarrow Fe^{\cdot\cdot}+H^{\cdot}$. Potassium nitrate solutions undergo considerable reduction in the glow discharge, nitrous acid, nitric and nitrous oxides, and nitrogen being formed, but no ammonia. It follows that electrolytic reduction by means of hydrogen can take place when the gas is not in contact with a metal electrode. L. L. Bircumshaw.

Primary decomposition of molecules in photochemical reactions. R. H. Gerke (J. Amer. Chem. Soc., 1927, 49, 2671—2677).—Photochemical reactions are divided provisionally into three classes according as the absorption of light produces excited atoms (or molecules), causes a decomposition of molecules into atoms (" primary decomposition reactions "), or excites a catalyst or sensitiser. A given photochemical reaction may belong to the first class in one region of the spectrum and to the second class in another region. Many examples are considered. Reactions of the second class, but not of the first class, have a quantum efficiency independent of the pressure and of the wave-length of the light.

S. K. Tweedy.

Photolytic formation of hydrogen peroxide. E. Baur and C. Neuweiler (Helv. Chim. Acta, 1927, **10**, 901—907).—Exposure of aqueous suspensions of zinc oxide in contact with air to sunlight results in the formation of hydrogen peroxide. According to the " molecular electrolysis " theory of photolysis (Baur, A., 1918, ii, 284) the process is represented by

$$ZnO\begin{cases}\oplus+OH'=\tfrac{1}{4}O_2+\tfrac{1}{2}H_2O\\ \ominus+H^{\cdot}+\tfrac{1}{2}O_2=\tfrac{1}{2}H_2O_2.\end{cases}$$

In presence of small amounts of glycerol, dextrose, or benzidine the yield of hydrogen peroxide is greatly increased. At the same time these added substances are themselves oxidised. Evidence has been obtained for the existence of dihydroxyacetone and possibly glycerose in exposed suspensions containing glycerol. Benzidine yields a brown, insoluble oxidation product. When zinc oxide is replaced by eosin or fluorescein formation of hydrogen peroxide is observed in presence of dextrose and benzidine, but not in presence of glycerol. J. S. Carter.

Hydrogen peroxide formation photo-sensitised by mercury vapour. A. L. Marshall (J. Amer. Chem. Soc., 1927, 49, 2763—2772).—The previous investigation (A., 1926, 252) was repeated with improved apparatus. The peroxide formed was removed practically undecomposed. The rate of hydrogen peroxide formation is proportional to the mol. fraction of hydrogen present and also to the arc current, and probably, therefore, to the light intensity. At high mercury vapour concentrations large quantities of mercuric oxide are formed and the yield of peroxide is correspondingly low; the optimum vapour concentration is 0·005 mm. The optimum concentration of mercury vapour in the lamp for obtaining the maximum amount of resonance light (λ2536·7 Å.) is 0·01 mm. The temperature coefficient of the reaction is 1·04. S. K. Tweedy.

Photochemical decomposition of hydrogen iodide. Mode of optical dissociation. B. Lewis (Proc. Nat. Acad. Sci., 1927, **13**, 720—726).—The number of molecules of hydrogen iodide decomposed per quantum absorbed, using the lines 2080 and 2530 Å. of zinc, is 2·36 and 2·25, respectively. W. E. Downey.

Modified sulphide-nuclei theory of photographic sensitivity. J. Southworth.—See B., 1927, 957.

Zinc oxide as a general sensitiser for photochemical reactions. A. K. Bhattacharya and N. R. Dhar (J. Indian Chem. Soc., 1927, **4**, 299—306).—Exposure of solutions of 40 dyes to sunlight in presence of zinc oxide shows that the dyes absorbing light of long wave-length, *i.e.*, blue, green, violet, are bleached rapidly, then fluorescent dyes, and lastly red, orange, and yellow dyes. Alizarin-blue and methyl-orange show a slight increase in concentration, probably owing to evaporation of the solution, and no bleaching action. A list is given of 37 reactions which are sensitised by zinc oxide. The remainder of the paper is a criticism of work published by Baur (A., 1924, ii, 857; 1925, ii, 1082). H. Burton.

Photochemical oxidation of leuco-malachite-green by uranyl nitrate in monochloroacetic acid solution. J. C. Ghosh and J. Mukherjee (J. Indian Chem. Soc., 1927, **4**, 343—352).—The oxidation of leuco-malachite-green by uranyl nitrate is a photochemical reaction. The reaction rate varies directly as the intensity of the light and concentration of the uranyl nitrate. The life period of the excited molecules is calculated as being $4 \cdot 9 \times 10^{-11}$ sec. There is no temperature coefficient for the reaction. Application of Einstein's law of photochemical equivalence shows that more than one quantum of energy is necessary to transform 1 mol. of the leuco-compound. The region 478—410 μμ is most suitable for the reaction; all measurements were made within this region. Light absorbed by the malachite-green formed during the oxidation has no effect on the rate of change of the reaction. The reciprocal of the reaction rate when plotted against the reciprocal of the concentration of the leuco-compound gives a straight line. H. Burton.

Dehydration of hydrated salts. IV. M. A. Razukin and D. A. Brodski.—See B., 1927, 875.

Distillation of alkali metals. R. J. Clark (Proc. Camb. Phil. Soc., 1927, **23**, 953—955).—The metal is washed in dry ether containing 4 or 5% of alcohol, wiped with filter-paper, and dropped into a glass still of special design. The metal is melted in a vacuum, separated from the skin of oxide, and is then thrice distilled in a vacuum. The method has been used for the purification of certain halides. W. E. Downey.

Chemical nature of precipitated basic cupric carbonate. J. R. I. Hepburn (J.C.S., 1927, 2883—2896).—The initial process which occurs on mixing equimolecular solutions of copper sulphate and sodium carbonate (cf. A., 1925, ii, 696) has been investigated, the concentration of the precipitants being varied from 1·0 to 0·00625*M*. The relationship between the carbon dioxide content of the precipitate and the concentration of carbon dioxide in the solution can be represented by a Freundlich adsorption isotherm, and the view is therefore advanced that the formation of basic cupric carbonate is due to adsorption of un-ionised carbonic acid by hydrated cupric oxide which is in a very active state. Other views regarding the nature of precipitated basic cupric carbonate are discussed. O. J. Walker.

Basic mercurous nitrate. S. Jajte (Rocz. Chem., 1927, **7**, 156—158).—*Basic mercurous nitrate*, $3Hg_2O,N_2O_5$, crystallised from a solution containing mercurous nitrate, silver nitrate, and nitric acid after a year. R. Truszkowski.

Separation of pure radium salts from isomorphous mixtures with barium salts. A. G. Eliseev (Ann. Inst. Anal. Physico-Chim. Leningrad, 1926, **3**, 443—454).—In presence of hydrogen chloride in proportions increasing up to 11 g. per 100 g. of water, the solubility of barium chloride at 25° diminishes practically linearly; subsequently the solubility isotherm approaches the axis of abscissæ asymptotically, the whole of the salt being precipitated when 30 g. of hydrogen chloride are present per 100 g. of water. At 0°, 100 g. of water dissolve 30·7 g. of barium chloride (cf. Engel, Ann. Chim. Phys., 1888, [vi], **13**, 371). Investigation of the isotherm at 25° of the system $RaCl_2$–$BaCl_2$–HCl–H_2O shows that the solubility of radium choride is diminished by the presence of hydrogen chloride to a greater extent than that of barium chloride, and that radium chloride does not influence appreciably the solubility of the barium salt. The curves indicating the quantities of radium and barium chlorides in equilibrium with definite proportions of hydrogen chloride show that, by addition of the acid to a solution of the mixed chlorides saturated at 25° and by removing small fractions, values exceeding 2 are obtainable for the coefficient of enrichment.

These results form the basis of the industrial treatment of an ore of the composition CaO 32·01, BaO 4·63, Fe_2O_3 7·06, Al_2O_3 4·41, CuO 3·1, Bi_2O_3 trace, PbO 0·08, U_3O_8 1·49, V_2O_5 3·29, P_2O_5 0·12, As_2O_3 0·02, SO_3 2·4, CO_2 25·49%, rare earths traces. The ore was treated with hydrochloric acid and the insoluble residue boiled with 2·5 times its weight of sodium carbonate in saturated aqueous solution, the carbonates thus obtained being decomposed by hydrochloric acid. Saturation of the solution of the mixed chlorides with hydrogen chloride gave a precipitate containing all the barium and radium, most of the admixed metals, especially the vanadium, uranium, calcium, and lead, remaining dissolved. The mixed barium and radium chlorides were then subjected to fractional precipitation by means of hydrogen chloride. T. H. Pope.

Boric acids and alkali borates. IV. Solid alkali perborates. H. Menzel [with J. Meckwitz and W. Kretzschmar] (Z. anorg. Chem., 1927, 167, 193—229; cf. A., 1927, 1043).—Addition of ethyl alcohol to a mixed solution of lithium monoborate and hydrogen peroxide precipitates *lithium perborate*, $LiBO_3,2H_2O$, or $LiBO_2,H_2O_2,H_2O$, from which, by recrystallisation from water, or by careful dehydration, the lower *hydrate*, $LiBO_3,H_2O$, or $LiBO_2,H_2O_2$, may be obtained. Further dehydration, *e.g.*, by heating at above 100° in a vacuum, leads to loss of active oxygen, and at the same time the substance acquires the property of reacting with water with liberation of oxygen, probably owing to the presence of some such substance as $(LiBO_2)_2,O_2$, and ultimately the monoborate remains. With entrance on this final stage, the crystal structure changes completely, which suggests that the perborate cannot be regarded merely as the monoborate with hydrogen peroxide of crystallisation. The perborates of potassium and ammonium apparently exist only in the form of the hemihydrates, *e.g.*, $KBO_3,0\cdot5H_2O$; other hydrates which have been reported are to be regarded as having been impure. Attempts to remove the water by heating lead to decomposition, as with the lithium salt, although in the case of the ammonium salt the changes are somewhat more complex, owing to oxidation and volatilisation of the cation. The structure of the alkali perborates has been considered in the light of Hermans' theory of the constitution of the borates (A., 1925, i, 500). It is considered that the only true alkali perborate is the anhydrous sodium salt (Le Blanc and Zellmann, A., 1923, ii, 415), this being a boryl derivative of sodyl hydroxide, NaO·OH, containing a boron atom with the co-ordination number 3. The other alkali perborates, on the other hand, are salts of dibasic acids containing two boron atoms with the co-ordination number 4, the lithium and hydrated sodium salts having the formula $M_2(B_2O_6,2H_2O)$ and the potassium and ammonium salts the formula $M_2(B_2O_6,H_2O)$. The division of the perborates into true and *pseudo*-salts on the basis of their reaction with potassium iodide, as suggested by Riesenfeld and Reinhold (A., 1910, ii, 33) for the percarbonates, must be rejected, as this test is influenced by purely physical factors such as solubility, and there are, moreover, all stages of transition between the two groups. R. Cuthill.

Rare earths. P. B. Sarkar (Ann. chim., 1927, [x], 8, 207—262).—By a critical examination of the data available in the literature and by the preparation of a number of new simple and complex salts of scandium an attempt is made to determine the analogies which exist between the compounds of this element and those of other tervalent elements, the iron and the rare-earth groups, respectively. From the point of view of the solubility of its salts scandium resembles in general the elements of the rare earths, but it also exhibits many close analogies with the iron group in the crystalline form and composition of many of its complex salts. Thus the acetylacetonates of scandium are isomorphous with those of iron, and the double alkali sulphates with those of aluminium, whilst it forms a series of double alkali sulphates corresponding with the anhydrous alums which are quite unknown in the rare-earth series; its basic nitrates closely resemble those of chromium. Spectroscopic evidence obtained using a very pure sample purified by the sublimation of scandium acetylacetonate confirms its relationship with the aluminium family. No such intimate relationship is found, however, between the simple salts of scandium and those of either the rare-earth or iron group of elements, scandium occupying a transitional position between the two groups. The following new salts of scandium are described: double *thiocyanates* of the type $M_3Sc(SCN)_6,4H_2O$ of *ammonium, potassium, d* 1·8480, and *sodium*; double *sulphates* of the type $MSc(SO_4)_2$ of *potassium, ammonium, rubidium,* and *cæsium*; double *sulphates* of the type $M_3Sc(SO_4)_3$ of *sodium* $+6H_2O$, and of *thallium*: the electrolytic conductivity of scandium sulphate $Sc_2(SO_4)_3$ suggests that it is really scandium scandisulphate $Sc[Sc(SO_4)_3]$; *potassium scandium selenate* $KSc(SO_4)_2,2H_2O$; *basic nitrates* of composition $Sc(OH)(NO_3)_2,3H_2O$ [erroneously described by Crookes (A., 1909, ii, 44) as the anhydrous normal nitrate], $Sc_2O(NO_3)_4,0\cdot5H_2O$ (stable between 90° and 115°), and $Sc_4O_5(NO_3)_2$ (stable between 120° and 200°). Scandium hydroxide forms a crimson lake with ammonium aurintricarboxylate (Hammett and Sottery, A., 1925, ii, 601), which, unlike the corresponding aluminium lake, is very soluble in ammonium carbonate solution, the sensitivity of the test being of the order of $2\cdot4\times10^{-7}$ g.-atom of scandium per c.c. A similar study of various new salts of gadolinium and europium shows that these elements resemble both the cerium and yttrium groups of the rare-earth elements and form a transition between the two groups. The following new salts of gadolinium are described: *formate*; *hydrogen tartrate* $+2H_2O$; normal *tartrate* $+5H_2O$; *citrate* $+5H_2O$ and $+4H_2O$; *acetylacetonate* $+3H_2O$, m. p. 143·5—145°; nitrate $+6H_2O$, m. p. in sealed tube 91° (not $6\cdot5H_2O$, as described by Benedicks, A., 1900, ii, 209); *basic nitrate*, $3Gd_2O_3,4N_2O_5,3H_2O$; *antipyrine additive* compound of the nitrate $Gd(NO_3)_3,3C_{11}H_{12}ON_2$; *hexamethylenetetramine additive* compound of the nitrate $Gd(NO_3)_2,2C_6H_{12}N_4,10H_2O$; *bromate* $+9H_2O$, m. p. 80°; *thiocyanate* $+7H_2O$; double *salt* with mercuric cyanide, $Gd(SCN)_3,3HgCN_2,12H_2O$; *orthophosphate* $+5\cdot5H_2O$; *iodate* $+5\cdot5H_2O$; *perchlorate* $+8H_2O$; *periodate* $+4H_2O$; *chlorate* $+10H_2O$; *double potassium oxalate*, $K_2C_2O_4,KGd(C_2O_4)_2,4H_2O$; *double carbonates* of the type $M_2CO_3,Gd_2(CO_3)_3,nH_2O$ of *potassium* $+12H_2O$, *ammonium* $+4H_2O$, and *sodium* $+13H_2O$; salts with *potassium ferrocyanide*, $KGdFe(CN)_6 5H_2O$; *ferricyanide* $+4\cdot5H_2O$; *sulphite* $+12H_2O$ and $+11H_2O$; *double potassium chromates*, $K_2CrO_4,Gd_2(CrO_4)_3,7H_2O$ and $5K_2CrO_4,2Gd_4(CrO_4)_3,10H_2O$. The following new salts of europium are described: *oxalate* $+10H_2O$ and $+5H_2O$; *nitrate* $+6H_2O$, m. p. in sealed tube, 85°; *citrate* $+5H_2O$; *hydrogen tartrate* $+2H_2O$; normal *tartrate* $+5H_2O$; *acetylacetonate* $+3H_2O$, m. p. 136—137°; *acetate* $+4H_2O$ and $+3H_2O$; *iodate* $+5\cdot5H_2O$; *cyanoplatinates* $+21H_2O$, $+18H_2O$, and $+H_2O$; *carbonate* $+3H_2O$; *double potassium oxalate* $+2H_2O$; *orthophosphate* $+4H_2O$.

J. W. Baker.

Double salt formation between thallous carbonate and carbonates of the rare earths. G. Canneri (Gazzetta, 1927, **57**, 732—735).—The preparation of crystalline double carbonates of the general formula $R_2(CO_3)_2,2Tl_2CO_3$ (also $+6H_2O$; R being lanthanum, cerium, neodymium, praseodymium, and yttrium) is described. R. W. Lunt.

Silicic acids. IV. R. Schwarz and H. Richter (Ber., 1927, **60**, [*B*], 2263—2270; cf. A., 1925, ii, 222; A., 1927, 634).—Fused mixtures, corresponding in composition with the formulæ $Na_4Si_3O_8$ and $Na_2Si_3O_7$, become crystalline after long preservation at 500°, and then exhibit the radially arranged needles of a monotropic substance. They are, however, only mixtures of meta- and di-silicate or disilicate and silicon dioxide, since the so-called granatic acid gives an *X*-ray spectrum very closely similar to that of disilicic acid, and its vapour tension isotherms, like those of " trisilicic acid " (which appears to give an individual *X*-ray spectrum), do not give any indication of the presence of a hydrate of the required composition. Granatic and trisilicic acids cannot therefore be regarded as chemical individuals. The presence of definite hydrates is not shown by the vapour-tension isotherms of silicic acid gels obtained by cautious neutralisation of 5% solutions of sodium meta- and di-silicates with hydrochloric acid followed by thorough washing of the precipitates. Dehydration of the gels by acetone under varied conditions results in the removal of water to a content of about 13%, thus indicating the presence of disilicic acid. Its production from sodium metasilicate is explained by the displacement of the equilibrium, $2Na_2SiO_3+H_2O \rightleftharpoons Na_2Si_2O_5+2NaOH$, towards the right during neutralisation with hydrochloric acid. Addition of barium chloride to solutions of sodium meta- or di-silicate or sodium hydrogen silicate results in the precipitation of a mixture of barium meta- and di-silicates; if a large excess of sodium hydroxide is present, homogeneous barium metasilicate is precipitated. Barium meta- and di-silicates are obtained from solutions of lithium orthosilicate even in the presence of a large excess of lithium hydroxide. The SiO_3'' and Si_2O_5'' ions appear to be the only ones present in solutions of alkali silicates; they form an equilibrium which usually is largely in favour of the disilicate ion (cf. Hägg, A., 1926, 924). H. Wren.

Germanium. XXI. Germanium tetrafluoride. L. M. Dennis and A. W. Laubengayer (Z. physikal. Chem., 1927, **130**, 520—531).—The most satisfactory method of preparation of germanium tetrafluoride is by the thermal decomposition of pure barium fluogermanate, prepared by dissolving germanium oxide in 48% hydrofluoric acid solution and adding a saturated solution of the theoretical quantity of barium chloride; the granular precipitate, after drying at 120°, rapidly evolves gas when heated at 700°. The product, purified by fractional distillation at −104°, is a colourless, fuming gas, condensible at the temperature of liquid air to a mass of white crystals which sublime on allowing the temperature to rise. Liquid germanium tetrafluoride is produced at −15° under its own vapour pressure of 3032 mm. On passage of the gas through water a clear acid solution is at first obtained, from which, as the operation is continued, a gelatinous precipitate of hydrated germanium dioxide separates; addition of potassium hydroxide to the clear solution causes the precipitation of potassium fluogermanate. Glass in presence of moisture is rapidly etched, but quartz is not attacked below 700°. There is no indication of dissociation at 1000°. Some evidence has been obtained for the production of germanium difluoride when the tetrafluoride is passed over heated germanium. H. F. Gillbe.

Germanium. XXIII. Germanium monosulphide. L. M. Dennis and S. M. Joseph (J. Physical Chem., 1927, **31**, 1716—1718; cf. A., 1927, 1156).—The optimum temperature for the preparation of germanium monosulphide by Winkler's method (A., 1886, 985) by the reduction of the disulphide in a current of hydrogen is approximately 480°. The product obtained consisted of very hard, black crystals, which were probably rhombic bi-pyramids having the faces 010, 1001, 001, 101, 110, together with thin tablets having a graphitic lustre and showing pleochroism in the thinnest flakes. The crystals are practically insoluble in mineral acids, but can be brought into solution by fusion with potassium hydroxide or by long digestion with an aqueous solution of the same reagent. L. S. Theobald.

Germanium. XXIV. Dihalides of germanium, tin, and lead. F. M. Brewer (J. Physical Chem., 1927, **31**, 1817—1823).—The properties of the halogen compounds of germanium, tin, and lead are compared. L. S. Theobald.

Production of zirconium oxide, and constitution of some zirconium salts. P. Schmid (Z. anorg. Chem., 1927, **167**, 369—384).—Zirconium ores are most satisfactorily opened up by fusion with lime, the temperature of a gas furnace being sufficient for the process. By treating the product with an appropriate amount of hydrochloric acid, the calcium, iron, and aluminium may be brought into solution, and then by warming the residue, which contains the whole of the zirconium as calcium zirconate, with more hydrochloric acid zirconium oxychloride is obtained. Alternatively, the mass resulting from the fusion may be treated with sulphuric acid, when the calcium remains undissolved. By the action of hydrochloric acid on solutions of the oxychloride, the *compounds* $ZrOCl_2,HCl,5H_2O$, and $ZrOCl_2,HCl,6H_2O$ may be obtained. By the action of ammonia on the oxychloride, hydrogen chloride is removed, and on drying the product at 110° crystalline metazirconic acid results. This reaction shows that the chlorine atoms in the oxychloride are probably present as loosely attached hydrogen chloride. Since, further, the two molecules of water in the oxychloride dihydrate cannot be removed without decomposition occurring, this water is apparently an integral part of the structure of the molecule. These facts, and the existence of Endemann's oxychloride (A., 1875, 1162), may be explained by supposing that the oxychloride is derived from the hydroxide by two of the hydroxo-groups binding hydrogen chloride, and the other two

holding water molecules by their subsidiary valencies, the formula being $[(H_2O)_3(OH)_2Zr(OHH)_2]Cl_2,2H_2O$.
R. CUTHILL.

Zirconium. J. H. DE BOER.—See B., 1927, 941.

Compound of lead iodide with stannous iodide. N. A. TANANAEV and I. TANANAEV (Z. anorg. Chem., 1927, 167, 341—344).—The reddish-orange compound obtained by the action of stannous chloride and potassium iodide on lead nitrate (A., 1925, ii, 324) appears to have the formula Pb_2SnI_6, although the exact composition varies somewhat with the conditions of formation. R. CUTHILL.

Constitution of nitrogen peroxide. M. BATTEGAY and W. KERN (Bull. Soc. chim., 1927, [iv], 41, 1336—1341).—Nitrogen peroxide reacts with certain anilides in such a way as to suggest that its constitution should be represented by the formula $O{:}N\cdot O\cdot NO_2$; thus with *p*-toluenesulphonyl-*p*-toluidide it gives first a mononitro-, then a dinitro-derivative, and finally a nitrosoamine of the latter. With *p*-toluenesulphonylmesidide in carbon tetrachloride nitrogen peroxide yields solely the N-*nitrosoamine*, $C_6H_2Me_3\cdot N(NO)\cdot SO_2\cdot C_6H_4Me$, pale brown crystals decomposed at 121—122°, and with the anilide, $CPh_3\cdot C_6H_2Me_2\cdot NH\cdot SO_2\cdot C_6H_4Me$, it yields the N-*nitrosoamine*, $CPh_3\cdot C_6H_2Me_2\cdot N(NO)\cdot SO_2\cdot C_6H_4Me$, pale yellow crystals decomposing at 110—120°. Other reactions of the peroxide, studied by Wieland and others, suggest the simple formula $O_2N\cdot NO_2$; it seems probable that the true explanation is that nitrogen peroxide in the liquid form exists in the above two tautomeric forms. A. R. POWELL.

Azido-carbon disulphide. III. Behaviour towards chlorine, bromine, and iodine. W. H. GARDNER and A. W. BROWNE (J. Amer. Chem. Soc., 1927, 49, 2759—2763).—Solid azido-carbon disulphide reacts explosively with chlorine and bromine, but not at all with iodine. By carrying out the former reactions in cooled non-aqueous solutions *compounds* are formed, probably $ClSCSN_3$ and $BrSCSN_3$. The former is a viscous, yellow oil, formed from a white solid first produced. In ethereal solution, bromine reacts with silver azido-dithiocarbonate to form a *tribromo-azido-dithiocarbonate*, Br_3SCSN_3; in chloroform and carbon tetrachloride solutions a mixture of this with the monobromo-derivative is produced. The hydrolysis of non-aqueous solutions of the monobromo-derivative with aqueous potassium hydroxide solution probably proceeds as follows: $BrSCSN_3+2KOH=KBr+KOSCSN_3+H_2O$; $2KOSCSN_3+2KOH=K_2S_2O_3+2KCNS+2N_2+H_2O$; $K_2S_2O_3+2KOH+2KOSCSN_3=2K_2SO_3+2KSCSN_3+H_2O$. Addition of iodine to concentrated aqueous sodium azido-dithiocarbonate solution causes the immediate formation of a heavy black oil. S. K. TWEEDY.

Decomposition of the vanadyl sulphates at high temperatures. C. EICHNER (Compt. rend., 1927, 185, 1200—1202).—In confirmation of previous results (A., 1921, ii, 554) it is shown that quadri- or quinque-valent vanadium, when heated in sulphuric acid solution, is oxidised or reduced, respectively, until a state of equilibrium is reached. Eventually most of the vanadium is precipitated as $VOSO_4$, and not as $V_2O_3(SO_4)_2$ as stated by Rosenheim and Mong (A., 1925, i, 1411). The remaining liquid contains a mixture of sulphates of quadri- and quinquevalent vanadium, tervalent vanadium (in the form of the compound $NH_4V(SO_4)_2$ of Rosenheim and Mong) being obtained only in the presence of ammonium sulphate at a temperature above 400°, when the latter decomposes and reduces the vanadium to the tervalent state. J. GRANT.

Thio-salts. III. Polyphenolic complexes. L. FERNANDES and F. PALAZZO (Gazzetta, 1927, 57, 567—574; cf. A., 1927, 636).—Ammonium thiomolybdate gives with phenols no compound or coloration, and from the oxythiomolybdate coloured syrups only are obtained; ammonium dithiomolybdate yields, however, with pyrocatechol the *compound* $[MoO_2S(C_6H_4O_2)](NH_4)H,3H_2O$, or in presence of pyridine the corresponding *pyridine* salt. Pyrogallol yields the *compound* $[Mo_2O_3S_3(C_6H_4O_3)_2](C_5H_5N)_2H_2,3H_2O$ (if the oxythio-salt is used, ammonium thiomolybdate separates), and gallic acid the *barium* salt, $[Mo_2O_3S_3(C_6H_2O_3\cdot CO_2)_2]BaH_2,12H_2O$. Salicylic acid does not yield such compounds.

The absorption spectra of molybdosalicylic acids, of pyrocatechol molybdates, and of thiomolybdates are compared. Compounds from thiomolybdates differ from those from molybdates in that addition of a second molecule of a phenol does not intensify the colour, the co-ordination valency of the molybdenum being already partly satisfied by the sulphur atom. It is concluded that co-ordinating capacity in derivatives of gallic acid, pyrogallol, 2 : 3-dihydroxybenzoic acid, pyrocatechol, and salicylic acid diminishes in this order. E. W. WIGNALL.

Coloration anomalies of ferric and alkali thiocyanates. E. KAHANE (Bull. Soc. chim., 1927, [iv], 41, 1403—1410).—The slow decolorisation of solutions of alkali thiocyanate containing small quantities of ferric salts is accelerated by boiling and is due to a reduction of the ferric salt to ferrous accompanied by the formation of perthiocyanic derivatives. Conversely, the pink colour that develops on exposing commercial preparations of alkali thiocyanates to ultra-violet light is due to oxidation of the small quantity of ferrous salt always present with the formation of ferric thiocyanate. This action is accelerated by the presence of oxidising agents and proceeds in the reverse direction when the coloured salt is kept in the dark. The removal of the traces of iron salts from preparations of thiocyanates is extremely difficult, but nearly pure preparations of the ammonium salt may be obtained by diluting alcoholic solutions with ether; the yield, however, is poor. Salts purified in this manner do not become coloured on exposure to direct sunlight.
A. R. POWELL.

Double compound of chromic and hydrogen chlorides. J. R. PARTINGTON and S. K. TWEEDY (J.C.S., 1927, 2899—2900).—By passing hydrogen chloride through a concentrated solution of green chromic chloride a heliotrope double *chloride*, $CrCl_3,HCl,xH_2O$ (where x is approximately 6), is precipitated. The substance is insoluble in ether

and in methyl and ethyl alcohols, and in water gives a pink solution which immediately turns green.
O. J. Walker.

Basic chromic compounds. N. Bjerrum and C. Faurholt (Z. physikal. Chem., 1927, **130**, 584—591).—The hexaquochromic ion, $Cr(H_2O)_6^{\cdots}$, may be determined by adding to the solution cæsium sulphate solution and precipitating cæsium alum by the addition of alcohol. The precipitate, after washing with alcohol, is oxidised with hydrogen peroxide in alkaline solution, potassium iodide and hydrochloric acid are added, and the liberated iodine is titrated with standardised thiosulphate solution. By this method the percentage of hexaquochromic ion has been determined in chromic nitrate solutions of concentrations 0·1—0·01*M* which have been heated at 75° for several days with or without the addition of sodium hydroxide. Determinations have also been made of the quantity of latent basic chromium compounds formed in the solutions by precipitation with sulphuric acid and alcohol. The formation of non-colloidal substances of this nature reaches equilibrium in a few days, whereas the colloidal forms are still being produced after heating for several months.
H. F. Gillbe.

Transformation of sodium chromate into dichromate by means of carbon dioxide. N. F. Yushkevich and J. N. Shokin.—See B., 1927, 936.

Oxide of fluorine or fluoride of oxygen ? B. Brauner (Nature, 1927, **120**, 842).—The substance obtained by Lebeau and Damiens (A., 1927, 1044) is regarded as oxygen difluoride, OF_2, differing in constitution and properties from chlorine monoxide, Cl_2O.
A. A. Eldridge.

Compounds of the halogens with each other, and with the halogen hydrides. K. H. Butler and D. McIntosh (Proc. Nova Scotian Inst. Sci., 1927, **17**, 23—25).—When bromine is dissolved in liquid chlorine the ebullioscopic constant is greater than for other solutes. To decide whether or not this is due to combination between solvent and solute, the f.-p. curve of the system chlorine–bromine has been determined. The curve is continuous and has no maximum.
M. S. Burr.

Behaviour of iron with other elements. G. Tammann and K. Schaarwächter (Z. anorg. Chem., 1927, **167**, 401—410).—The heating and cooling curves of mixtures of iron with various other elements have been determined. Sulphur, selenium, tellurium, antimony, zinc, and aluminium do not react appreciably below their m. p., but with calcium, boron, silicon, and graphite reaction commences even below the m. p. of the eutectics. Red phosphorus and arsenic begin to react when their vapour pressure approaches 1 atm.
R. Cuthill.

Univalent iron. W. Manchot (Annalen, 1927, **459**, 47—52).—Polemical against Reihlen and von Friedolsheim (A., 1927, 951).
J. W. Baker.

Univalent iron, nickel, and cobalt. III. Reduction process in the case of iron. W. Manchot and H. Gall (Ber., 1927, **60**, [*B*], 2318—2322; cf. A., 1927, 1157).—Ferrous mercaptide is conveniently prepared by reducing ferric chloride in aqueous solution with ethyl mercaptan and subsequent addition of ammonia, ethyl mercaptan, and alcohol to the solution, all operations being conducted in the absence of air. The compound is very readily oxidised and, in presence of oxygen, transforms ethyl alcohol into acetaldehyde. It very rapidly absorbs nitric oxide, yielding the compound $Fe(NO)_2{\cdot}SEt$, m. p. 78°, and ethyl thionitrite. Reduction of the mercaptides of iron, nickel, and cobalt is attributed to the chemical affinity of sulphur for nitric oxide and occurs according to the scheme: $X(SR)_2+nNO=(NO)_{n-1}XSR+NO{\cdot}SR$. In the cases of Roussin's salts the change appears to be $Fe(SK)_2+3NO=(NO)_2Fe{\cdot}SK+NO{\cdot}SK$; in confirmation, it is observed that a red, oily substance apparently very closely analogous to ethyl thionitrite is obtained from potassium hydrogen sulphide and ethyl nitrite. The action of ferrous sulphate, potassium hydrogen sulphite, and potassium nitrite yields directly the black salt $(NO)_7Fe_4S_3K$, but this is a secondary compound from the red salt $(NO)_2Fe{\cdot}SK$ and $(NO)FeCl_2$.
H. Wren.

Thiosulphatocobalt complexes. II. Potassium thiosulphatocobaltipentacyanide. P. R. Rây (J. Indian Chem. Soc., 1927, **4**, 325—330).—Thiosulphatopentamminecobaltic chloride (A., 1927, 742) is decomposed by concentrated potassium cyanide solution, yielding *potassium thiosulphatocobaltipentacyanide*, $K_4[S_2O_3,Co(CN)_5]$. This complex salt is neutral, gives no reaction for cobalt ions, yields precipitates with most metallic salts, is slowly hydrolysed in aqueous solution to the aquo-salt, $K_2[H_2O,Co(CN)_5]$, and is diamagnetic. Mol. wt. determinations show that in 1·5—2% aqueous solution the salt is not completely dissociated. The coagulating power of its ion is greater than that of the ferrocyanide ion. The pentamminecobaltic chloride is decomposed by sodium nitrite, yielding *cobalt trinitrotriammine* $[(NO_2)_3,Co(NH_3)_3]$.
H. Burton.

Complex compounds of tervalent iridium. V. V. Lebedinski (Ann. inst. platine, 1926, No. 4, 235—242).—When sodium chloroiridate dodecahydrate (1 g.) is heated with ethylenediamine monohydrate (2 c.c.) and water (10 c.c.) in a sealed tube at 140°, and the product treated with potassium iodide, *triethylenediamine iodoiridite*, $[en_3\,Ir]I_3,H_2O$, rose-yellow, is obtained. *Precipitates* are obtained with: sodium chloroplatinite (yellow), ammonium chloroplatinate (pink), sodium cyanoplatinite (white), bromoplatinic acid (yellow), sodium chloro-osmate (yellowish-green), potassium ferrocyanide (yellow), potassium ferricyanide (orange-yellow), sodium picrate (canary-yellow), $[en_2\,Ir][C_6H_2(NO_2)_3O]_3$.
Chemical Abstracts.

Preparation of platinum. V. V. Lebedinski and V. G. Chlopin (Ann. inst. platine, 1926, No. 4, 317—323).—1—1·2 Litres of a mixture of nitric acid (*d* 1·4), hydrochloric acid (*d* 1·19), and water (1 : 3 : 4 vols.) is added, first at 70—80°, then at the b. p., to the ore (100 g.), and evaporated at 30 mm. The residue, including osmium, iridium, etc., is heated on a water-bath for 2—2·5 hrs. and on a sand-bath at 140—142° with concentrated sulphuric acid until hydrogen chloride is removed. The diluted solution (500—600 c.c.), after heating for 30 min. on the water-bath, yields ammonium chloroplatinate with ammonium chloride (150 g.), the precipitate being washed with saturated ammonium chloride solution, ice-water, and alcohol. CHEMICAL ABSTRACTS.

Use of electrolytic bridge for determining soluble salts. R. O. E. DAVIS (U.S. Dept. Agric. Circ. 423, 1927, 13 pp.).—The construction and use of a simple form of Wheatstone's bridge suitable for approximate determination of the conductivity of drainage waters and wet soils are described. Tables are provided to enable the amount of soluble matter to be calculated from the conductivity. If a large quantity of organic matter is present, the results are untrustworthy. R. CUTHILL.

Accuracy of titration of acids and alkalis. T. MIŁOBĘDZKI (Rocz. Chem., 1927, 7, 295—308).—Sources of error in the titration of various acids and alkalis using various indicators are discussed. The accuracy of titration of 0·1*N*-hydrochloric acid with 0·1*N*-sodium hydroxide is from 0·01 to 0·03%, and the titre found is accurate to 99·8—99·9%. R. TRUSZKOWSKI.

Differential electrometric titration as a precision method. D. A. MACINNES (Z. physikal. Chem., 1927, 130, 217—221).—The method of differential electrometric titration (A., 1927, 35) is applicable to the determination of end-points in titrations of high precision, such as those of oxalic acid and potassium permanganate, hydrochloric acid and sodium hydroxide, and arsenious oxide and iodine. The curve obtained by this method for the reaction of a base with an acid in the presence of quinhydrone shows two maxima, indicating two points of inflexion in the curve obtained by the usual method, which, if not clearly recognised, may lead to error in its use. L. S. THEOBALD.

Colouring matters operating in the presence of neutral salts, and the construction of a scale of indicators with varying mass indices for the comparison of saline solutions. F. VLÈS, P. REISS, and (MLLE.) M. GEX (Compt. rend., 1927, 185, 1127—1130; cf. this vol., 14).—The behaviour of indicators of various types in a number of saline solutions has been investigated spectrophotometrically, and their mid-point values (mass indices) have been determined colorimetrically by means of the comparator with reference to potassium chloride. The indicators fall into groups which appear to correspond with their constitutions. The authors' concentration–absorption equation (*loc. cit.*) holds for the various indicators in potassium chloride solutions. J. GRANT.

Automatic apparatus for the determination of moisture [by distillation with benzene etc.]. H. RÖSSLER.—See B., 1927, 895.

Determination of halogens by Volhard's method. G. LEIMBACH (Caliche, 1927, 8, 428—430).—After filtration, an aliquot part of the filtrate is titrated; much nitrate causes only slightly high results, and iodates do not interfere. CHEMICAL ABSTRACTS.

Micro-determination of iodine in potable waters. M. SETTIMJ.—See B., 1927, 958.

Determination of iodates in the presence of iodides, nitrates, nitrites, and chlorides. G. LEIMBACH (Caliche, 1927, 8, 409—411).—Sufficient silver nitrate is added to precipitate the iodide and part of the chloride, and the acidified filtrate is boiled with a slight excess of chlorine or sodium hypochlorite and phenol to remove the nitrite. Some of the iodate, however, becomes decomposed. CHEMICAL ABSTRACTS.

Determination of sulphur in ores. K. K. JÄRVINEN.—See B., 1927, 910.

Rapid determination of sulphur in iron ores. C. C. HAWES.—See B., 1927, 939.

Microtitration of sulphate ions and of barium ions by a centrifugal method. R. F. LE GUYON (Bull. Soc. chim., 1927, [iv], 41, 1387—1389).—Barium and sulphate ions may be determined by centrifugovolumetry, using sulphuric acid and barium chloride, respectively, in the way previously described (cf. A., 1926, 927). A determination takes 8—10 min. and the end-point may be observed within 0·05 c.c. A. R. POWELL.

Determination of sulphur trioxide in the presence of sulphur dioxide. J. R. ECKMAN.—See B., 1927, 876.

Determination of sulphuric acid in drinking water by the use of benzidine. F. RASCHIG.—See B., 1927, 894.

Determination of selenium and tellurium by means of titanous chloride. O. TOMIČEK (Bull. Soc. chim., 1927, [iv], 41, 1389—1399).—Tellurates and tellurites may be titrated potentiometrically with titanous chloride in the presence of hydrochloric acid, the end-point being marked by a sharp change of potential when all the tellurium is precipitated in the elementary form. In sulphuric acid solution two breaks are obtained in titrating telluric acid, the first corresponding with reduction to tellurous acid and the second with total reduction to tellurium. For the gravimetric determination of tellurium the reduction to the element is carried out in a solution containing 30 c.c. of 20% hydrochloric acid per 100 c.c., using 3 c.c. of a 20% titanous chloride solution for every 0·1 g. of tellurium present as tellurate. The precipitate is washed with dilute acid, then with water, dried at 105°, and weighed. Selenium may be determined potentiometrically in selenates in a similar manner to tellurium in tellurates, but only one potential change occurs in sulphuric acid solutions. A. R. POWELL.

Reaction of tellurium. O. TOMIČEK (Bull. Soc. chim., 1927, [iv], 41, 1399—1403).—The reduction of tellurates and tellurites to tellurium by titanous chloride in hydrochloric acid solutions (cf. preceding abstract) is sufficiently delicate to serve as a test for tellurium in the absence of gold, copper, selenium, and the platinum metals; in 5 c.c. of concentrated hydrochloric acid 0·00005 g. of tellurium gives with 2 c.c. of 2% titanous chloride solution a grey cloud which slowly flocculates. In the presence of a large quantity of sodium or ammonium acetate and a little acetic acid titanous or chromous chloride reduces tellurium compounds to hydrogen telluride, which may be detected by the production of a mirror when the gas is passed through a heated tube, as well as by its characteristic disagreeable odour. Selenium, phosphorus, arsenic, antimony, bismuth, tin, and lead give a similar reaction. A. R. Powell.

Simplified apparatus for micro-Kjeldahl determinations. J. G. van der Sande (Chem. Weekblad, 1927, 24, 558).—The apparatus is provided with a dropping funnel fused on to the tube connecting the steam flask with the Kjeldahl flask, so that the sodium hydroxide solution may be added to the latter in position. The condenser is arranged vertically, with its end drawn out to a capillary, and dipping below the surface of the standard acid solution.

S. I. Levy.

Improved micro-Kjeldahl ammonia distillation apparatus. G. Kemmerer and L. T. Hallett.—See B., 1927, 958.

Spectrophotometric detection of boron. W. C. Holmes.—See B., 1927, 936.

Determination of small quantities of carbon monoxide in air. N. Komar.—See B., 1927, 936.

Colorimetric method for the field determination of the carbon dioxide tension and free carbon dioxide, hydrogen carbonates, and carbonates in natural waters. I. Theoretical. E. B. Powers.—See B., 1927, 958.

Determination of carbon disulphide in its emulsions. H. J. Fisher.—See B., 1927, 876.

Systematic qualitative analysis of cations without the use of hydrogen sulphide or its derivatives. O. Macchia (Z. anal. Chem., 1927, 72, 180—185).—The substance is heated with nitric acid to destroy iodides and organic substances, the solution is evaporated to dryness, the residue gently heated to carbonise organic matter, and the resulting mass (or the original substance if free from organic substances) digested with aqua regia. Irrespective of whether the substance is completely dissolved or not, nitric acid is added and the mixture evaporated nearly to dryness. After slight dilution, ammonia to alkalinity, ammonium carbonate, hydrogen peroxide, and ammonium phosphate are added, the solution is boiled and filtered, and the precipitate, *A*, digested with aqua regia whilst the filtrate, *B*, is acidified with nitric acid whereby silver is precipitated as chloride and removed by filtration. The solution of *A* is concentrated and digested hot with sodium hydroxide, peroxide, and carbonate, giving precipitate *C* and filtrate *D*. The former is washed with saturated sodium carbonate solution and dissolved in a mixture of formic and nitric acids, part of the solution being tested for manganese by boiling with lead peroxide and the remainder being treated with ammonia, ammonium chloride, and hydrogen peroxide, giving precipitate *E* and filtrate *F*. The latter is tested for the alkaline-earths and magnesium in the usual way, whilst *E* is dissolved in sulphuric acid and hydrogen peroxide and the iron and bismuth are separated from the manganese by means of ammonia and dextrose, and from one another by reduction of the iron with sulphur dioxide and precipitation with ferricyanide, followed by precipitation of bismuth with sodium hydroxide. Filtrate *D* is treated with sulphuric acid, which removes lead, then with sodium carbonate to precipitate antimony, tin, and aluminium, leaving chromate in solution. Tin and aluminium are extracted from the precipitate by treatment with formic acid, and tin alone is precipitated by addition of citric acid followed by ammonia. Filtrate *B* is divided, a small portion being tested for mercury with a clean piece of copper foil and a second small portion for arsenic by heating with aluminium and sodium hydroxide and allowing the hydrogen to impinge on silver nitrate test paper; the main portion is evaporated to dryness and the residue ignited to expel ammonium, mercury, and arsenic compounds, and extracted with bromine water to dissolve alkali metal salts. The insoluble material is collected and dissolved in nitric acid, and the solution digested with sodium hydroxide and bromine and filtered. The filtrate, if yellow, contains chromate, which is confirmed by the hydrogen peroxide test, and zinc, which is confirmed by addition of ferrocyanide to the acidified solution. The precipitate is dissolved in hydrochloric acid, copper removed by treatment with sulphur dioxide and thiocyanate, nickel with dimethylglyoxime in ammoniacal solution, cadmium as a white precipitate of hydroxide on adding sodium hydroxide and hydrogen peroxide to the cold filtrate from the nickel, and cobalt by boiling the filtrate from the cadmium to precipitate black cobaltic hydroxide.

A. R. Powell.

Determination of potassium in mixtures of salts, especially in Chile saltpetre, by the perchlorate method. G. Leimbach.—See B., 1927, 874.

Microchemical detection of rubidium. E. Burkser and S. Rubloff (Mikrochem., 1927, 5, 137—145).—A solution of a rubidium salt in concentrated hydriodic acid yields with equal volumes of a 14% solution of silver iodide in the same acid and of a 4·5% solution of gold in iodine and hydriodic acid black, hexagonal crystals of the *compound* $3AuI,AuI_3,4RbI,AgI$ when the rubidium is in excess, and of the *compound* $3AuI,AuI_3,3RbI,2AgI$ when an excess of the reagents is used. The formation of these black crystals forms a delicate test for rubidium in the presence of potassium or ammonium salts, as little as $1—3\times10^{-8}$ g. of rubidium in one drop of a solution on a microscope slide giving a detectable reaction; cæsium interferes, as it gives a similar reaction, but the crystals have a pronounced tendency to collect into stellar aggregates. The method is far more delicate than the corresponding tests using chlorides or bromides of gold and silver. The gold iodide solution is made by allowing fine filings of gold to remain for 1 week in contact with iodine, hydriodic acid (*d* 1·5), and a little ether, and the silver solution by dissolving freshly precipitated and washed silver iodide in hydriodic acid.

A. R. Powell.

Rapid potentiometric determination of silver and zinc in the same solution. E. Müller and H. Hentschel (Z. anal. Chem., 1927, 72, 188—195).—The neutral nitrate solution of the two metals is titrated at 75° with 0·1*N*-potassium bromide solution,

using a silver indicator electrode and a normal calomel electrode with an opposing potential of +0·176 volt. Without filtering the silver bromide the solution is then titrated with ferricyanide for zinc, using a platinum indicator electrode and an opposing potential of +0·31 volt, until the galvanometer registers zero.
A. R. Powell.

Influence of ammonia on the results of the determination of magnesium by Schmitz' method. J. Majdel (Arh. Hemiju, 1927, 1, 216—217; cf. Technic List., 1925, 6, 16).—The completeness of precipitation of magnesium as pyrophosphate depends on the concentration of ammonium salts present, the best results being given by the addition of one fifth of the volume of 10% ammonia.
R. Truszkowski.

Determination of traces of impurities in lead. B. S. Evans.—See B., 1927, 911.

Rapid potentiometric determination of lead and cadmium in the same solution. E. Müller and W. Prée (Z. anal. Chem., 1927, 72, 195—200).—The neutral nitrate solution of the two metals is divided and one portion is titrated at 75° with 0·1N-sodium ferrocyanide solution, using a platinum indicator electrode and an opposing potential of +0·18 volt, until the galvanometer registers zero. The sum of the lead and cadmium is thus obtained; cadmium alone is determined in the second portion by a similar titration at 60°, using an opposing potential of +0·2 volt, after precipitating the lead by addition of sodium sulphate and alcohol. A. R. Powell.

Determination of cuprous oxide and copper in mixtures containing both. W. D. Bonner and B. D. Kaura.—See B., 1927, 940.

Volumetric determination of cerium. G. Autié (Bull. Soc. chim., 1927, [iv], 41, 1535—1546).—The accuracy of the various methods which have been proposed from time to time for the volumetric determination of cerium has been examined. The only satisfactory methods are those involving oxidation of a cerous salt with alkaline permanganate (Meyer and Schweitzer, A., 1907, ii, 581), or with a persulphate (von Knorre, A., 1900, ii, 576), and the potentiometric method (Tomiček, A., 1925, ii, 716). In using von Knorre's method, the ceric salt formed by oxidation should, when the excess of persulphate has been destroyed by boiling, be determined with hydrogen peroxide in concentrated nitric acid solution, as otherwise errors arise owing to the precipitation of what appears to be a form of ceric hydroxide.
R. Cuthill.

Volumetric determination of aluminium. A. Wöhlk (Dansk Tidsskr. Farm., 1927, 1, 525—536).—The method depends on the formation of the complex salt, $Al(C_2O_4)_3K_3$, which is neutral in solution. The dilute solution of the aluminium salt is heated to boiling and precipitated with approximately N-ammonia, methyl-red being used as indicator. The precipitate is collected, washed back into the beaker with boiling water, and stirred thoroughly until all lumps are broken up. A little ammonium chloride and two drops of methyl-red are added, and ammonia solution is added drop by drop until the colour of the solution changes to yellow. The liquid is heated to boiling, the aluminium hydroxide collected on the original paper and washed, first with ammonium nitrate containing a few drops of ammonia, and finally with neutral ammonium nitrate. The paper and precipitate are returned to the beaker, and the precipitate is dissolved by warming with a measured volume of a standardised solution of oxalic acid. After cooling and diluting to 100 c.c., 1—2 g. of neutral potassium or sodium oxalate are added, and the excess of oxalic acid is titrated with 0·5N- or N-sodium hydroxide, using methyl-red as indicator.

A solution of borax may be used in place of sodium hydroxide for titrating the oxalic acid, or, if only small amounts of aluminium are to be determined, a solution of potassium iodide and iodate may be added, and the liberated iodine determined by titration with thiosulphate solution.
H. F. Harwood.

Analytical consequences of the region of stability of cryolite. A. Travers (Compt. rend., 1927, 185, 1043—1046; cf. A., 1927, 1141).—The liberation of hydroxyl ions in the equilibrium $Al(OH)_3+6F' \rightleftharpoons AlF_6+3OH'$ may be used to demonstrate the dissociation of heated kaolin into free silica and alumina, and to detect free hydrated alumina in certain clays. For the separation of silica and fluorine (*e.g.*, in rock analysis) the method of Berzelius and that involving the formation of potassium fluosilicate are incorrect in the presence of alumina. If the ratio Al_2O_3/SiO_2 is less than $\frac{1}{3}$, and if the rock is attacked by fused alkali carbonates alone, the alumina may be removed as an insoluble permutite, and the fluorine may be determined accurately in the water extract. When the p_H value of the water extract is higher (*e.g.*, with mica or topaz), the permutite decomposes and the alumina passes into solution as aluminate, and is subsequently precipitated after neutralisation as a complex fluoride. J. Grant.

Potentiometric determination of indium. U. B. Bray and H. D. Kirschman (J. Amer. Chem. Soc., 1927, 49, 2739—2744).—Acidified indium chloride solution, 0·05N or less with respect to hydrochloric acid, is titrated with potassium ferrocyanide, the end-point being determined potentiometrically. An insoluble *compound*, presumably $KIn_5[Fe(CN)_6]_4$, is formed. Since the composition of the analogous zinc compound is known (Treadwell and Chervet, A., 1923, i, 764) the ferrocyanide solutions may be standardised with respect to indium by means of pure metallic zinc. S. K. Tweedy.

"Potassium chlorate" method for determining manganese. IV, V, and VI. M. Marqueyrol and L. Toquet (Ann. Chim. analyt., 1927, [ii], 9, 324—330; cf. A., 1927, 1162).—By using nitric acid (*d* 1·332) and carrying out the precipitation on a water-bath, manganese in any concentration can be determined accurately. The advantages of the method are that large quantities of the metal can be used, that no empirical constant is involved, and that the completeness of the precipitation can always be verified. C. W. Gibby.

Separation of manganese in rock analysis. E. V. Holt and H. F. Harwood (Min. Mag., 1927, 21, 318—323).—The manganese present in small amount (usually less than 1%) in rocks interferes with the separation of alumina, lime, and magnesia. The various methods of separation are mentioned and preference is given to that in which the manganese is precipitated with the alumina and ferric oxide by ammonia in the presence of an oxidising agent. As oxidising agents trials were made with ammonium persulphate, hydrogen peroxide, chlorine, and bromine. The last of these—bromine water added gradually to the boiling alkaline solution—gave the best results.

L. J. Spencer.

Rapid determination of manganese in steels. A. Quartaroli.—See B., 1927, 910.

Analysis of nickel–chromium and nickel–chromium–iron alloys. D. Harvey.—See B., 1927, 879.

Detection of uranium by a photo-luminescence test. J. Papish and L. E. Hoag (Proc. Nat. Acad. Sci., 1927, 13, 726—728).—Uraniferous material is fused with potassium fluoride and the resulting mass examined by near ultra-violet light. An orange-yellow luminescence is characteristic of uranium. Sodium fluoride gives a similar result, but niobic acid also produces fluorescence in this case.

W. E. Downey.

Gravimetric and volumetric micro-determination of bismuth. R. Strebinger and W. Zins (Mikrochem., 1927, 5, 166—192).—The nitrate solution is evaporated to dryness, the residue dissolved in 0·1—0·15 c.c. of 3*N*-nitric acid and 2—2·5 c.c. of water, and the solution treated with potassium iodide, added a small crystal at a time until the liquid above the black precipitate of bismuth tri-iodide appears yellow. A further 2·5 c.c. of water are added and the mixture is heated slowly on the water-bath until the black precipitate is converted into copper-coloured, glistening crystals of bismuth oxy-iodide. Another 5 c.c. of water are added and heating is continued until the precipitate settles and the supernatant liquid is colourless; the solution is treated with 2—2·5 c.c. of 1% sodium acetate solution, cooled, and filtered, and the precipitate is washed with cold water, then with alcohol, dried at 105°, and weighed as BiOI. Alternatively, the dried precipitate may be heated in a current of air or oxygen and the liberated iodine collected in potassium iodide and titrated with thiosulphate.

A. R. Powell.

Volumetric determination of bismuth. H. Kubina and J. Plichta (Z. anal. Chem., 1927, 72, 201—207).—The cold bismuth solution is treated with 0·1 g. of aluminium dust and 40 c.c. of 3*N*-potassium hydroxide solution. After gently shaking for 20 min. the mixture is heated to boiling until the precipitated bismuth flocculates and the aluminium is completely dissolved. The precipitate is washed by decantation and dissolved in 15 c.c. of a solution containing 200 g. of ferric chloride and 250 c.c. of concentrated hydrochloric acid per litre. The resulting ferrous chloride is titrated with permanganate after addition of the usual solution containing manganese sulphate and phosphoric acid. Good results are also obtained by precipitation of the bismuth in acid solution with copper in an atmosphere of carbon dioxide followed by titration of the cuprous chloride with potassium bromate; in this method lead does not interfere (cf. Reissaus, A., 1927, 334).

A. R. Powell.

Separation and determination of metals by means of 8-hydroxyquinoline. VI. Determination of bismuth. R. Berg (Z. anal. Chem., 1927, 72, 177—179; cf. A., 1927, 848).—In acetic acid or in ammoniacal tartrate solutions containing bismuth, 8-hydroxyquinoline produces an orange-yellow, crystalline precipitate of $Bi(C_9H_6ON)_3,H_2O$, stable at 105°, but becoming anhydrous after prolonged heating at 130—140°. The limit of sensitivity of the test is 1 part of bismuth in 300,000 parts of a dilute acetic acid or in 270,000 parts of an ammoniacal tartrate solution. For quantitative work the solution of bismuth salt must be free from halides; it is heated at 60—70° and treated with an excess of a cold saturated solution of the reagent in alcohol or acetone. The precipitate is collected, washed with hot water, dried at 100° or at 140°, and weighed as the monohydrate or anhydrous compound. Alternatively, the precipitate may be dissolved in hydrochloric acid and titrated with bromide–bromate solution.

A. R. Powell.

Analytical chemistry of tantalum, niobium, and their mineral associates. IX. Separation of titanium from tantalum and niobium. W. R. Schoeller and E. C. Deering.—See B., 1927, 940.

Refractometer for determining the refractive indices of gem-stones, crystals, and liquids. B. J. Tully (Min. Mag., 1927, 21, 324—328).—A convenient box-form of instrument contains a hemisphere of dense glass and a system of lenses and reflecting prisms. The shadow-edge of total reflexion is thrown on to a scale, giving in the eyepiece a direct reading of the refractive index.

L. J. Spencer.

Silvering of glass plates for optical instruments. J. J. Manley (Phil. Mag., 1927, [vii], 4, 1322—1323).—A film of silver which will endure polishing may be obtained by carrying out the whole of the deposition from the usual solutions at 0°. An equally satisfactory deposit, which does not require polishing, is produced by allowing the silvering solutions to act for 10—15 min. at the ordinary temperature, then stopping the deposition by passing a current of water through the silvering bath.

R. Cuthill.

Explosions in the coating of mirrors. W. Meyer.—See B., 1927, 913.

Sodium flame for polarimetric work. T. McLachlan and A. W. Middleton (Analyst, 1927, 52, 639).—A brilliant sodium flame may be maintained by using a pencil obtained by mixing 33% of sodium chloride, 33% of sodium bromide, and 14% of magnesium oxide with sufficient water to obtain a damp mass, kneading it into 20% of sodium silicate, rolling out, and drying.

D. G. Hewer.

Composite yellow. J. Papish and F. E. Agel (J. Physical Chem., 1927, 31, 1746—1747; cf. Rayleigh, Nature, 1871, 3, 234).—Difficulties were encountered in preparing composite yellow by Rayleigh's method (*loc. cit.*), but it can readily be obtained by placing together cells containing a saturated solution of potassium chromate, and a solution of neodymium chloride containing the equivalent of 4 g. of the sesquioxide per 100 c.c.

L. S. Theobald.

Monochromatic colour filters. F. Weigert and H. Staude (Z. physikal. Chem., 1927, **130**, 607—615).—The preparation is described of practically monochromatic colour filters, based, not on selective absorption, but on selective refraction. Although very simple to make, much greater intensity of light may be obtained than is given by expensive monochromators. H. F. Gillbe.

Transmission properties of some filters. E. Pettit (Astrophys. J., 1927, **66**, 43—58).—Transmission curves of 44 filters are given from 0·23 to 2·3 μ, and in some cases to longer wave-lengths. The effect of sunlight on green celluloid, glass, silver, and gold films was observed. A. A. Eldridge.

Simple form of automatic siphon. D. C. Harrison (J.C.S., 1927, 2896—2897).—A glass siphon of diameter not greater than 5 mm. contains inside the bend about eight capillaries of diameters from 0·25 to 1 mm., projecting about 7 cm. into the shorter limb. The longer limb extends well below the capillaries and is coated with paraffin wax on the inside to within about 4 cm. of the ends of the capillaries. A rapid flow of liquid through the siphon is possible. O. J. Walker.

Laboratory evaporation and filtration. J. H. Linschoten (Chem. Weekblad, 1927, **24**, 558—559).—Simple apparatus is described for the automatic continuous feeding of large quantities of liquids for evaporation or filtration. S. I. Levy.

Differential ebulliscope. W. Swientoslawski (Z. physikal. Chem., 1927, **130**, 286—288).—A differential ebullioscope is described which overcomes variations in atmospheric pressure and avoids the use of two sets of b.-p. apparatus. The apparatus can also be used for the measurement of the coefficient *dp/dt*, and for the comparison of Beckmann thermometers. A diagram is given. L. S. Theobald.

Rapid mercury still. R. J. Clark (Proc. Camb. Phil. Soc., 1927, **23**, 956—958).—A modification of Hulett's still (Physical Rev., 1905, [i], **21**, 288). A second air inlet admits air above the mercury surface. A boiler of 500 c.c. capacity can distil 1500 g. of mercury per hr. W. E. Downey.

Adhesion phenomenon of mercury, and a new manometer. C. Hagen (Physikal. Z., 1927, **28**, 735—737).—A piece of wide tubing is connected at one end to a vacuum and at the other to a movable mercury container. A side arm is connected to two similar vertical capillary tubes, one of which is closed and the other connected to a second side arm, restoring connexion with the main tube. When the vacuum is high the level of mercury can be raised so as to fill the closed capillary, and on lowering the container slowly the mercury adheres in the closed capillary but descends in the open one. The resultant difference in level varies with the pressure; *e.g.*, at 1×10^{-5} mm. it is 6 mm., at 3×10^{-5} about 1 mm., and at 9×10^{-5} mm. it is zero. The sealed end of the capillary must not be conical with a sharp angle, or adhesion will not occur.

The phenomenon has been utilised in devising a modified McLeod gauge sensitive to low pressures.

R. A. Morton.

Specific heats at low temperatures. Apparatus for the rapid determination of specific heats of solids at low temperatures. F. Simon and M. Ruhemann (Z. physikal. Chem., 1927, **129**, 321—338).—A method is described for determining by a rapid series of measurements the mean specific heat of a substance over a very small temperature interval, and results are given for a number of metals at temperatures between 71° and 83° Abs. The following characteristic temperatures have been determined from the atomic heat at constant volume: tantalum 243·5°, chromium 486°, cobalt 383°, nickel 368°, and beryllium 1035°. H. F. Gillbe.

Sucrose solution for the calibration of viscosimeters. E. von Mühlendahl (Z. angew. Chem., 1927, **40**, 1318—1320).—Paraffin or castor oil is not entirely suitable for calibration purposes owing to their variable chemical characteristics, and glycerol, although a well-defined compound, is hygroscopic. Sucrose is therefore used to calibrate an Ostwald capillary viscosimeter. Tables are given for water and sucrose solutions (60, 62, 64, 66%) at temperatures of 16—30°. The logarithm of the viscosity is proportional to the concentration and inversely proportional to the temperature. W. G. Carey.

Chinese alchemy. B. E. Read (Nature, 1927, **120**, 877—878).—Evidence supporting the view that Chinese alchemy originated independently of, and antedated, the Egyptian school is adduced.

A. A. Eldridge.

Geochemistry.

Theory of the upper atmosphere and meteors. H. B. Maris (Nature, 1927, **120**, 839).

Rôle of ozone in the atmosphere. J. Lévine (Compt. rend., 1927, **185**, 962—963).—Dobson's conclusion (Proc. Roy. Soc., 1924, **A**, **114**, 521) that the ozone content of the atmosphere depends on the distribution of the atmospheric pressure, being higher during depressions than during anticyclones, is in agreement with that of the author (Compt. rend., 1923, **176**, 705). J. Grant.

Natural mineral waters in the light of modern research. O. Baudisch and D. Davidson (Arch. Int. Med., 1927, **40**, 496—520).—The catalase and peroxidase activities of Saratoga mineral waters disappear when the water is irradiated by ultraviolet light in the presence but not in the absence of oxygen. These waters give no blue coloration with potassium ferricyanide but give a green coloration with nitrosophenol, apparently dependent on the presence of ferrous iron in a combined condition. After irradiation in presence of oxygen the waters no longer give a green colour with nitrosophenol and therefore the catalytic activity appears to be dependent on the presence of ferrous iron. Simple solutions of ferrous salts such as ferrous hydrogen carbonate do not, however, behave similarly to the mineral waters. W. O. Kermack.

Chemical composition of the interior of the earth and the moon. S. Mohorovičić (Arh. Hemiju, 1927, **1**, 95—104).—From seismological, petrological, and astronomical-geodetic considerations it is concluded that the earth consists mainly of iron, magnesium, silicon, and oxygen, whilst the moon contains in addition relatively more aluminium and calcium. The rigidity of the earth is a little more than three times as great as that of the moon. Venus and Mercury probably possess a similar composition to the earth, whilst that of Mars is closer to that of the moon. The planetoids are of similar composition to meteorites, whilst the planets more distant from the sun probably resemble the fixed stars in composition, this being unknown. R. Truszkowski.

Radioactivity and the temperature of the interior of the earth and the moon. S. Mohorovičić (Arh. Hemiju, 1927, **1**, 226—236).—From a consideration of the thickness of the Sial granite substratum and its radioactivity, thermal conductivity, and elasticity, it is concluded that at a depth of 50 km. the rocks of the moon exist only in the liquid state, whilst at 70 km. only the gaseous phase can exist. In the earth, a temperature high enough to liquefy rocks (2500°) is attained at a depth of 50 to 60 km. below high mountains.

R. Truszkowski.

Case of pseudopolychroism in calcite. B. Dimitrievitch (Compt. rend., 1927, **185**, 1143—1144).—Pseudopolychroism has been detected in a colourless calcite (from Avala, Serbia), found in the form of plates in the fissures of rocks and associated with non-polychroic calcite or with felspars. The calcite behaves as a rectilinear polariser, but the action of hydrochloric acid (5%) removes the active agent and leaves an opaque non-pseudopolychroic residue of isotropic corpuscles. Since the calcite is derived from felspars, these corpuscles are probably composed of kaolin or gelatinous silica contained in the calcite in the form of a mechanical mixture.

J. Grant.

Exploitation of the magnesian lakes of the Crimean peninsula. S. F. Shemtschushni (Ann. Inst. Anal. Physico-Chim. Leningrad, 1926, **3**, 370—378).—Figures are given showing the compositions of the saline contents of five lakes of the Perekopski group at different times. The salts contain predominating proportions of magnesium chloride and their use as sources of magnesium compounds is discussed. T. H. Pope.

Chemical nature of natural hydrates of ferric oxide. N. S. Kurnakov and E. J. Rode (Ann. Inst. Anal. Physico-Chim. Leningrad, 1926, **3**, 305—332).—Investigation of the heating and dehydration curves of natural hydrates of ferric oxide indicates that the only existing hydrate of definite composition is the monohydrate, Fe_2O_3,H_2O, which probably corresponds with natural göthite and lepidokrotite. The natural hydrated forms of ferric oxide may be separated into three classes: (1) Hydrohæmatites, constituting the α-phase of variable composition. The water present varies within wide limits up to about 8% and is of zeolitic type, forming solid solutions with hæmatite. The heating curves exhibit a break at about 129—150°, corresponding with commencement of the dehydration of the solid solutions. (2) Göthites, lepidokrotites, limonites, bog iron ores, representing the β-phase of variable composition and containing 9·9—13·2% of water, probably contain the definite hydrate, Fe_2O_3,H_2O (10·1% H_2O) with any excess of water in the form of a solid solution. The heating curve shows clearly the göthite halt, corresponding with a change in the properties of the substance, and also, when the water-content is sufficiently high, a change in direction at 125—135°, indicative of decomposition of the göthite or β-solid solution. The dehydration curves change direction at 200—250°, at which temperature equilibrium between the two solid α- and β-phases is established; the lower branch corresponds with the solid solution of water and göthite and the upper with that of water and hæmatite. (3) Xanthosiderites, limonites, which form the γ-phase, with water-content 13·8% or more. With these, the heating curves exhibit, in addition to the göthite halt, a second break in the continuity at 120—150°, sometimes accompanied by reheating. At this point there probably exists a mixture of the β- and γ-solid solutions. T. H. Pope.

Structure of felspars and of mica. M. Dominikiewicz (Rocz. Chem., 1927, **7**, 345—356).—The kaolin nucleus is an integral part of the molecule of felspar and of mica, anorthite being normal calcium kaolinate and orthoclase a silicate of potassium kaolinate. In the process of kaolinisation of felspar the potassium silicate split off combines with the aluminate, but not with the silicate fragment of the molecule. Kaolinisation takes place, not only under the influence of atmospheric agencies, but also by the action of volatile acids, steam, etc. The conversion of alkaline felspar into mica is explicable on the basis of hydrolytic or pneumalytic elimination of 8 alkali silicate nuclei, the silicate molecules of which are replaced by hydrogen atoms. Acid micas possessing various alumina and silica contents are products of the progressive disintegration of the kaolin nuclei. The existence of mixtures of these various disintegration compounds is quite possible. The simplest micas may be considered as being built up of natrolite nuclei, whence the space formula of lepidolite is derived. By substitution of the free —SiO— radicals of the natrolite nucleus by magnesia the simplest biotites and phlogopite are obtained. Other biotites may be regarded as substitution products of the natrolite or kaolin nuclei by magnesium silicate, silicate molecules combining with the aluminate portion of these nuclei. R. Truszkowski.

Action of dilute acid and of sodium carbonate solution on mica. A. Fioletova (Ann. Inst. Anal. Physico-Chim. Leningrad, 1926, 3, 426—433).—A sample of black mica (biotite) was decomposed when treated with 10% hydrochloric acid for 10 hrs., whereas more than one half remained undecomposed after three successive treatments, each of 2 hrs.' duration, with 2% hydrochloric acid. Preliminary heating of the biotite to dull redness renders the decomposition more difficult. With clay containing a large proportion of biotite, a certain but not a complete separation is possible by means of 2% hydrochloric acid, if the material is previously heated to dull redness for not more than 2—3 hrs.; when the clay contains the usual small proportion of mica in thin pieces, it is probable that this treatment effects dissolution of the whole of the mica. A suggested structure for mica is given. T. H. Pope.

Formation of radioactive manganiferous deposits from Tanokami, and the source of manganese in the deep-sea nodules. S. Iimori (Bull. Chem. Soc. Japan, 1927, 2, 270—273; cf. A., 1926, 380, 494).—Analyses of manganiferous deposits from Tanokami and of deep-sea nodules are compared and discussed. C. W. Gibby.

Green kaolin from Tanokami. S. Iimori (Bull. Chem. Soc. Japan, 1927, 2, 274—278).—An analysis of green kaolin from Tanokami has been made. The elements present in the chromosphere are also the universal minor constituents of igneous rocks.

C. W. Gibby.

Temperature-range of formation for tourmaline, rutile, brookite, and anatase in the Dartmoor granite. A. Brammall and H. F. Harwood (Min. Mag., 1927, 21, 205—220).—The association of tourmaline with both α-quartz and β-quartz (transition at 575°) proves that some of the tourmaline was formed below 575° and some above that temperature, possibly up to 800°. The stability range of rutile corresponds with that of tourmaline, and is higher than that of anatase and still higher than that of brookite. L. J. Spencer.

Chemical classification of the mica group. III. Molecular volumes. A. F. Hallimond (Min. Mag., 1927, 21, 195—204).—The molecular volumes of a number of analysed micas belonging to different groups (A., 1925, ii, 819; 1926, 815) are tabulated and plotted against the RO-content. A good agreement is shown with the volumes calculated as an additive property of the constituent oxides.

L. J. Spencer.

Study of bituminous rocks. G. Testi and G. Inardi (Annali Chim. Appl., 1927, 17, 446).—Many substances which do not exhibit fluorescence when exposed to ultra-violet rays show marked fluorescence if dissolved in a suitable solvent. The presence of hydrocarbons in rocks may be detected by this means. Two or three g. of the powdered rock are shaken with 20—30 c.c. of a solvent for petroleum in either a flat-bottomed glass dish or a quartz test-tube. In presence of hydrocarbons, the liquid gradually develops increasing fluorescence on exposure to ultra-violet rays, the phenomenon being observed more readily if the solution is absorbed by filter-paper. In absence of hydrocarbons, either no fluorescence or one of different character appears. A sample of ichthyolic shale gave, however, no fluorescence, possibly owing to the presence of sulphur.

T. H. Pope.

Occurrence of the platinum metals. J. L. Howe (Science, 1927, 66, 220—221).—It is probable that all meteorites contain the platinum metals. An attempt is made to calculate the relative amounts of the metals of the eighth periodic group in the earth.

A. A. Eldridge.

Organic Chemistry.

Chemical reactivity of atoms and groups in organic compounds. J. F. Norris.—See this vol., 26.

Future development of organic chemistry. C. F. van Duin (Z. physikal. Chem., 1927, 130, 353—364).—A large number of otherwise inexplicable reactions may be interpreted by means of the principle of induced alternate polarity, which is held to be of great importance for the future development of organic chemistry. The following problems, among others, are considered from the point of view of the theory: substitution in the benzene nucleus; the heat of combustion of isomeric benzene derivatives; the activation of halogen atoms; the acidity of acids and the basicity of amines; the elimination of halogen hydrides, *e.g.*, hydrogen chloride from 3 : 4′-dinitrostilbene dichloride (cf. Harrison and Wood, A., 1926, 604); various additive reactions, including the addition of bromine to *m*- and *p*-sulphocinnamic acid, the addition of nitric acid to αα-diphenylethylene, the addition of water to 3 : 4′-dinitro- and -diamino-tolanes. L. L. Bircumshaw.

Atmospheric oxidation of hydrocarbons. A. Kailan and L. Olbrich (Monatsh., 1927, 48, 537—541).—The oxidation of paraffin wax at 183—184° and of toluene at 99·4° by a current of purified air passed at the rate of 6 litres/hr. has been studied for varying periods and the amount of oxidation determined by investigations of the acid values, oxygen content, hydrolysis and acetylation, and densities of the products. Oxidation of paraffin wax proceeds more rapidly in the second period of 25 hrs. than in the first, and after 100 hrs. 8% of the residue is hydrolysable, whilst a distillate containing fatty acids, alcohols, and aldehydes is obtained. The amount of carbon dioxide produced increases proportionately to the duration of the oxidation. Naphthalene is less readily oxidised than paraffin wax by atmospheric oxygen under the same conditions, although double the amount of carbon dioxide is produced in this case. Increase of the velocity at which the air is passed to 60 litres/hr. decreases the amount of oxidation produced by a given volume of air. In this case oxidation is most rapid in the earlier stages and mercury acts only as a very feeble catalyst. In spite of the lower temperature the velocity of oxidation of toluene is greater than that of naphthalene, and here again the velocity of oxidation is greater during the second period of 25 hrs. than during the first. No increase in the velocity of oxidation was observed in the presence of manganese dioxide.

J. W. Baker.

Action of acetylene on metals yielding explosive acetylides. J. F. Durand and M. Banos.—See this vol., 28.

Action of acetylene on the oxides of carbon. C. Sandonnini (Gazzetta, 1927, 57, 781—792).—A dry mixture of acetylene and carbon dioxide passed through a glass tube at 400° remained unchanged in the absence of a catalyst. On the surface of copper some water, carbon monoxide, and saturated hydrocarbons were formed in small quantity. Nickel–copper and cobalt–copper catalysts were only slightly more effective. A nickel catalyst caused 20% reaction at 175°, and 60% at 300°; at the latter temperature, a mixture of 630 c.c. of acetylene with 370 c.c. of carbon dioxide gave 140 c.c. of carbon dioxide unchanged, 10 c.c. of unsaturated hydrocarbons, 15 c.c. of hydrogen, and 65 c.c. of saturated hydrocarbons. Cobalt gave similar results; iron was inefficient, as were catalysts containing aluminium.

For acetylene–carbon monoxide mixtures, nickel and cobalt were the most efficient catalysts. The products contained water, carbon dioxide, formaldehyde, acetaldehyde, acraldehyde, and a mixture of unsaturated hydrocarbons, b. p. 135—150°. The carbonaceous mass remaining on the catalyst had Ni 15·2%, H 1·32%, C 78·4%, O 5·18%, or Co 21·55%, H 2·83%, C 65·92%, O 9·70%. It is assumed that oxygen is adsorbed by the carbon.

E. W. Wignall.

[Action of cyanogen bromide on dimagnesium acetylene dibromide.] H. Biltz (Ber., 1927, 60, [*B*], 2413).—The dibromoacetylidene, reported as obtained by Nekrassov (A., 1927, 1051), has been shown to be dibromoacetylene (cf. Biltz, A., 1913, i, 241).

H. Wren.

Action of polyhalogenated compounds of methane and of ethane on magnesyl derivatives. IV. R. Binaghi (Gazzetta, 1927, 57, 669—675).—An attempt to prepare hexaphenylethane from hexachloroethane by the action of magnesium phenyl bromide was unsuccessful; of *s*-di- and tetra-chloroethylene and *s*-tetrachloroethane, only the last reacts with magnesium phenyl bromide on heating, yielding a product decomposed by water to give *s*-tetraphenylethane.

With magnesium ethyl bromide hexachloroethane yields equal volumes of ethylene and ethane and a product decomposed by water to give equal volumes of ethylene and acetylene, some ethyl bromide and ethyl chloride being also formed (as in most of the following reactions). *s*-Tetrachloroethane yields ethane, and a product decomposed to give equal volumes of ethylene and acetylene. Tetrachloroethylene yields equal volumes of ethylene and ethane, and a product decomposed to give equal volumes of ethylene and acetylene. *s*-Dichloroethylene yields ethane, and a product decomposed to acetylene and ethylene; it is supposed that in the initial reaction acetylene is formed, and that this reacts with magnesium ethyl bromide to give ethane and the compound $\mathrm{MgBr{\cdot}C{\vdots}C{\cdot}MgBr}$.

E. W. Wignall.

Synthesis of αζ-dibromo-*n*-hexane and its action on *p*-toluenesulphonamide. A. Müller and A. Sauerwald (Monatsh., 1927, 48, 521—527).—Hexane-αζ-diol is prepared in 55% yield by the vigorous reduction of methyl adipate with sodium in boiling absolute alcohol, the reaction being completed by heating in an oil-bath at 110—120°. On steam distillation of the product the diol passes over completely with the aqueous-alcoholic distillate, from which it is obtained by distillation in a vacuum, the diol boiling at 136—138°/11 mm. When hydrogen bromide is passed for 3·5 hrs. into the diol at 120—130° αζ-dibromo-*n*-hexane is obtained in 70% yield. When the dibromohexane is treated with *p*-toluenesulphonamide in the presence of alcoholic potassium hydroxide (cf. Müller and Sauerwald, A., 1927, 884) the products are *NN′-bis*-p-*toluenesulphonyl-αζ-diamino*-n-*hexane*, $(\mathrm{C_6H_4Me{\cdot}SO_2{\cdot}NH})_2(\mathrm{CH_2})_6$, m. p. 151·4°, which, when heated with hydrochloric acid (*d* 1·19) for 5 hrs. in a sealed tube at 170°, is hydrolysed to the hydrochloride of αζ-diamino-*n*-hexane (Curtius and Clemm, A., 1901, i, 68) and a *substance*, m. p. 72°, which on hydrolysis with hydrochloric acid (*d* 1·19) for 6·5 hrs. at 160° yields a *hydrochloride*, m. p. 234° [*chloroplatinate*, m. p. 196—197° (decomp.); *methiodide*, m. p. 265°], isomeric but not identical with the corresponding salts of α-pipecolin [hydrochloride, m. p. 210°; methiodide, m. p. 320—321° (uncorr.) (von Braun, A., 1910, i, 821, describes the product as 1-methyl-2-pipecolin methiodide, m. p. 255°)]. The original condensation product, m. p. 72°, is therefore isomeric but not identical with *N*-p-*toluenesulphonyl-α-pipecolin*, m. p. 54·5—55°, which was synthesised by the action of *p*-toluenesulphonyl chloride on α-pipecolin. All m. p. are corrected.

J. W. Baker.

Symmetrical dichlorodimethyl sulphate, chloromethoxysulphonyl chloride, and similar derivatives of formaldehyde. K. Fuchs and E. Katscher (Ber., 1927, 60, [*B*], 2288—2296; cf. A., 1924, i, 1164).—The action of 1 mol. of paraformaldehyde on 1¼ mols. of chlorosulphonic acid at a temperature not exceeding 70° leads to the production of *chloromethoxysulphonyl chloride*, b. p. 49—50°/14 mm., 153—155°/750 mm. (slight decomp.), *d* 1·63, and methylene sulphate, m. p. 153°; with 2½ mols. of chlorosulphonic acid the quantity of formaldehyde corresponding with the methylene sulphate is transformed into methoxysulphonyl chloride. If the products obtained from 1 mol. of paraformaldehyde and 1¼ mols. of chlorosulphonic acid are poured on to ice previous to distillation, a mixture of dichloromethyl ether, b. p. 101·5—102°, polymeric formaldehyde, hydrogen chloride, and *chloromethyl sulphate*, $(\mathrm{CH_2Cl})_2\mathrm{SO_4}$, b. p. 96—97°/

14 mm., is obtained; in contrast with methyl sulphate, the latter substance is completely non-poisonous, strongly antibactericidal, almost odourless, and sweet in taste. Removal of unchanged chlorosulphonic acid and sulphuric acid may advantageously be accomplished by the use of sodium chloride in place of ice if the temperature is not allowed to exceed 70—80°. After similar use of anhydrous potassium sulphate the main isolable product is chloromethoxysulphonyl chloride with smaller amounts of dichloromethyl ether and chloromethyl sulphate. As expected, mixtures of chloromethyl sulphate and chlorosulphonic acid are converted by distillation in a vacuum either into chloromethoxysulphonyl chloride and methylene sulphate or entirely into chloromethoxysulphonyl chloride according to their relative proportion in the mixture. Under similar conditions, methylene sulphate is converted by chlorosulphonic acid into chloromethoxysulphonyl chloride. Dichloromethyl ether is transformed by chlorosulphonic acid at 60—70° and subsequent distillation exclusively into chloromethoxysulphonyl chloride; if, however, the product is treated with ice, a mixture of chloromethyl sulphate and chloromethoxysulphonyl chloride is produced. If attempts are made to distil a solution of small amounts of methylene sulphate in chloromethoxysulphonyl chloride or non-homogeneous chloromethyl sulphate, carbonisation occurs at a temperature not exceeding 70° although pure methylene sulphate does not char at 155°; similar effects are produced by a large number of organic compounds (ether, acetone, ethyl acetate, benzene, etc.) at 80—100°.

The reactions are adequately explained by the hypothesis that formaldehyde and chlorosulphonic acid yield primarily chloromethyl hydrogen sulphate and chloromethyl alcohol, in support of which it is observed that polymeric formaldehydes dissolve slowly in chlorosulphonic acid at 0°, yielding products which are almost completely soluble in water. Further, an equilibrium appears to exist between chloromethyl hydrogen sulphate and chloromethyl alcohol, since the maximum yield of products insoluble in water is only 70% of that calculated on the formaldehyde and distillation of the residue obtained after decomposition of excess of chlorosulphonic acid by ice gives the fission products of chloromethyl alcohol (polyoxymethylenes and hydrogen chloride).

H. Wren.

Synthesis of partly acylated glycerides. B. Helferich and H. Sieber (Z. physiol. Chem., 1927, **170**, 31—37).—The rapid hydrolysis of triphenylmethyl (=trityl) ethers of glycerol by hydrobromic–acetic acid at 0° provides a means of obtaining partly acylated glycerides. Glycerol α-monotrityl ether (Helferich, Speidel, and Toeldte, A., 1923, i, 331) gives, when treated with benzoyl chloride in pyridine, the *dibenzoate*, m. p. 90—92°, which by hydrolysis with hydrobromic–acetic acid at 0° is converted into glyceryl αβ-dibenzoate, m. p. 59·5—60°. From glycerol αγ-ditrityl ether are obtained the *benzoate*, m. p. 108° (+1·5H_2O) or 130—132° (anhyd.; corr.), and glyceryl β-benzoate, the latter being identified by conversion into glyceryl β-benzoate αγ-di-*p*-nitrobenzoate, m. p. 152—152·5°. Glycerol αγ-ditrityl ether forms a p-*toluenesulphonate*, m. p. 163°.

C. Hollins.

Autocatalytic oxidation of sulphydryl compounds. D. C. Harrison (Biochem. J., 1927, **21**, 1404—1415).—Both the aërobic and anaërobic oxidation of sulphydryl compounds are catalysed by pure metal-free dithiodiglycollic acid, and this catalysis is not inhibited by cyanide. On the other hand, when the –S·S– linking of dithiodiglycollic acid is destroyed the catalytic action of the compound disappears. A mechanism is suggested by which the catalysis may take place.

S. S. Zilva.

Varying valency of platinum with respect to mercaptanic radicals. VI. (Sir) P. C. Rây, K. C. Bose-Ray, and N. B. Adhikari (J. Indian Chem. Soc., 1927, **4**, 467—475).—Ammonia decomposes the complex compound, $PtCl_3,(C_2H_4)_3S_2$ (Rây, J.C.S., 1922, **121**, 1283), forming tetrammineplatinous dichloride. Benzylamine reacts yielding *tetrabenzylammineplatinous dichloride*, $[(CH_2Ph{\cdot}NH_2)_4Pt]Cl_2$, m. p. 195°, whilst with ethylenediamine there are formed three *compounds*, $Pt_2Cl_6,3C_2H_4(NH_2)_2,(C_2H_4)_3S_3$, $PtCl_2,(C_2H_4)_2S_2$, and $PtCl_2,2C_2H_4(NH_2)_2$. Pyridine converts the original substance into tetrapyridineplatinous dichloride, dipyridineplatinous chloride (cf. A., 1926, 1023), and the *compound* $(C_5H_5N)_4Pt_2Cl_7$. Dimethylaniline yields the *compound* $NPhMe_2,PtCl_2$, piperidine gives the *compound* $3C_5H_{11}N,PtCl_2$, tripropylamine affords the *substance* $(C_2H_4)_2S_2,PtCl_2$, diethylamine furnishes the *compound* $2NHEt_2,PtCl_2$, which on crystallisation from acetone passes into the complex *compound*, $NHEt_2,PtCl_2,Me_2CO$, and *p*-phenylenediamine yields the *compound* $4C_6H_4(NH_2)_2,PtCl_3$. From these results it is concluded that the original complex is best represented by the formula $[(C_2H_4)_3S_2PtCl_2]Cl$.

H. Burton.

Mechanism of the hydrolysis of organic compounds. S. C. J. Oliver and G. Berger (Rec. trav. chim., 1927, **46**, 861—865).—In cases of hydrolysis of esters, ethers, and acid anhydrides where the reaction is catalysed by hydrogen ions, it is suggested that the reaction takes place through the addition of the ion to the oxygen atom of the group C·O·C. When this oxygen atom becomes induced positive by the presence of negative substituents, the reaction velocity depends on the concentration of water and no longer on that of the ion (A., 1927, 835). The very rapid addition of water to the doubly-linked oxygen atom in acetic anhydride prevents the detection of the influence of hydrogen ions, whereas it is detectable in the case of benzoic anhydride.

G. A. C. Gough.

Strength of the linkings between hydrocarbon radicals and oxygen in simple and mixed ethers; mechanism of esterification and hydrolysis of esters. B. V. Tronov, L. N. Diakonova-Schulic, O. J. Gulaeva, and N. S. Nikiforova (J. Russ. Phys. Chem. Soc., 1927, **59**, 545—562).—A *résumé* of earlier work on the stability of carbon–oxygen linkings in ethers, acetals, and esters. The decomposition of these compounds at the ordinary temperature by hydrogen bromide in glacial acetic acid solution under constant conditions was investigated, in order to determine the effect of different hydrocarbon radicals on the carbon–oxygen linking. The time required for the decomposition of a definite fraction of the compound was taken as a measure of the stability of the linking.

For ethers and esters the ease of elimination of hydrocarbon radicals is in the order: $CH_2Ph>Me>Et>C_5H_{11}>Ph$. The behaviour of the esters of inorganic acids is similar. The ease of decomposition of the esters of the same alcohol was in the order: H_2SO_4 and $HNO_3>H\cdot CO_2H>Et\cdot CO_2H>H_2CO_3>Me\cdot CO_2H>Ph\cdot CO_2H>CH_2Cl\cdot CO_2H>(CO_2H)_2>(CH_2\cdot CO_2H)_2$. The mineral acid esters are much more reactive than the others.

Different members of the ether and acetal series did not vary much in reactivity, with the exception of some methyl compounds.

The hydrolysis of esters by alkalis was also investigated, in order to elucidate the nature of the reaction, and various theories of its mechanism are discussed.

M. Zvegintzov.

Decomposition of fatty acids by sulphuric acid. J. B. Senderens and J. Aboulenc (Compt. rend., 1927, **185**, 1087—1090).—Acetic acid and some of its homologues were decomposed by heating with five times their volume of sulphuric acid. Carbon monoxide was the first gas to be evolved, with increasing proportions of carbon dioxide and sulphur dioxide as the temperature was raised, and, finally, separation of carbon. The temperatures at which gas was first evolved were: with acetic, butyric, valeric, and hexoic acids, about 200°; *iso*butyric and *iso*valeric acids, 140°; *iso*hexoic acid, 150°; α-ethylbutyric acid, 130—140°. Thus the proximity of a side-chain to the carboxyl group facilitates decomposition.

B. W. Anderson.

Rate of reaction between bromine and unsaturated fatty acids as evidence of stereoisomerism. C. A. Knauss and J. G. Smull (J. Amer. Chem. Soc., 1927, **49**, 2808—2815).—The rates of bromination, in carbon tetrachloride at the ordinary temperature, of oleic, linoleic, and linolenic acids decrease in this order, *i.e.*, the rate decreases with increase in unsaturation. The rates of bromination of the mixed fatty acids of poppy-seed, soya-bean, linseed, and perilla oils is in direct relation to the acid constituents. Under the influence of ultra-violet light, the bromination of both pure and mixed fatty acids proceeds beyond the bromination in the dark, indicating apparently the presence of unsaturated isomerides (10—15%) which are less readily brominated.

F. G. Willson.

Acetylated sulphates of sesquioxides. A. Recoura (Compt. rend., 1927, **185**, 992—994).—After prolonged treatment with powdered acetic anhydride, white ferric sulphate forms a *compound*, $(Fe_2O_3,3H_2SO_4)_6,3SO_3,3Ac_2O$, which loses its 3 mols. of acetic anhydride in dry air, but recovers them in an atmosphere of acetic anhydride, in which it is stable. Ferric alum similarly forms a *compound*, $Fe_2(SO_4)_3,(NH_4)_2SO_4.H_2O,3Ac_2O$; in a dry atmosphere 2 mols. of the anhydride are lost rapidly, the third very slowly. The *compound*, $Al_2(SO_4)_3.2H_2O,3Ac_2O$, formed by ammonium alum, behaves similarly. Aluminium sulphate, $Al_2(SO_4)_3,15H_2O$, gives the *substance* $2Al_2(SO_4)_3,6H_2O,3Ac_2O$, which in dry air loses 1 mol. of anhydride rapidly, the second slowly, the third still remaining after 3 years' preservation.

B. W. Anderson.

Di-*n*-hexoyl peroxide and per-*n*-hexoic acid, and the detection of peroxides by electrolysis of potassium hexoate. F. Fichter and R. Zumbrunn (Helv. Chim. Acta, 1927, **10**, 869—885; cf. A., 1926, 807).—Treatment of *n*-hexoic anhydride with freshly-prepared barium peroxide in moist ether yields, in addition to barium hexoate, some *di*-n-*hexoyl peroxide*, a colourless oil which does not solidify on cooling. The peroxide when heated evolves gas at 64—65° and explodes at 84—85°. It is soluble in organic solvents and forms a red dye with *p*-toluidine. With phenylhydrazine there is formed *n*-hexoylphenylhydrazide, m. p. 95·6—96·5° (cf. Autenrieth, A., 1888, i, 250). Treatment of an ice-cold mixture of *n*-hexoic anhydride and 100% sulphuric acid with 93% hydrogen peroxide (cf. D'Ans and Frey, A., 1912, i, 601) yields *per*-n-*hexoic acid*, b. p. 62—63°/13 mm., 41—42°/0·5 mm., m. p. 15°, which on heating evolves gas at 75°, and afterwards explodes. Explosive decomposition of the peroxide furnishes carbon dioxide, *n*-decane, *n*-amyl alcohol, and hexoic acid, whilst slow decomposition at 65—70° yields pentene, *n*-amyl alcohol, and hexoic acid. The rate of hydrolysis of the peroxide is increased by borax or sodium hydrogen carbonate (cf. Böeseken and Gelissen, A., 1926, 166). Explosive decomposition of perhexoic acid at 240° gives carbon dioxide, pentene, and *n*-amyl hexoate, whilst slow decomposition at 75° affords small quantities of carbon dioxide and *n*-amyl hexoate, the main products being hexoic acid and oxygen. Electrolysis of potassium hexoate–hexoic acid solution, with platinum and graphite electrodes, shows that the reaction proceeds through the peroxide. This intermediate either decomposes at the anode yielding *n*-decane and carbon dioxide, or is hydrolysed to hexoic and perhexoic acids, followed by decomposition of the latter to *n*-amyl alcohol (cf. Petersen, A., 1898, i, 352) and carbon dioxide. The amyl alcohol furnishes pentene and *n*-amyl hexoate. The main product of electrolysis with a platinum anode is *n*-decane.

H. Burton.

Derivatives of trichloroacrylic acid. IV. Pentachloropropionic acid. V. Electrolytic dissociation constant. Salts. J. Böeseken (Rec. trav. chim., 1927, **46**, 841—843, 844—846).—IV. *Pentachloropropionic acid*, m. p. 210—215° (on heated mercury), prepared by passing chlorine through a carbon tetrachloride solution of trichloroacrylic acid in sunlight, gives *barium*, *calcium*, *potassium*, and *sodium* salts which are decomposed rapidly in aqueous solution with the formation of tetrachloroethane, carbon dioxide, and the metallic chloride. The acid decomposes in a similar manner in aqueous solution and possesses a strength comparable with the mineral acids.

V. Trichloroacrylic acid has κ_{25} 0·07. The normal *barium* ($+3\frac{1}{2}H_2O$), *calcium* ($+3\frac{1}{2}H_2O$), *strontium* ($+5H_2O$), *magnesium* ($+3\frac{1}{2}H_2O$), *zinc* ($+6H_2O$ and

$+3\frac{1}{2}H_2O$), *cadmium* ($+2H_2O$), and *mercury* salts (anhydrous) are described. G. A. C. Gough.

_iso_Erucic acid. T. J. Marchandani and J. L. Simonsen (J. Indian Inst. Sci., 1927, **10A**, 57—63).—See A., 1927, 339.

Configurational relationships of α-hydroxybutyric and lactic acids. G. W. Clough (J. Biol. Chem., 1927, **75**, 489—490).—A question of nomenclature (cf. Clough, J.C.S., 1918, **113**, 533, and Levene and Haller, A., 1927, 1053).

C. R. Harington.

Preparation of β-hydroxybutyric acid. A. Wacker, Ges. f. Elektrochem. Ind., G. Basel, and F. Kaufler.—See B., 1927, 924.

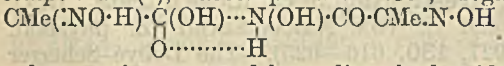
Sulphomethylsuccinic acids. I. H. J. Backer and J. Buining (Rec. trav. chim., 1927, **46**, 847—854).—α-Sulphopropane-βγ-dicarboxylic acid ($+H_2O$), m. p. 89° (decomp.), may be obtained either by the interaction of potassium pyrosulphite and ammonium hydrogen itaconate in aqueous solution at 108° or by the interaction of ammonium α-bromopropane-βγ-dicarboxylate and ammonium sulphite. The acid is best isolated by means of the *barium* salt ($+6H_2O$). The *calcium* ($+7H_2O$), *lead* ($+6H_2O$), *copper* ($+6H_2O$), *nickel* ($+7H_2O$), and *cobalt* ($+6H_2O$) salts are described. Crystallisation of the *strychnine* salt ($+3H_2O$) followed by decomposition to the sodium salt gives a partly active product.

G. A. C. Gough.

Specific action of the oxime group on metallic salts. I. Reactions of cobalt, nickel, and copper salts with aldoximes. II. Reactions of ketoximes with metallic salts. W. Hieber and F. Leutert (Ber., 1927, **60**, [*B*], 2296—2310, 2310—2317).—I. The behaviour of metals towards oximes appears to depend on the nature of the metallic salt and the constitution and configuration of the organic component. The oximes offer two centres for addition, but the oxygen and nitrogen atoms have a mutually weakening effect and hence only metallic salts which have a relatively pronounced specific affinity towards nitrogenous addenda and not too great lattice energy may be expected to yield additive compounds with oximes. In general, aldoximes unite readily with the halides of cobalt, nickel, and copper in the presence of alcohol, acetone, or chloroform. The compounds thus produced are immediately decomposed by water or ammonia. They are unchanged by attempted electrolysis in chloroform or acetone. Determinations of mol. wt. in ethylene dibromide do not give very definite results, since the compounds appear to be decomposed with liberation of the oxime but without precipitation of the metallic salts, thus indicating that additive compounds exist in solution which contain less than 4 mols. of oxime. The substances appear therefore to have the structure $[Hal_2X(\cdots N(OH){:}CHR)_{2\text{ or }4}]$. Among stereoisomeric aldoximes, only the labile β-varieties react immediately with metallic salts; since the α- and β-forms ultimately yield the same additive compounds, the reaction of the former is preceded by isomerisation to the β-derivatives. This behaviour of the oximes is in harmony with Meisenheimer's views on their constitution. Corresponding with the pronounced basicity of the nitrogen atom, only a feeble tendency towards salt formation is to be expected. This is observed only with the salts of heavy metals with weak acids or in alkaline solution. Copper acetate and α-benzaldoxime yield a substance which, however, is not a copper salt in the usual sense, the acetic acid residue being only partly replaced by the oxime groups. Acetaldehyde affords the *compounds* $4CHMe{:}N\cdot OH,CoCl_2$, $4CHMe{:}N\cdot OH,CoBr_2$, $4CHMe{:}N\cdot OH,NiCl_2$, $4CHMe{:}N\cdot OH,NiBr_2$, and $2CHMe{:}N\cdot OH,CuCl_2$. The *substances* $4CHPr^{\beta}{:}N\cdot OH,CoCl_2$, $4CHPr^{\beta}{:}N\cdot OH,NiCl_2$, and $4CHPr^{\beta}{:}N\cdot OH,CuCl_2$ are derived from *iso*butaldoxime. Benzaldoxime gives the additive *compounds*, $4CHPh{:}N\cdot OH,CoCl_2$, $4CHPh{:}N\cdot OH,CoBr_2$, $4CHPh{:}N\cdot OH,NiCl_2$, $4CHPh{:}N\cdot OH,NiBr_2$, $2CHPh{:}N\cdot OH,CuCl_2$. The *substances* $4CHPh{:}CH\cdot CH{:}N\cdot OH,CoCl_2$ and $2CHPh{:}CH\cdot CH{:}N\cdot OH,CuCl_2$ are derived from β-cinnamaldoxime. The sodium derivative of benzaldoxime and copper chloride in alcoholic solution yield a *substance* containing oxime and copper in the ratio 1 : 1; similarly β-cinnamaldoxime and copper acetate give the *compound* $(CHPh{:}CH\cdot CH{:}NO)_2Cu$. If a methyl-alcoholic solution of sodium hydroxide is treated with a little acetaldoxime, *iso*butaldoxime, β-benzaldoxime, or β-cinnamaldoxime and a trace of cobalt chloride or copper chloride is added, a characteristic colour is developed which usually passes into the organic medium after addition of chloroform and water. Complex metal–oxime anions appear to be produced. α-Benzildioxime and cupric chloride yield the *substance* $C_{14}H_{12}O_2N_2,CuCl_2,2H_2O$.

II. The ability of ketoximes to form additive compounds with metallic salts is notably less than that of aldoximes, and the peculiarities of the metallic salt are therefore more obvious. The formation of additive compounds is immediately observed when cobalt chloride or bromide is covered with a solution of acetoxime in chloroform; the appearance of the blue colour is specific and the reaction is very sensitive. Homogeneous products cannot, however, be isolated. Quantitative differences in the additive power of metallic salts to acetoxime are investigated by observing the changes of f. p. caused by the addition of the metallic bromide to a solution of the oxime in ethylene bromide. If addition with more than 1 mol. of oxime occurs the molecular concentration is lowered and the f. p. rises. The tendency to form compounds is found to increase in the series, cobalt, nickel, copper, which harmonises with the preparation of the *compounds* $CMe_2{:}N\cdot OH,CuCl_2$ and $CMe_2{:}NOH,(AcO)_2Cu$. Acetoxime adds bromides more readily than chlorides; with iodides, the isolation of the *compounds* $CoI_2,2CMe_2{:}N\cdot OH,0{\cdot}5Me_2CO$ and $NiI_2,2(?\beta)CMe_2{:}N\cdot OH$ has been effected. In harmony, the more or less complete replacement of iodine by the oxime residue is observed when acetoxime reacts with cobalt iodide in alcoholic solution whereby crystalline substances of the type $Co(I,CMe_2{:}N\cdot OH)_2$ are obtained. Methyl butyl ketoxime resembles acetoxime in giving a very sensitive colour reaction with cobalt chloride and chloroform. Fatty aromatic ketoximes have markedly less additive power. Acetophenoneoxime does not react with cobalt or nickel halides, but with copper chloride in chloroform gives compounds, $CuCl_2,1$—$2CMePh{:}N{\cdot}OH$. Feigl's "copper salt" of acetophenoneoxime is an additive compound. Benzophenone gives only a faint reaction with copper acetate, whereas with cupric chloride it affords the *compound* $CPh_2{:}N{\cdot}OH,CuCl_2$. H. WREN.

Dioximes. XLIII. G. PONZIO and I. DE PAOLINI (Gazzetta, 1927, 57, 633—648).—The action of bromine on α-hydroxy-β-methylglyoxime yields a *compound* (I), decomp. 122—135°, regarded as



$CMe({:}NO{\cdot}H){\cdot}\underset{\overset{\|}{O}}{C}(OH)\cdots\underset{\overset{|}{H}}{N}(OH){\cdot}CO{\cdot}CMe{:}N{\cdot}OH$

This substance is converted by sodium hydroxide solution into α-oximinopropionic acid and hydroxymethylglyoxime, and by hydrogen chloride in alcohol into the latter, with ethyl α-oximinopropionate; the action of nitrogen tetroxide yields ethylnitrolic acid (benzoyl derivative, new m. p. 131°); that of hydroxylamine, hydroxymethylglyoxime. The colour reactions of (I) with copper solutions under varying conditions are in harmony with the above formula; the compound has one hydrogen atom replaceable by metals, giving a *silver* salt, unchanged in boiling water, a *copper* salt regarded as co-ordinated with the α-oximino-nitrogen atom, soluble in ammonia solution to a violet-blue solution which changes to reddish-brown on adding hydroxylamine, ammonium dimethylhydroxyglyoxime cuprate being formed.

When heated with aniline, (I) gives *α-oximinopropionanilide*, (II), m. p. 144—145°, also obtained from pyruvanilide and hydroxylamine; the position of the oximino-group is found by treatment with bromine to give *α-oximinopropion-*p*-bromoanilide*, m. p. 206—208°, hydrolysed by sodium hydroxide solution to *p*-bromoaniline and α-oximinopropionic acid. The anilide (II) yields an *acetyl* derivative, m. p. 95° ($+H_2O$), 77—78° (anhyd.), and a *benzoyl* derivative, m. p. 105—107° ($+H_2O$), 98—100° (anhyd.).

Benzoyl chloride converts (I) into a *dibenzoyl* derivative, $CMe({:}N{\cdot}OBz){\cdot}C_2H_3O_4N{\cdot}CMe{:}N{\cdot}OBz$, m. p. 151° (decomp.) or, after washing with alcohol, 162° (decomp.). This with aniline at 50—60° yields benzanilide and α-oximinopropionanilide; in the cold, however, α-benzoyloximinopropionanilide and *α-oximino-β-benzoyloximinopropyl alcohol*, (III), m. p. 122—123° (decomp.), are formed, and it is suggested that the dibenzoyl derivative yields first the monobenzoyl derivatives of α-oximinopropionic acid and α-hydroxy-β-methylglyoxime. The compound (III) gives an intense cherry-red colour with ferric chloride, unchanged by hydrochloric acid, forms a copper derivative, is hydrolysed by sodium hydroxide solution to benzoic acid and hydroxymethylglyoxime, with benzoyl chloride gives α-hydroxydi-*N*-benzoyl-β-methylglyoxime, $CMe({:}N{\cdot}OBz){\cdot}C({:}N{\cdot}OBz){\cdot}OH$, and with acetic anhydride gives *α-acetyloximino-β-benzoyloximinopropyl alcohol*, m. p. 104—105°.

The product formulated by Ponzio (A., 1927, 134) as $CMe({:}N{\cdot}OBz){\cdot}C({:}N{\cdot}OH){\cdot}OH$, m. p. 146—147° (decomp.), is now regarded as the "*l*-derivative," *i.e.*, as α-benzoyloximino-β-oximinopropyl alcohol. It forms a *copper* derivative containing 2 mols. of the organic compound; acetic anhydride yields *α-benzoyloximino-β-acetyloximinopropyl acetate*, m. p. 86—87°.

α-Hydroxy-β-phenylglyoxime yields a molecular *compound* (IV), analogous to (I), decomp. at 125—135° to give 5-hydroxy-3-phenylazoxime, m. p. 200—202°; (IV) yields *ammonium* (m. p. 107—108°, decomp.), *silver*, and nickel salts; it is hydrolysed by sodium hydroxide to give hydroxyphenylglyoxime and *phenyloximinoacetic acid*, m. p. 135° (decomp.). With aniline in the cold, (IV) yields oximinophenylacetanilide, m. p. 154—155°, with hydroxyphenylglyoxime. E. W. WIGNALL.

Dioximes. XLIV. (SIGNA.) M. AYMARETTO (Gazzetta, 1927, 57, 648—655).—Oximinoacetic acid forms copper, *nickel*, and *cobalt* salts, $[CH({:}N{\cdot}OH)CO_2]_2M,2H_2O$. α Oximinopropionic acid yields similar *copper*, *nickel*, and *cobalt* ($-3H_2O$) salts, and a basic *copper* salt; the *sodium* salt is prepared by the action of sodium ethoxide on an alcoholic solution of the acid. α-Oximinobutyric acid yields an *ammonium* salt, m. p. 158° (decomp.), and *sodium*, *potassium* ($+H_2O$), *copper* ($+H_2O$), *cobalt* ($+2H_2O$), and *nickel* ($+2H_2O$) salts; the last-named also gives two *complexes*, in which the water is replaced by 2 mols. of ammonia and of pyridine, respectively. Oximinophenylacetic acid yields a *nickel* salt ($+0{\cdot}5H_2O$, replaceable by $3C_5H_5N$), a *cobalt* salt ($+2H_2O$), and a *copper* salt. These salts are considered to be co-ordinated, thus: $M{=}[{-}CO_2{\cdot}CR{:}N(OH)\cdots]_2$. E. W. WIGNALL.

Mutarotation. VIII. Mutarotation of mannose. C. N. RIIBER and J. MINSAAS (Ber., 1927, 60, [*B*], 2402—2412; cf. A., 1926, 1228).—The possibility of the existence of more than two modifications of a given sugar in its aqueous solution cannot be satisfactorily examined by observations based on a single physical constant; for this purpose it is necessary to determine more than one additive property when, if only two forms are present, the ratio $k_1/k_2=K$ must be constant for each property. Thus for mannose the value K is 0·50 and 0·47 as deduced from observations on specific rotation and molecular solution volume, whereas determination of the index of refraction leads to the value $K=0{\cdot}64$. Hence more than two modifications of mannose are present in the aqueous solution in which, however, the known α- and β-varieties predominate. Hudson's classification of sugars into α- and β-varieties in accordance with optical activity alone is open to criticism, since contradictory results are obtained when other physical constants are made the basis of division. Precise directions for the preparation of crystalline α- and β-mannose are given.

H. WREN.

Constitution of the disaccharides. XVI. Cellobiose. W. N. HAWORTH, C. W. LONG, and J. H. G. PLANT (J.C.S., 1927, 2809—2814).—*Methyl octamethylcellobionate*, b. p. 169—171°/0·05 mm., n_D^{14} 1·4609, furnishes on hydrolysis with hydrochloric acid 2 : 3 : 4 : 6-tetramethylglucose, m. p. 93—94° (92·7% yield), and 2 : 3 : 5 : 6-tetramethylgluconolactone, m. p. 26—27° (Haworth and Long, A., 1927, 450), in 80% yield. The phenylhydrazide of 2 : 3 : 5 : 6-tetramethylgluconic acid, prepared from the above lactone, is identical with that obtained from methyl octamethylmaltobionate and 2 : 3 : 5 : 6-tetramethyl-(γ)-glucose.

These results confirm the structure of cellobiose as a glucose β-glucoside previously advocated (Charlton, Haworth, and Peat, A., 1926, 273) and removes the need for any reservation in favour of an alternative formulation as a γ-glucose β-glucoside. S. Coffey.

Production of cellobiose from cellobiose octa-acetate. F. C. Peterson and C. C. Spencer (J. Amer. Chem. Soc., 1927, **49**, 2822—2825).—Finely-powdered cellobiose octa-acetate (10 g.) is incorporated during 1 hr., with stirring, with 85 c.c. of 10% sodium ethoxide in 95% alcohol. The precipitated sodium salt is collected, washed with absolute alcohol, dissolved in the minimum of water, and the filtered aqueous solution acidified with glacial acetic acid, whereon the cellobiose separates, in crystalline form, in 95% yield. It is purified by dissolving in the minimum of water, filtration, and reprecipitation with acetone. The yield of purified product, m. p. 225°, is 85%. F. G. Willson.

Glucosides of *Fatsia japonica*, Dcne. et Planc. I. *Fatsia* sapotoxin. II. Fatsin. III. Biological. K. Ohta (Kitasato Arch. Exp. Med., 1926, **7**, 301—313).—The *sapotoxin*, $C_{37}H_{62}O_{10}$, was obtained by extracting the powdered, air-dried leaves with warm alcohol, purifying the extract with lead acetate, and treating the alcoholic residue with 98% methyl alcohol. When heated with 1% sulphuric acid in 50% alcohol, a clear yellow solution and an insoluble *sapogenin*-I, $C_{32}H_{54}O_4$, were obtained. Fatsin, $C_{31}H_{53}O_{20}$, when heated with excess of 2% sulphuric acid, is hydrolysed to sugar, a volatile organic acid, ether-soluble α-*sapogenin*, $C_{18}H_{30}O_3$, and ether-insoluble β-*sapogenin*, $C_{16}H_{25}O_5$. Neither *Fatsia* sapotoxin nor fatsin eliminates sugar under the action of taka-diastase. Chemical Abstracts.

Cellulose space lattice of plant fibres. O. L. Sponsler (Nature, 1927, **120**, 767).—The two different types of *X*-ray diffraction patterns obtained respectively by Herzog and the author from cellulose fibres are discussed. Their lack of agreement is considered, and it appears that the values used for the *a* axis and the *b* axis of the elementary cell proposed by Herzog were both produced by the same set of planes. When the value 4·30 Å. is discarded, Herzog's axial dimensions must also be discarded, together with the conclusions (*a*) that four anhydro-glucose units are contained in the elementary cell, and (*b*) that certain interference maxima are produced by impurities in the fibre, or that there are two types of carbohydrates embodied in the cellulose of the fibre. The correspondence between the value 4·30 and a certain interference maximum obtained from mercerised cellulose likewise has no significance. A. A. Eldridge.

Characteristics of celluloses, oxycelluloses, and hydrocelluloses. L. Camilleri (Anal. Fís. Quím., 1927, **25**, 434—439).—Cotton cellulose and α-cellulose from rice-straw (*a*) and the oxycelluloses (*b*) and hydrocelluloses (*c*) derived from them, were examined. The following measurements are recorded: Cotton cellulose; *d* (by three methods): (*a*) 1·5945—1·6017, (*b*) 1·5805—1·5847, (*c*) 1·6051—1·6109; calorific value: (*a*) 4789·6, (*b*) 4865, (*c*) 4783·8. α-Cellulose; *d*: (*a*) 1·5847—1·5947, (*b*) 1·5766—1·5804, (*c*) 1·6064—1·6101; calorific value: (*a*) 4779·4, (*b*) 4868·6, (*c*) 4783·4. The products of distillation were analysed. The gaseous products showed distinct differences in amount, about 7% being obtained from the hydrocelluloses and 14% from the celluloses and oxycelluloses. Slightly less liquid was obtained from the celluloses. R. K. Callow.

***X*-Ray investigation of cellulose nitrate.** R. O. Herzog and S. von Náray-Szabó (Z. physikal. Chem., 1927, **130**, 616—625).—The Debye–Scherrer diagrams given by specimens of cellulose nitrate prepared in different ways and of different nitrogen content all exhibit the same interference. It is therefore concluded that the various cellulose nitrates are in reality mixtures of cellulose trinitrate and unchanged cellulose. Consideration of the kinetics of the nitration and of nitration in general favours the theory of the exclusive production of cellulose trinitrate. The latter belongs to the quadratic system, the lattice constants being $a=14·75$, $b=7·88$, and $c=10·30$ Å.; the elementary cell contains four molecules. H. F. Gillbe.

Cryoscopic behaviour of cellulose acetate. A correction. K. Hess (Annalen, 1927, **457**, 307—308; cf. Hess and Schultze, A., 1927, 753).—Certain errors in values for rotatory power are corrected. C. Hollins.

Lignin. II. W. Küster and E. Schoder [with A. Bahl, R. Daur, W. Schairer, and K. Massong] (Z. physiol. Chem., 1927, **170**, 44—59; cf. Küster and Schnitzler, B., 1926, 151).—"Merolignin," isolated from the product of heating lignin with β-naphthol and a trace of hydrochloric acid (*loc. cit.*), is now found to be dinaphthapyran, $C_{21}H_{14}O$, a molecule of formaldehyde being supplied by the lignin (cf. Freudenberg, A., 1926, 935). Under similar conditions merolignin is also formed from β-naphthol and formaldehyde–resorcinol resin (but not formaldehyde–phenol resin, in which pyran rings are absent). Merolignin from primary lignin prepared by Friedrich's method (A., 1926, 824) is free from fluorescent compounds, but resinified pine sawdust, freed from wood gum by treatment with 5% sodium hydroxide, yields in addition to merolignin a fluorescent hydrocarbon, m. p. 249—250°, which is probably chrysene. This is also obtained from lignin prepared by Willstätter and Zechmeister's method.

Dinaphthapyran, m. p. 201° [picrate, m. p. 181—183° (lit. 172°)], best synthesised by Wolff's method (A., 1893, i, 222), gives a *perbromide*, $C_{21}H_{13}Br_3$, which is converted by alcoholic potassium hydroxide into a *compound*, m. p. 271° (decomp.).

Starch and sucrose both yield, when heated with β-naphthol and a little hydrochloric acid, no merolignin but a yellow, crystalline *compound*, $C_{14}H_{10}O$, m. p. 337° (sublimes). C. Hollins.

Amino-derivatives of isoprene and of ethyl butyl ether. J. Supniewski (Rocz. Chem., 1927, **7**, 176—182).—The following dimethylallyl derivatives are prepared: *γ-methyl-Δ^{β}-butenylamine* $(CMe_2{:}CH{\cdot}CH_2{\cdot}NH_2)_3$, b. p. 80—90°/35 mm.: n-*butyl-di-γ-methyl-Δ^{β}-butenylamine*, b. p. 70—100°/25 mm.; *γ-methyl-Δ^{β}-butenyl cyanamide*, b. p. 142—145°/20 mm.; *methyl γ-methyl-Δ^{β}-butenyl ether*, b. p. 85—90°; *γ-methyl-Δ^{β}-butenyl thiocyanate*, b. p. 65—70°/35 mm.; *ethoxybutylamine*, b. p. 142—145°, and *dibutylethoxybutylamine*, b. p. 203—208°. R. TRUSZKOWSKI.

Triacetonamine hydrate. F. FRANCIS (J.C.S., 1927, 2897—2898).—A satisfactory method for the preparation of the above (yield 20—26%) is described. Nitrosotriacetonamine is decomposed catalytically by alkalis, giving a quantitative yield of phorone. S. COFFEY.

Stereoisomerism and anæsthetic action. Separation of methylethyldimethylaminomethylcarbinol into its two enantiomorphs and preparation of the two optically active stovaines. E. FOURNEAU and I. RIBAS (Anal. Fís. Quím., 1927, 25, 401—408).—Optically active forms of "stovaine" (hydrochloride of methylethyldimethylaminomethylcarbinol benzoate) have been prepared from the active carbinols, separated with the aid of α-(2-naphthoxy)propionic acid (Fourneau and Balaceano, A., 1926, 288).

d-*Methylethyldimethylaminomethylcarbinol* l-α-(2-*naphthoxy)propionate* and the l-*base*-d-*acid* salt, m. p. 125—126°, $[\alpha]^{20}_{D}$ −57·3° and +57·7° in alcohol, were obtained in turn by crystallisation from a solution of the *r*-carbinol salt of the *l*-acid followed by conversion of the residue into the salt of the *d*-acid. Hydrolysis yielded d- and l-*methylethyldimethylaminomethylcarbinols*, b. p. 55°/15 mm., $[\alpha]^{20}_{D}$ +7·7° and −7·6° in water, which yielded, respectively, d- and l-*stovaines*, m. p. 186—187°, $[\alpha]^{20}_{D}$ ±8·5° in water. These separated with alcohol of crystallisation and effloresced rapidly. Inactive stovaine (m. p. 174—175°), which crystallises without alcohol, is probably pseudo-racemic. Physiological tests show that *d*-stovaine is a more powerful anæsthetic than *l*-stovaine. R. K. CALLOW.

Decomposition of amino-acids and aminopurines by methylglyoxal and related substances. C. NEUBERG and M. KOBEL (Biochem. Z., 1927, 188, 197—210).—Data are given for the amounts of carbon dioxide, ammonia, and aldehyde (or ketone) formed when a solution of methylglyoxal is boiled for varying periods with certain amino-acids in an atmosphere of nitrogen. The following amino-acids were used and the following aldehydes (or ketones) formed: *dl*-alanine (acetaldehyde), *dl*-amino*iso*butyric acid (acetone), *dl*-leucine (*iso*valeraldehyde), phenylglycine (benzaldehyde), cystine (acetaldehyde), aspartic acid (acetaldehyde), asparagine (acetaldehyde), glutamic acid (propaldehyde and acetaldehyde), glycine (formaldehyde). Data are also given for the deamination effected by methylglyoxal on guanidine, creatine, creatinine, adenine, guanine, and guanidine. E. A. LUNT.

Reaction of chloroacetic acid with ammonia, and the preparation of glycine. G. R. ROBERTSON (J. Amer. Chem. Soc., 1927, 49, 2889—2894).—Glycine is obtained in 50% yield from chloroacetic acid by dissolving 1 mol. of the latter in 4 litres of ammonia solution (*d* 0·90), and keeping the solution for 24 hrs. at 30° or at least 2 days at 20°. The solution is then evaporated to 500 c.c. to recover ammonia, and the flocculent silver oxide obtained from 170 g. of silver nitrate by means of aqueous sodium hydroxide is added. After removal of the precipitated silver chloride, the filtrate is again evaporated, with stirring, to about 200 c.c., to decompose silver–ammonia complexes. The filtered residue should then give no turbidity with hydrobromic acid, any traces of silver remaining being precipitated by adding water and re-evaporating. The silver-free solution is finally decolorised with charcoal, and the glycine precipitated by adding an equal volume of 95% alcohol. To remove ammonia, the product is dissolved in water (200 c.c.), shaken with 10 g. of granular permutite, and reprecipitated with 250 c.c. of 95% alcohol. The silver is conveniently recovered by suspending the chloride in 400 c.c. of boiling aqueous 25% sodium hydroxide and adding dextrose gradually until precipitation of the metal is complete. F. G. WILLSON.

Synthesis of local anæsthetics of the novocaine group. J. SUPNIEWSKI (Rocz. Chem., 1927, 7, 163—171).—The following substances are prepared: *ethyl* n-*butylaminoacetate*, b. p. 174—176°/20 mm.; *ethyl* n-*butylallylaminoacetate*, b. p. 150—160°/7 mm.; n-*butylallylaminoethyl alcohol*, b. p. 214—215°/745 mm.; *pyrrolidinoethyl* p-*nitrobenzoate hydrochloride*, m. p. 188—189°, and *pyrrolidinoethyl* p-*aminobenzoate hydrochloride*, m. p. 199—200°. R. TRUSZKOWSKI.

Preparation of taurine in considerable quantity. W. O. KERMACK and R. H. SLATER (Biochem. J., 1927, 21, 1065—1067).—Sodium tauroglycocholate is boiled with hydrochloric acid, the whole filtered, concentrated, and then precipitated with alcohol; 5 kg. of the sodium salt yielded 173 g. of taurine. S. S. ZILVA.

Nitrile esters of dicarboxyglutaconic acid. Y. URUSHIBARA (Bull. Chem. Soc. Japan, 1927, 2, 278—287).—The condensation of diethyl ethoxymethylenemalonate with sodiomalononitrile yielded *diethyl sodio-αα-dicyano-α-carboxyglutaconate*, m. p. 238—239°, from which *diethyl αα-dicarbamyl-α-carboxyglutaconate*, m. p. 139—140°, was obtained. These products are identical with the corresponding compounds obtained by condensing diethyl sodiomalonate with ethoxymethylenemalononitrile. Similarly, the condensation of ethyl ethoxymethylenecyanoacetate with sodiomalononitrile, and of ethyl sodiocyanoacetate with ethoxymethylenemalononitrile yielded in each case *ethyl sodio-ααγ-tricyanoglutaconate monohydrate*, m. p. 190°, from which *ethyl ααγ-tricyanoglutaconate*, m. p. 241—242°, was obtained. By similar reactions *triethyl sodio-γ-cyano-α-carboxyglutaconate*, *triethyl γ-cyano-α-carboxyglutaconate*, *sodio-ααγγ-tetracyanopropylene*, and *tetracyanopropylene* were obtained. This last compound is strongly acidic and soluble in water, and as the reaction of its sodio-derivative with hydrochloric acid is reversible, the compound was obtainable only by extraction with ether of the acid solution. In the preparation of tetracyanopropylene a *compound*, $C_7H_2N_4$,EtOH, m. p. 211—212°, was formed incidentally. B. W. ANDERSON.

Active component of the Bertram root [*Radix pyrethri*]. E. Ott and A. Behr (Ber., 1927, **60**, [*B*], 2284—2287).—The powdered root is extracted with alcohol and the residue left after removal of the solvent is treated with ether. The ethereal solution is shaken with sodium hydroxide and, after evaporation, affords crude pyrethrine, which is divided by light petroleum into insoluble pyrethrine and a portion rendered soluble by the presence of fats. Mild hydrolysis removes the latter, which are derived to a considerable extent from stearic acid. Pyrethrine cannot be purified by means of tin tetrabromide (cf. A., 1924, i, 418). The non-homogeneous material, which contains hydrocarotin, $C_{18}H_{30}O$, m. p. 137°, is hydrolysed to *iso*butylamine and undecadienoic acid and hence is the *iso*butylamide and not the piperidide of the latter acid. The term " pyrethrine " has been applied to the active component of *Radix pyrethri* since the first examination of the drug; its application by Staudinger and Ruzicka (cf. A., 1924, i, 758) to two dissimilarly constituted components of another plant is therefore criticised. H. Wren.

Action of organo-magnesium derivatives on tetraethyloxamide. R. Barré (Compt. rend., 1927, **185**, 1051—1052; cf. A., 1927, 447).—The condensation of ethyl oxalate with magnesium diethylamine bromide gives a 70—75% yield of *tetraethyloxamide*, m. p. 35—36°, b. p. 142°/4 mm. In the cold, magnesium ethyl bromide reacts with this amide to form 70% of propionylformdiethylamide and 20% of α-*diethylaminobutyrdiethylamide*, b. p. 98—99°/3 mm. (*picrate*, m. p. 114°), with traces of dipropionyl and evolution of ethylene. At 90°, in toluene, a greater proportion of the second compound is formed and perceptible amounts of dipropionyl. The sole product of the reaction between magnesium phenyl bromide and tetraethyloxamide is α-*diethylaminodiphenylacetdiethylamide*, b. p. 182—184°/3 mm. (*perchlorate*, m. p. 177°), which, on hydrolysis, forms hydroxydiphenylacetdiethylamide. B. W. Anderson.

M. p. of the chloroplatinates of monomethyl- and *as*-dimethyl-guanidine. M. Schenck and H. Kirchhof (Ber., 1927, **60**, [*B*], 2412—2413; cf. Werner and Bell, J.C.S., 1922, **121**, 1790; Philippi and Morsch, A., 1927, 1175).—Methylguanidine chloroplatinate and *as*-dimethylguanidine chloroplatinate have m. p. 190—192° and decomp. 225° respectively. H. Wren.

Magnesylurethane. I. R. Binaghi (Gazzetta, 1927, **57**, 676—689).—The action of magnesium ethyl bromide on urethane yields ethane and the " *magnesylurethane* " $MgBr \cdot NH \cdot CO_2Et$ (*urethanomagnesium bromide*). This forms *compounds* with ether and with pyridine; it is decomposed completely by water, is converted by acetyl chloride into acetylurethane, by benzoyl chloride into benzoylurethane, and is decomposed by acetaldehyde and by benzaldehyde, additive compounds having probably been formed. Acetophenone, benzophenone, ethyl acetate, and benzyl acetate have a similar action. " *Magnesylphenylurethane* " (*phenylurethanomagnesium bromide*) gives stable crystalline products. E. W. Wignall.

Organoberyllium halides. H. Gilman and F. Schulze (J. Amer. Chem. Soc., 1927, 49, 2904—2908).—Beryllium methyl iodide could not be obtained by the method of Durand (A., 1926, 718), but is obtained by heating beryllium with ethereal methyl iodide in presence of mercuric chloride at 80—90° for 15 hrs. *Beryllium ethyl* and n-*butyl iodides* are obtained similarly, and *beryllium phenyl iodide* is obtained by heating beryllium with ethereal iodobenzene and mercuric or beryllium chloride at 150—175°. *Beryllium ethyl bromide* was prepared analogously at 80—90°. The beryllium alkyl halides are decomposed by water with formation of the corresponding hydrocarbons. Carbon dioxide does not appear to react with beryllium methyl iodide, but the latter yields some beryllium dimethyl when heated, so that the equilibrium $2BeRX \rightleftharpoons BeR_2+BeX_2$ appears to be set up under certain conditions (cf. Gilman and Schulze, following abstract). Beryllium methyl iodide and phenylcarbimide yield acetanilide. The beryllium alkyl halides are generally less reactive than the beryllium dialkyls and Grignard compounds. F. G. Willson.

Beryllium dialkyls. H. Gilman and F. Schulze (J.C.S., 1927, 2663—2669).—Beryllium dialkyls were not obtained by heating beryllium with mercury alkyls although this method succeeds with mercury aryls. The alkyls are obtained in good yield (90%) by allowing anhydrous beryllium chloride to react with magnesium alkyl halides in ether, air and oxygen being rigidly excluded. After removing most of the solvent the mixture is distilled for a long period at 150—200°. A concentrated ethereal solution of the dialkyl distils over, from which the latter may be obtained by sublimation in ether. *Beryllium dimethyl*, a solid, subliming at about 200°, and *beryllium diethyl*, m. p. −13° to −11°, b. p. 93—95°/4 mm., 110°/15 mm., are spontaneously inflammable in air, but *beryllium di*-n-*butyl*, b. p. 170°/25 mm., is rapidly oxidised to beryllium *n*-butyl oxide. The alkyls react violently with water, forming the corresponding hydrocarbon and beryllium oxide. With carbon dioxide in ethereal solution beryllium dimethyl gives acetic acid, whilst the diethyl affords triethylcarbinol. Beryllium dialkyls with phenylcarbimide or α-naphthylcarbimide form the corresponding anilides or naphthalides, and show an immediate positive colour reaction with Michler's ketone (cf. A., 1925, ii, 1011). Beryllium dimethyl reacts with benzophenone, giving diphenylmethylcarbinol (identified as αα-diphenylethylene), and with benzoyl chloride, giving phenyldimethylcarbinol, whilst the corresponding diethyl reduces benzophenone to benzhydrol. Beryllium alkyls afford beryllium alkyl iodides with iodine and when treated with anhydrous beryllium chloride, beryllium diethyl furnishes beryllium ethyl chloride. Hence the equilibrium $BeR_2+BeX_2 \rightleftharpoons 2BeRX$ probably exists under certain conditions. S. Coffey.

Action of vanadium salts on Grignard's reagents. J. Supniewski (Rocz. Chem., 1927, 7, 172—175).—The addition of vanadium salts to Grignard's reagents leads to the formation of hydrocarbons, no organic vanadyl derivatives being produced. R. Truszkowski.

Mechanism of reactions accompanying the formation of Cadet's oil. A. Valeur and P.

Gailliot (Compt. rend., 1927, 185, 956—958; cf. A., 1927, 1176).—When arsenious acid and potassium acetate are heated to form Cadet's oil, methyl arsenide, AsMe, b. p. 190°/5 mm., is formed, probably by a reaction between potassium acetate and arsenic suboxide. The decomposition of this compound gives rise to the cacodyl, cacodyl oxide, trimethylarsine, and hepta- and penta-methyltriarsine which are found in Cadet's oil. A red polymeride of methyl arsenide has been isolated. B. W. Anderson.

Dehydrogenation by selenium. II. O. Diels and A. Karstens (Ber., 1927, 60, [*B*], 2323—2325).—Sulphur may frequently be replaced by selenium as dehydrogenating agent with great advantage since hydroaromatic systems are frequently converted into uniform dehydrogenated products by the latter substance, whereas they are completely decomposed by the former; the yields of the products are also greatly improved. The examples cited include abietic acid to retene, dodecahydro-9 : 10-benzophenanthrene to 9 : 10-benzophenanthrene and cadinene to cadaline (cf. Ruzicka and Meyer, A., 1921, i, 573). H. Wren.

Oxidation of cyclic hydrocarbons by an acetic acid solution of hydrogen peroxide. G. Charrier and A. Moggi [with C. Ferri] (Gazzetta, 1927, 57, 736—741).—Hydrogen peroxide in acetic acid solution attacks benzene with difficulty, but on prolonged boiling oxidises it to carbon dioxide (oxalic acid is unstable under the conditions employed) and a yellow, resinous substance. Naphthalene is oxidised fairly quickly to resinous products and phthalic acid; acenaphthene yields acenaphthenequinone and naphthalic acid. Phenanthrene yields phenanthraquinone, followed by diphenic acid and much resin; similarly, 2-phenyl-αβ-naphtho-1 : 2 : 3-triazole yields 4-*o*-carboxyphenyl-2-phenyl-1 : 2 : 3-triazole-5-carboxylic acid; anthracene gives anthraquinone. E. W. Wignall.

Spectroscopic determination of very small amounts of benzene. H. Ley and F. Vanheiden (Ber., 1927, 60, [*B*], 2341—2344).—Solutions of benzene in ethyl alcohol obey Beer's law within the concentration 0·089 and 0·0044%. The presence of less than 0·001% of benzene can be determined spectroscopically, the measurements being preferably made with reference to the second and third long wave-length benzene bands. Benzene was found to the extent of 0·0074% and more in samples of ethyl alcohol dehydrated by Young's method. H. Wren.

Halogenation. III. Bromination. P. S. Varma and B. Narayan (J. Indian Chem. Soc., 1927, 4, 283—289; cf. A., 1927, 452).—Moderately good yields of bromobenzene can be obtained by brominating benzene in presence of fuming nitric–nitrosulphonic acids (50%). Brominations in presence of concentrated and fuming sulphuric acids, concentrated and fuming nitric acids, concentrated and fuming nitric–sulphuric acids, and sodium nitrite and concentrated or fuming sulphuric acid have been studied, and the results are given. The presence of acetic acid has no appreciable effect on the reactions. H. Burton.

Orienting influence of free and bound ionic charges on attached simple or conjugated unsaturated systems. III. Nitration of *m*-nitrophenylbenzylsulphone. B. Chatterjee and R. Robinson (J.C.S., 1927, 2780—2784).—The nitration of this compound has been studied in connexion with the theory of electrostriction of the sulphonium ions (see this vol., 71). The double dipole $-\overset{++--}{\mathrm{SO}_2}$ may be compared with the single dipole $-\overset{+-}{\mathrm{NO}_2}$, and *m*-nitrophenylbenzylsulphone is selected because the group $-C_6H_4{\cdot}NO_2(m)$ should be almost neutral; the results are to be ascribed, therefore, to the influence of the sulphone group. The following sulphones are prepared from the corresponding benzyl chlorides and sodium *m*-nitrobenzenesulphinate: m-*nitrophenylbenzylsulphone*, m. p. 101—102°; m-*nitrophenyl*-o-*nitrobenzylsulphone*, m. p. 192—193°; m-*nitrophenyl*-m-*nitrobenzylsulphone*, m. p. 194—195°; m-*nitrophenyl*-p-*nitrobenzylsulphone*, m. p. 180—181°. The nitration of *m*-nitrophenylbenzylsulphone with nitric acid (*d* 1·5) furnishes approximately 25, 28, and 40%, respectively, of the above *o*-, *m*-, and *p*-nitrobenzylsulphones. The three isomerides are so sparingly soluble in most organic solvents that the proportions had to be determined colorimetrically by the following reactions. An alcoholic solution of the *p*-isomeride gives a carmine coloration with 10% aqueous sodium hydroxide. The *o*-isomeride gives an intense violet coloration with concentrated alkalis in alcoholic acetone, whilst the *m*-compound develops a brownish-red tint only on keeping. All three isomerides develop characteristic colorations when solid potassium hydroxide is added to cold acetone solutions, but when water is added the colours due to the *o*- and *p*-derivatives are discharged, whilst that due to the *m*-isomeride persists. The views expressed by Ingold, Ingold, and Shaw (A., 1927, 550) regarding the effect of the sulphone group on substitution are criticised. S. Coffey.

Orienting influence of free and bound ionic charges on attached simple or conjugated unsaturated systems. IV. Nitration of toluene-ω-sulphonic acid and toluene-ω-sulphonyl chloride. A. C. Bottomley and R. Robinson (J.C.S., 1927, 2785—2790; cf. preceding abstract and A., 1927, 550).—Sodium toluene-ω-sulphonate, when treated at 0° with nitric acid (*d* 1·5), affords an 88% yield of sodium nitrotoluene-ω-sulphonates (minimum yield, *m*-isomeride 9·2%), whilst the free ω-sulphonic acid furnishes 63·6% of mixed sodium nitrotoluene-ω-sulphonates (minimum yield, *m*-isomeride 8·9%). In the nitration of toluene-ω-sulphonyl chloride the proportion of *m*-isomeride obtained varies with the efficiency of the method of salting out the sodium nitrotoluene-ω-sulphonates, the results being: yields of mixed isomerides 63 and 73·5%, minimum yields of *m*-isomeride 28 and 39%. *o*- and *m*-Nitrotoluene-ω-sulphonates, either separately or when mixed, develop no coloration when heated with concentrated aqueous potassium hydroxide solution, whereas the *p*-isomeride gives a yellowish-orange solution, which is more intense in the presence of *o*-isomeride and still more intense in the presence of *m*-isomeride. A colorimetric examination based on this reaction showed that the nitration product from toluene-ω-sulphonyl chloride contains less than 5% of *o*-isomeride and approximately 55% of *m*- and 45% of *p*-isomerides. The nitration products from toluene-ω-sulphonic acid and its sodium salt are identical in composition and equivalent to 10% of *m*-, 48% of *p*-, and 42% of *o*-nitrotoluene-ω-sulphonate. Dinitrotoluene-ω-sulphonates were absent.

From these results it is concluded that the sulphonic ion group, $-\overset{-}{S}O_3$, although negatively charged, still retains a higher electron affinity than a hydrogen atom, hence its *m*-directive effect is due to a general electric effect. S. COFFEY.

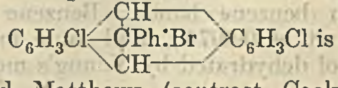
Some derivatives of diphenylmethane. K. N. MENON (J. Indian Chem. Soc., 1927, 4, 437—439).—4 : 4′-Dibromodiphenylmethane is nitrated in acetic anhydride to 4 : 4′-*dibromo*-3 : 3′-*dinitrodiphenylmethane*, m. p. 238—240°. Attempts to obtain ring closure from this compound and from 4 : 4′-*di-iododiphenylmethane*, m. p. 93—93·5°, were unsuccessful. H. BURTON.

Structure of the hydrocarbon $C_{17}H_{18}$ obtained by the dehydration of diphenyl-*tert*.-butylcarbinol. D. E. BATEMAN and C. S. MARVEL (J. Amer. Chem. Soc., 1927, 49, 2914—2919).—α-Diphenylpropaldehyde was oxidised with alkaline permanganate to α-diphenylpropionic acid, and the latter converted, through the acid chloride, into the *methyl ester*, b. p. 149—152°/3 mm., d_4^{20} 1·1206, n_D^{20} 1·5691. When treated with ethereal magnesium methyl iodide, this yields *γγ-diphenyl*-β-*methyl*-Δ^{α}-*butene*, b. p. 132—133°/4·5 mm., d_4^{20} 1·0060, n_D^{20} 1·5757, identical with the hydrocarbon obtained by the dehydration of diphenyl-*tert*.-butylcarbinol (cf. Ramart-Lucas, A., 1913, i, 1325), which is conveniently prepared by heating the latter with a small proportion of *p*-toluenesulphonic acid for 2 hrs. on the steam-bath. *s*-Tetraphenyldi-*tert*.-butylethane could not be obtained by the usual methods from diphenyl-*tert*.-butylmethyl chloride. F. G. WILLSON.

2-Methylnaphthalene. II. Synthesis of hydrocarbons of the benzanthracene group. K. DZIEWOŃSKI and E. RITT (Bull. Inter. Acad. Polonaise, 1927, 3 A, 181—192).—The pyrogenic transformation of 2-methylnaphthalene derivatives results in the formation of 1 : 2-benzanthracene and its methyl derivatives. When 1-benzyl-2-methylnaphthalene, b. p. 221°/17 mm., obtained by the interaction of benzyl chloride and 2-methylnaphthalene in the presence of anhydrous zinc chloride, is distilled over zinc dust, the principal product is 1 : 2-benzanthracene, m. p. 158—159°, whilst 2 : 3-benzanthracene, m. p. 335—336°, is obtained in small amount. If, however, 1-benzoyl-2-methylnaphthalene is subjected to the same process in the presence of a current of hydrogen, 1 : 2-benzanthracene alone is formed. This pyrogenic transformation is applicable to the preparation of similar hydrocarbons; *e.g.*, from 2-methylnaphthalene and *o*- or *p*-toluoyl chloride in the presence of aluminium chloride, 1-*o*-toluoyl-2-methylnaphthalene and 1-*p*-toluoyl-2-methylnaphthalene can be prepared and converted into the corresponding 6- or 8-methyl derivative of 1 : 2-benzanthracene. These compounds may be converted into the corresponding methyl-1 : 2-benzanthraquinone derivatives by means of chromic acid. The following substances are described: 1 : 2-*Benz*-9 : 10-*anthraquinone*, m. p. 168°; 1-*benzoyl*-2-*methylnaphthalene*, b. p. 233°/13 mm., m. p. 74°; 3-*benzoyl*-4-*methylphthalic acid*, m. p. 184°; 1-p-*toluoyl*-2-*methylnaphthalene*, m. p. 106—107°; 6-*methyl*-1 : 2-*benzanthracene*, m. p. 127°; 6-*methyl*-1 : 2-*benz*-9 : 10-*anthraquinone*, m. p. 174°; 1-o-*toluoyl*-2-*methylnaphthalene*, b. p. 238°/14 mm.; 8-*methyl*-1 : 2-*benzanthracene*, m. p. 145°. R. A. MORTON.

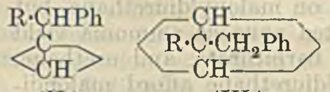
Action of hydrogen peroxide and of hypochlorous acid on anthracene. G. CHARRIER and G. B. CRIPPA [with E. SARAGA] (Gazzetta, 1927, 57, 741—748).—When anthracene is suspended in water and heated with hydrogen peroxide, anthraquinone is formed, with another product, m. p. 250—270°, which when treated with zinc and sodium hydroxide gives dianthrone, m. p. 235—245°, also obtained when a similar suspension is exposed to sunlight and extracted with zinc and sodium hydroxide.

Anthracene suspended in water and treated with hypochlorous acid yields a product, m. p. 180—185°, decomp. from 150°, which contains chlorine and dissolves in organic solvents to strongly fluorescent solutions, from which a substance, m. p. 230—250°, free from chlorine, crystallises; the latter when prepared by long boiling of the reaction product with alcohol has m. p. 235—250°, and is considered to be dianthranolyl ether, $(HO{\cdot}C_{14}H_8)_2O$ (Liebermann and Mamlock, A., 1905, i, 521). E. W. WIGNALL.

Alkylanthracenes and "transannular tautomerism." III. 1 : 5-Dichloro-9-benzylanthracene. E. DE B. BARNETT, J. W. COOK, and M. A. MATTHEWS (Ber., 1927, 60, [*B*], 2353—2366; cf. A., 1926, 1030; 1927, 140).—1 : 5-Dichloroanthrone is converted by magnesium benzyl chloride into 1 : 5-*dichloro*-9-*hydroxy*-9-*benzyl*-9 : 10-*dihydroanthracene*, m. p. 154°, transformed by hydrochloric and glacial acetic acids into 1 : 5-*dichloro*-9-*benzylanthracene*, m. p. 127°. The latter substance reacts with bromine to form a colourless *dibromide*, which readily loses hydrogen bromide, giving the pale yellow *compound*, $C_{21}H_{13}Cl_2Br$, m. p. 184°, to which the endocyclic constitution  $C_6H_3Cl\left<\begin{matrix}CH—\\ |\\ CPh{:}Br\\ CH—\end{matrix}\right>C_6H_3Cl$ is ascribed by Barnett and Matthews (contrast Cook, following abstract). The bromine atom of this compound is unusually reactive (wherefore it is regarded as impossible that the compound should be 1 : 5-dichloro-10-bromo-9-benzylanthracene) and is readily replaced by OH, OMe, OEt, or OAc by boiling with aqueous acetone, alcohols, or sodium acetate, respectively; if the solution is kept neutral by addition of calcium carbonate the following colourless *compounds* are obtained: $C_{21}H_{14}OCl_2$, m. p. 205—207°, unchanged by diazomethane, hydroxylamine, or zinc dust and ammonia, converted by phenylcarbimide into the *phenylurethane*, m. p. 104—106° (decomp.); $C_{22}H_{16}OCl_2$, m. p. 167°; $C_{23}H_{18}OCl_2$, m. p. 190°;

$C_{23}H_{16}O_2Cl_2$, m. p. 247—248°. To these an endocyclic structure is also ascribed. If precautions are not taken to maintain the solution neutral, the following yellow compounds are obtained in place of the colourless series. They are regarded (Barnett and Matthews) as ω-substituted 1 : 5-dichloro-9-benzylanthracenes on account of their colour, fluorescence, and absorption spectrum, and the conversion of the methoxy-compound into an unstable *dibromide* which decomposes into benzaldehyde and 1 : 5-*dichloro-9-bromoanthracene*, m. p. 158—159°. *Substances*, $C_{21}H_{13}Cl_2\cdot OH$, m. p. 155° (obtained also by boiling the colourless hydroxy-compound with acetone and sulphuric acid), which does not react with phenylcarbimide or diazomethane but, like the colourless isomeride, is converted by hydrogen bromide in toluene into the original bromide; $C_{21}H_{13}Cl_2\cdot OAc$, m. p. 187—188°, also obtained from the colourless or yellow hydroxy-compound and glacial acetic acid or by isomerisation of the colourless acetate; $C_{21}H_{13}Cl_2\cdot OMe$, m. p. 156—157°, also derived from the colourless methoxy-compound or the yellow hydroxy-derivative by treatment with methyl alcohol and hydrochloric acid; $C_{21}H_{13}Cl_2\cdot OEt$, m. p. 113°, also obtained from the colourless or yellow hydroxy-compounds and ethyl alcohol and sulphuric acid. The bromo-compound is converted by the following bases into colourless *compounds* probably constituted similarly to the colourless series: by diethylamine in chloroform into the *substance*, $C_{25}H_{23}NCl_2$, m. p. 125°; by piperidine into the *compound*, $C_{26}H_{23}NCl_2$, m. p. 171—172°; by aniline into the *derivative*, $C_{27}H_{19}NCl_2$, m. p. 162°; by dimethylaniline into the *substance*, $C_{29}H_{23}NCl_2$, m. p. 237—238°. The bromo-compound gives a *pyridinium* salt, $C_{26}H_{18}NCl_2Br,EtOH$, m. p. 190—193° (decomp.), which loses the pyridine residue when heated with aqueous acetone, methyl or ethyl alcohol giving the colourless derivatives obtained from the bromide. The following transformations are suffered by the respective substances when suspended or dissolved in chloroform and treated with an excess of nitrogen peroxide followed by addition of light petroleum: 1 : 5-dichloro-9-benzylanthracene to a *dinitro*-compound, $C_{21}H_{14}O_4N_2Cl_2$, m. p. 177° (decomp.), converted by pyridine into a *mononitro*-derivative, $C_{21}H_{13}O_2NCl_2$, m. p. 176°; monobromo- and colourless ethoxy-compound into a *trinitro*-derivative, $C_{21}H_{13}O_6N_3Cl_2$, m. p. 168° (decomp.), transformed by cold pyridine into a *dinitro*-compound, $C_{21}H_{12}O_4N_2Cl_2$, m. p. 157° (decomp.); yellow methoxy-compound to a *dinitro*-derivative, $C_{22}H_{16}O_5N_2Cl_2$, m. p. 170° (decomp.), converted by warm pyridine into the *mononitro*-compound, $C_{22}H_{15}O_3NCl_2$, m. p. 145°. H. WREN.

Isomeric derivatives of 1 : 5-dichloro-9-benzylanthracene. J. W. COOK (Ber., 1927, **60**, [*B*], 2366—2369; cf. A., 1926, 838, 953, 1131).—The author does not agree with Barnett and Matthews in assigning to the series of colourless compounds (preceding abstract) the endocyclic structure but regards them as having the constitution  $\left\langle\begin{matrix}C(\dot{:}CHPh)\\CHR\end{matrix}\right\rangle$ (I), for the following reasons. The substituents in the colourless series have the great reactivity characteristic of groups in the position 10 in 9 : 10-derivatives of dichloroanthracene; the hydroxy-compound (R=OH) is methylated by short treatment with methyl-alcoholic hydrogen chloride and easily acetylated by glacial acetic acid; the pyridinium group of the salt ($R=NC_5H_5\cdot Br$) is unusually labile. The distribution of affinity of the carbon atom in compounds of the types (II) and (III) is such that weakened activity must be expected from the colourless forms if they actually have the endocyclic constitution, whereas the reverse is the case. The endocyclic structure of the colourless series is not in harmony with the observation that the colourless hydroxy-compound readily yields a phenylurethane, whereas the yellow isomeride is indifferent towards phenylcarbimide. The behaviour is explained if the colourless compound has the structure I (R=OH) and steric hindrance is assumed to be operative with the yellow variety. The ready transformation of the colourless into the yellow isomerides is assumed to occur through dissociation into the free radicals, $\cdot CHPh\dot{:}C\langle\rangle CH\cdot + R$, isomerisation of the complex radical into its more stable form, $CH\langle\rangle C\cdot CHPh\cdot$, and union of R with the new radical. H. WREN.



(II.) (III.)

Rubrene : ψ-rubrene. C. MOREU, C. DUFRAISSE, and G. BERCHET (Compt. rend., 1927, **185**, 1085—1087).—When rubrene in benzene solution is treated with gaseous hydrogen iodide it is completely transformed into a colourless isomeride, *ψ-rubrene*, m. p. 278°. Iodine is liberated during the transformation, but in amounts bearing no relation to the simple hydrogenation of rubrene, and the end-product does not contain added hydrogen or iodine. ψ-Rubrene evolves violet vapours when heated, and gives an intense green solution in hot sulphuric acid. When crystallised from benzene it contains 1 mol. of solvent, which it loses at 210°. Rubrene remains unattacked by the usual methods of hydrogenation, but ψ-rubrene, when heated in a sealed tube with hydrogen iodide at 200°, forms an uncrystallisable oil. B. W. ANDERSON.

Dissociation of rubrene peroxide. C. MOUREU and C. DUFRAISSE (Z. physikal. Chem., 1927, **130**, 472—479).—Rubrene in solution is readily oxidised to a stable, colourless peroxide, which in the solid state or in solution at 100—150° readily dissociates into rubrene and oxygen. The light absorption of rubrene, examined in the range 5610—4100 Å., is characterised by maxima at 5300, 4920, and 4700 Å. In benzene solution cryoscopic measurements lead to values of $M=485$ (theory 532), in ethylene bromide $M=364$. It is therefore thought to exhibit dissociation in solution similar to that of hexaphenylethane. R. W. LUNT.

Urethanes. IV. Acyldiurethanes and their reactions with ammonia and amines. S. BASTERFIELD, E. L. WOODS, and M. S. WHELEN (J. Amer. Chem. Soc., 1927, **49**, 2942—2948; cf. A., 1926, 1132).—Treatment of oxalyldiurethane with cold, concentrated, aqueous ammonia affords oxamide and urethane, together with a small proportion of carbamide. Dry ammonia at 90—100° affords similarly urethane. Ethylamine and oxalyldiurethane afford diethyloxamide in 70% yield, together with urethane, whilst aniline at 150—190° yields similarly mainly oxanilide, with some carbanilide. At 100°, a 60% yield of oxanilide is produced, together with, apparently, *α-carbethoxy-β-phenyloxamide*, m. p. 224°, and phenylcarbamide and urethane. Dry ammonia at 100° is without action on malonyldiurethane, but the latter and concentrated aqueous ammonia yield malonamide, ammonium barbiturate, and urethane. Ethylamine and malonyldiurethane afford malondiethylamide in 92% yield. Aniline at 190° yields malonanilide and carbanilide; at 150°, the foregoing products are obtained, together with, apparently, *α-phenyl-β-phenylcarbamylmalonamide*, m. p. 234—235°; at 120°, the latter compound is produced in larger proportion, with malonanilide and phenylcarbamide, carbanilide not being produced, whilst at 100° no reaction takes place in several hours. Aqueous ammonia and phthalyldiurethane afford urethane and phthalamide. Aniline at 190° affords carbanilide and phthalanil, whilst at 100° (8 min.) the main product is, apparently, *α-phenyl-β-carbethoxyphthalamide*, m. p. 225°. Carbonyldiurethane and aqueous ammonia afford mainly urethane, which is subsequently converted to a large extent into carbamide, biuret, and cyanuric acid. Ethylamine and carbonyldiurethane yield ethylurethane, carbamide, and a *substance*, m. p. 155°, together with a 75% yield of ethyl allophanate. The courses of the above reactions appear to be connected with a tendency to the formation of the amides of acids stronger than carbonic, rather than to the formation of carbamides.

F. G. WILLSON.

Preparation of monohalogenophenylimides of dichloromaleic, tetrachlorosuccinic, and dibromosuccinic acids, and their molecular stability. A. SANNA and E. MACCIOTTA (Gazzetta, 1927, 57, 772—776; cf. this vol., 26).—*p*-Bromophenyl- (m. p. 130°) and *m*-bromophenyl- (m. p. 125°) αβ-dibromosuccinamic acids give on treatment with acetic anhydride the corresponding *imides*, m. p. 155° and 74—75°, respectively. *o*-, *m*-, and *p*-Chlorophenylsuccinimides are converted by phosphorus pentachloride first into the o-, m-, and p-*chlorophenyldichloromaleinimides*, m. p. 120°, 172—173°, and 212°, respectively, and the latter into the o-, m-, and p-*chlorophenyltetrachlorosuccinimides*, m. p. 132—133°, 185°, and 205°, respectively.

Solubility considerations prevent a study of the stability of these compounds; the introduction of halogen is, however, seen to stabilise the heterocyclic ring. E. W. WIGNALL.

Preparation of halogenodiphenylsuccinamides. A. SANNA and (SIGNA.) G. REPETTO (Gazzetta, 1927, 57, 777—780).—Succinic acid reacts with *o*-, *m*-, and *p*-chloroaniline to give oo′-, mm′-, and pp′-*dichloro*-s-*diphenylsuccinamides*, m. p. 202° (decomp.), 232°, and 246°, respectively; mm′- and pp′-*dibromo*-s-*diphenylsuccinimides*, m. p. 222° and 271°, respectively, are similarly prepared. E. W. WIGNALL.

Dimorphism of 2-chloroaceto-*p*-toluidide. M. SCHOFIELD (J.C.S., 1927, 2903; cf. A., 1912, i, 1027).—2-Chloroaceto-*p*-toluidide, m. p. 83°, crystallises from benzene, alcohol, and many other solvents in needles. When crystallised from light petroleum it is converted into a second form, m. p. 104° (plates), which may be transformed into the lower-melting, more soluble form by crystallisation from benzene. G. A. C. GOUGH.

***p*-Cymene. IX. Nitration of 2-amino-*p*-cymene.** A. S. WHEELER and F. P. BROOKES (J. Amer. Chem. Soc., 1927, 49, 2832—2834; cf. this vol., 55).—Treatment of 2-acetamido-*p*-cymene in sulphuric acid with nitric acid at 0° affords 5-*nitro*-2-*acetamido*-p-*cymene*, yellow, m. p. 148°, which, on hydrolysis with hydrochloric acid, yields 2-*amino*-5-*nitro*-p-*cymene*, b. p. above 250° (*hydrochloride*). Reduction of the *benzoyl* derivative, m. p. 215—218°, of the latter with tin and hydrochloric acid in alcohol affords 5-*amino*-2-*benzamido*-p-*cymene*, m. p. 115° [*hydrochloride*, m. p. above 200° (decomp.); *acetyl* derivative, m. p. 120°]. 1-(5-*Nitrocarvacrylazo*)-2-*naphthol*, red, m. p. 245°, and *sodium* 2-(5-*nitrocarvacrylazo*)-1-*naphthol*-4-*sulphonate*, red, were prepared. F. G. WILLSON.

Preparation and base strengths of some amines. W. H. CAROTHERS, C. F. BICKFORD, and G. J. HURWITZ (J. Amer. Chem. Soc., 1927, 49, 2908—2914).—The hydrolysis constants ($K_{\text{hyd}} \times 10^{10}$), and dissociation constants ($K_B \times 10^5$) of the following amines have been determined by measuring the p_H of solutions of the bases in water in presence of definite added fractional equivalents of hydrochloric acid, and are quoted below in the above order: benzylamine, 4·26, 2·35; β-phenylethylamine, 1·48, 6·78; γ-phenylpropylamine, 0·63, 15·9; δ-phenylbutylamine, 0·40, 24·8; ε-phenylamylamine, 0·33, 30·6; *o*-methylbenzylamine, 5·89, 1·70; *m*-methylbenzylamine, 4·24, 2·40; *p*-methylbenzylamine, 3·98, 2·55; *o*-methoxybenzylamine, 1·81, 5·56; *m*-methoxybenzylamine, 6·46, 1·56; *p*-methoxybenzylamine, 3·10, 3·22; benzylmethylamine, 2·63, 3·80; benzylethylamine, 2·10, 4·75; benzyl-*n*-propylamine, 2·40, 4·18; and β-phenylethylmethylamine, 0·75, 13·9. In amines of the type $Ph \cdot [CH_2]_x \cdot NH_2$, the continuous decrease of $K_{\text{hyd.}}$ with increase in x is not quite regular, and the results do not accord with Derick's rule (A., 1911, ii, 713) or Simms' equation (A., 1926, 681). In the methoxy- and methyl-benzylamines the effects of the ring substituents are slight and vary irregularly with change of position. It is concluded that Bourgeaud and Dondelinger's values of K_B for benzylmethylamine and benzylethylamine are erroneous (A., 1925, ii, 117).

m-*Methoxybenzylacetamide*, m. p. 58·5—59°, b. p. 191—198°/11 mm., was prepared by catalytic reduction of *m*-anisonitrile in acetic anhydride, and hydrolysed by heating with methyl-alcoholic sodium hydroxide at 140—150° to m-*methoxybenzylamine*, b. p. 131°/26 mm., 140°/37 mm. The following *NN′-p*-toluenesulphonamides are described: *benzylmethyl*-, m. p. 94·4—94·8°; *benzylethyl*-, m. p. 49—50°; *benzylpropyl*-, m. p. 46—47°; β-*phenylethylmethyl*-, m. p. 44—45°; *dibenzyl*-, m. p. 161°, and *di*-β-*phenylethyl*-p-*toluenesulphonamide*, m. p. 101°. The *N*-monosubstituted *p*-toluenesulphonamides are not soluble in aqueous alkali, but dissolve in aqueous-alcoholic

(1 : 2) sodium hydroxide, by means of which they can be separated from the corresponding disubstituted derivatives. F. G. Willson.

Crystalline compounds obtained by the action of aromatic amines on semicarbazide and its derivatives. J. Macurevitsch (J. Russ. Phys. Chem. Soc., 1927, 59, 579—592).—See A., 1927, 1061. M. Zvegintzov.

Investigation by means of thermal analysis of the reaction for obtaining naphthylamines from naphthols. B. N. Menschutkin and N. A. Butkov (Ann. Inst. Anal. Physico-Chim. Leningrad, 1926, 3, 405—420).—Thermal analysis of the binary systems involved in the reaction $C_{10}H_7{\cdot}OH+NH_3\longrightarrow C_{10}H_7{\cdot}NH_2+H_2O$ in presence of zinc chloride or calcium chloride is complicated by the difficulty of obtaining the naphthylamines and naphthols pure and by their proneness to resinification. Hence aniline and mono- and di-methylaniline have been used in addition to the naphthylamines, and zinc bromide, which is more readily dehydrated than the chloride, has also been used.

The solubility curve of the system zinc bromide–aniline shows a maximum corresponding with the compound $ZnBr_2,2NH_2Ph$, m. p. 270°, which is readily obtained, with considerable development of heat, when the components are mixed. The eutectic point between this compound and zinc bromide is at 172° and corresponds with 81·6% of zinc bromide. With mono- and di-methylanilines, zinc bromide forms the compounds $ZnBr_2,2NHMePh$, decomp. 285°, and $ZnBr_2,2NMe_2Ph$, decomp. above 280°. With the system zinc bromide–α-naphthylamine, the maximum solubility corresponds with the compound $ZnBr_2,4C_{10}H_7{\cdot}NH_2$, m. p. 241°; the eutectic point between this compound and zinc bromide is at about 225° and about 35% of the bromide, the other eutectic point, about 47°, corresponding with about 0·5% of zinc bromide. For the system zinc bromide–β-naphthylamine, the maximum of the solubility curve is at 261° and the composition that of the compound $ZnBr_2,2C_{10}H_7{\cdot}NH_2$, m. p. 261°; the eutectic point on the zinc bromide side, about 200°, corresponds with about 60% of the bromide. For the system zinc chloride–α-naphthylamine, the maximum of the solubility curve corresponds with the compound $ZnCl_2,4C_{10}H_7{\cdot}NH_2$, m. p. 253°, the eutectic points being 220° and about 47° (38% and about 0·1% of zinc chloride). The system zinc chloride–β-naphthylamine forms the compound $ZnCl_2,2C_{10}H_7{\cdot}NH_2$, m. p. 275°; the eutectic points are about 205° (about 62% of zinc chloride) and about 111° (very little zinc chloride). β-Naphthol and β-naphthylamine form the compound $2C_{10}H_7{\cdot}OH,C_{10}H_7{\cdot}NH_2$, m. p. 120°, the eutectic points of the system being 116° and 101° with 5% and 84% of the amine (cf. Kremann and Strohschneider, A., 1919, ii, 54).

Recent work increases the probability that, with organic reactions proceeding catalytically, the formation of molecular compounds of the catalyst with the reacting substances or with the products of the reaction retards the reaction, and this is undoubtedly the case in the formation of naphthylamines from naphthols. T. H. Pope.

p-Cymene. VIII. p-Cymylene-2 : 5-diamine. Dyes derived from 2-amino- and 5-bromo-2-amino-p-cymene. A. S. Wheeler and L. F. P. Cutlar (J. Amer. Chem. Soc., 1927, 49, 2819—2822; cf. A., 1927, 352).—2-*Amino*-p-*cymene nitrate*, m. p. 140° (decomp.), *hydrobromide*, m. p. 169° (decomp.), and *trichloroacetate*, m. p. 162° (decomp.), are described. Treatment of diazotised sulphanilic acid with 2-amino-*p*-cymene affords 5-(4′-*sulphobenzeneazo*)*carvacrylamine hydrochloride*, red, m. p. 282°, which, on reduction with stannous chloride, yields *p*-cymylene-2 : 5-diamine. When boiled with methyl-alcoholic *p*-nitrosodimethylaniline, 2-amino-*p*-cymene yields *dimethylaminocymylphenazine*, blue, m. p. 48° (decomp.). The following *dyes*, prepared by coupling diazotised 5-bromo-2-amino-*p*-cymene (*sulphate*, m. p. 123°, decomp.) with the substances mentioned, are described: *o*-cresol, brown, m. p. 112°; pyrocatechol, brown, m. p. 235°; phloroglucinol, red, m. p. 280°; carvacrol, brown, m. p. 192°, and *p*-toluidine (*hydrochloride*, brown, m. p. 188°). *Dyes* were also prepared from 5-bromo-2-amino-*p*-cymene and diazotised sulphanilic acid [*hydrochloride*, deep chrome, m. p. above 300° (decomp.)] and anthranilic acid (*hydrochloride*, brown, m. p. 189°). F. G. Willson.

Interaction of chloral and arylhydrazines. F. D. Chattaway and R. Bennett (J.C.S., 1927, 2850—2853).—2 : 4-Dihalogen-substituted phenylhydrazines react smoothly with chloral in alcoholic solution to afford the 2 : 4-dihalogen-substituted phenylhydrazone of the corresponding alkyl glyoxylate, $C_6H_3X_2{\cdot}NH{\cdot}N{:}CH{\cdot}CO_2R$ (I). If, however, the reaction takes place in aqueous or acetic acid solution one molecule of water and one molecule of hydrogen chloride are eliminated and αα-dichloro-β-2 : 4-dihalogenobenzeneazoethylenes, $C_6H_3X_2{\cdot}N{:}N{\cdot}CH{:}CCl_2$, are formed which yield β-bromo-substitution compounds on bromination and 2 : 4-dihalogenoanilines on reduction. With alcohols they afford compounds of the type I. In this way the following are prepared: *ethyl glyoxylate* 2 : 4-*dichlorophenylhydrazone*, m. p. 121·5° (hydrolysis gives ethyl alcohol and glyoxylic acid 2 : 4-dichlorophenylhydrazone); 2 : 4-*dichlorophenylhydrazones* of *methyl*, m. p. 136·5, n-*propyl*, m. p. 65°, and n-*butyl glyoxylate*, m. p. 59°; 2 : 4-*dibromophenylhydrazones* of *methyl*, m. p. 136°, *ethyl*, m. p. 119°, and n-*propyl glyoxylate*, m. p. 75°; *ethyl glyoxylate* 2-*chloro*-4-*bromophenylhydrazone*, m. p. 120°; *ethyl glyoxylate* 4-*chloro*-2-*bromophenylhydrazone*, m. p. 115°; αα-*dichlorobenzeneazoethylene*, m. p. 84·5° (scarlet); αα-*dichloro*-β-*bromo*-β-2 : 4-*dichlorobenzeneazoethylene*, m. p. 90° (red); αα-*dichloro*-β-2 : 4-*dibromo*-, m. p. 96·5, αα-*dichloro*-β-2-*chloro*-4-*bromo*-, m. p. 84°, and αα-*dichloro*-β-4-*chloro*-2-*bromo-benzeneazoethylene*, m. p. 81°. Glyoxylic acid reacts with 2 : 4-dichloro- and 2 : 4-dibromo-phenylhydrazine to give *glyoxylic acid* 2 : 4-*dichlorophenylhydrazone*, decomp. about 150°, and 2 : 4-*dibromophenylhydrazone*, decomp. about 150°, respectively. Several alkyl glyoxylate dihalogenophenylhydrazones prepared from bromal were identical with the corresponding compounds prepared from chloral. G. A. C. Gough.

Manufacture of carbazides and thiocarbazides of the naphthalene series. Brit. Dyestuffs Corp., Ltd., G. M. Dyson, F. A. Mason, and A. Renshaw.—See B., 1927, 902.

Di-*p*-xylylguanidine. W. Scott, Assr. to E. I. du Pont de Nemours & Co.—See B., 1927, 924.

Halogenation of phenols. II. Iodination. F. G. Soper and G. F. Smith (J.C.S., 1927, 2757—2761; cf. A., 1926, 831).—Examination of the kinetics of the iodination of phenol over the hydrogen-ion concentration range $0{\cdot}5\times10^{-7}$ to 4×10^{-7} shows that no iodination is effected by iodine, although the ionisation constant of the iodine into positive iodine ions is 30 times that of hypoiodous acid. Interaction probably occurs between both the phenoxide ion and un-ionised phenol and the hypoiodous acid; the former reaction is 180 times as rapid as the latter.

G. A. C. Gough.

Action of nitric acid and mercury on aromatic hydrocarbons and a few of their derivatives. F. Blechta and K. Pátek (Z. ges. Schiess- u. Sprengstoffw., 1927, 22, 314—317; cf. Holdermann, A., 1906, i, 439).—When toluene is nitrated at 95° with 50% nitric acid containing 2% of mercury, nitrotoluene is produced together with *p*-nitrobenzoic acid, m. p. 237—238° (corr.), in 10% yield and trinitro-*m*-cresol, m. p. 105—106°. Neither trinitro-*o*- or -*p*-cresol nor nitrosalicylic acid is formed under these conditions (cf. Wolffenstein and Böters, A., 1913, i, 353). Benzoic acid on nitration in presence of mercury yields chiefly *m*-nitrobenzoic acid together with a small amount of 2 : 4 : 6-trinitro-*m*-hydroxybenzoic acid (cf. Wolffenstein and Paar, A., 1913, i, 363), whilst benzene itself yields nitrobenzene, dinitrophenol, and trinitrophenol. The use of mixed acid instead of nitric acid alone in the nitration of benzene or toluene in presence of mercury has no effect on the course of the reaction. The further nitration of aromatic nitrohydrocarbons is facilitated by the presence of mercury. In the nitration of nitrobenzene with 85% nitric acid the yield of dinitrobenzene is increased from 48·8% to 71·8% under comparable conditions on addition of 2% of mercury to the acid, no nitrophenol being formed. The rate of nitration is also increased, and the improvement is still more marked if 5% of mercury is used. Similarly, the yield of dinitrotoluene obtained by the nitration of *o*-nitrotoluene with 75% nitric acid is with mercury 70·8%, and without mercury 50·3%, a small amount (about 1%) of *o*-nitrobenzoic acid being produced. With *p*-nitrotoluene, the yield of dinitrotoluene is increased from 30·1% to 58·4%, and about 2% of *p*-nitrobenzoic acid is formed. The accelerating action of mercury in the nitration and oxidation of aromatic hydrocarbons is probably due to the intermediate formation of mercury aryl nitrates (cf. Dimroth, A., 1899, i, 428; 1902, i, 656). Mercury tolyl nitrate, which may be prepared as a brown viscous mass by heating together toluene and mercuric nitrate, regenerates toluene when heated with dilute sulphuric acid, but with 30% nitric acid nitrotoluene and nitrocresol are produced. The suggestion is made that in the latter case the mercury tolyl nitrate first decomposes, yielding toluene in the nascent state which is more readily nitrated and oxidised by dilute nitric acid than the normal product. Mercury aryl nitrates or acetates are liable to cause painful skin blisters and should be handled with care.

W. J. Powell.

Halogenation of *p*-hydroxydiphenylamine. II. A. E. Bradfield, L. H. N. Cooper, and K. J. P. Orton (J.C.S., 1927, 2854—2864).—The reaction of chlorine or bromine on *p*-hydroxydiphenylamine may result in substitution or in oxidation to the quinoneanil (benzoquinonephenylimine) if the hydrogen bromide is removed (cf. Orton and Smith, *ibid.*, 1908, 93, 314). The chlorine-substitution products are prepared from the *O*-acyl derivatives by the chloroamine method (Orton and King, *ibid.*, 1911, 99, 1185; A., 1927, 645) and their constitutions are determined by oxidation to the quinoneanils followed by oxidation of these compounds to chlorobenzoquinones and chloroanilines. Thus *p*-benzoyloxydiphenylamine (p-*toluenesulphonyloxy*-derivative, m. p. 126·5°) affords 4′-*chloro*-4-*benzoyloxydiphenylamine*, m. p. 148·5°, which on hydrolysis with aqueous potassium hydroxide gives 4′-*chloro*-4-*hydroxydiphenylamine*, m. p. 91° (p-*toluenesulphonyloxy*-derivative, m. p. 93—94°). The latter on oxidation gives 4-*chlorobenzoquinoneanil*, m. p. 83·5°. 2 : 2′ : 4′-*Trichloro*-4-*benzoyloxydiphenylamine*, m. p. 114°, and 2 : 2′ : 4′-*trichloro*-4-p-*toluenesulphonyloxydiphenylamine*, m. p. 130·5° (*hydroxy*-compound, m. p. 128°), are prepared from the 4-acyloxy-compounds or from their monochloro-derivatives; the latter compound yields on further chlorination 2 : 6 : 2′ : 4′-*tetrachloro*-4-p-*toluenesulphonyloxydiphenylamine*, m. p. 126° (tetrachlorohydroxy-compound, m. p. 113°; *benzoyloxy*-compound, m. p. 114·5°), and 2 : 6 : 2′ : 4′ : 6′-*pentachloro*-4-p-*toluenesulphonyloxydiphenylamine*, m. p. 156·5° (also prepared by passing chlorine through an acetic acid solution of 4-*p*-toluenesulphonyl oxydiphenylamine; *pentachlorohydroxy*-compound, m. p. 156°; *monoacetyl* derivative, m. p. 126°; *benzoyloxy*-derivative, m. p. 133—134°). 2 : 2′ : 4′-Trichlorobenzoquinoneanil, m. p. 72·5°, bronzy-red, 2 : 6 : 2′ : 4′-*tetrachlorobenzoquinoneanil*, m. p. 143°, violet, and 2 : 6 : 2′ : 4′ : 6′-*pentachlorobenzoquinoneanil*, m. p. 163°, bronze coloured, are described. 2 : 3 : 6 : 2′ : 4′ : 6′-*Hexachloro*-4-*hydroxydiphenylamine*, m. p. 114° (*benzoyloxy*-derivative, m. p. 125°; p-*toluenesulphonyloxy*-derivative, m. p. 141°), and *heptachloro*-4-*hydroxydiphenylamine*, m. p. 158—159° (*benzoyloxy*-derivative, m. p. 164°), are described. 2 : 3 : 6 : 2′ : 4′ : 6′-*Hexachlorobenzoquinoneanil*, m. p. 141°, which gives trichlorobenzoquinone and *s*-trichloroaniline on hydrolysis with 1% sulphuric acid, and *heptachlorobenzoquinoneanil*, m. p. 114°, which gives tetrachlorobenzoquinone and *s*-trichloroaniline, are prepared in the usual ways. The pentachlorobenzoquinoneanil, when treated with a glacial acetic acid solution of concentrated hydrochloric acid, affords hexachlorohydroxydiphenylamine; the hexachlorobenzoquinoneanil gives similarly pentachlorohydroxydiphenylamine. 4′-*Bromo*-4-*benzoyloxydiphenylamine*, m. p. 150·5° (*hydroxy*-compound, m. p. 108°, and 4-*bromobenzoquinoneanil*, m. p. 100—104°, scarlet, probably dimorphous, described), is prepared by the interaction of bromine in glacial acetic acid with a solution of *p*-benzoyloxydiphenylamine and sodium acetate in the same solvent. 2 : 2′ : 4′-*Tri*-

bromo-4-p-*toluenesulphonyloxydiphenylamine* is prepared similarly by bromination at 50°, whilst the corresponding tribromobenzoyloxy-compound (Smith and Orton, J.C.S., 1908, **93**, 314) is best prepared by the Schotten–Baumann method or by bromination of 4-benzoyloxydiphenylamine. 2 : 6 : 2′ : 4′ : 6′-*Pentabromo*-4-p-*toluenesulphonyloxydiphenylamine*, m. p. 210° (*hydroxy*-compound, m. p. 206—207°; *benzoyloxy*-compound, m. p. 141—142°; *benzoquinoneanil*, m. p. 184—185°), is prepared from the tribromo-compound by exposure to bromine vapour in the presence of sodium phosphate or borate. An attempt to sulphonylate the heptabromo-compound (Smith and Orton, *loc. cit.*) yielded a *substance*, m. p. 188°. All attempts to sulphonylate the 2 : 5 : 2′ : 4′-tetrabromo- and the 2 : 3 : 5 : 2′ : 4′-pentabromohydroxy-compounds failed.

6 : 6′-*Dichloro*-2 : 2′ : 4′-*tribromo*-4-p-*toluenesulphonyloxydiphenylamine*, m. p. 185° (*hydroxy*-compound, m. p. 166°; *benzoquinoneanil*, m. p. 150°), and the corresponding *benzoyl* compound, m. p. 153°, are prepared from the tribromo-compounds by chlorination by the chloroamine method in acetic acid suspension. 2 : 2′ : 4′-*Trichloro*-6 : 6′-*dibromo*-4-p-*toluenesulphonyloxydiphenylamine*, m. p. 174° (*hydroxy*-compound, m. p. 180°; *benzoquinoneanil*, m. p. 170°), and the corresponding *benzoyloxy*-compound, m. p. 134°, are prepared by bromination of the trichloro-derivatives by the borate method. 2 : 2′ : 4′-*Trichloro-5-bromo-4-hydroxydiphenylamine*, m. p. 127—128° (*benzoyloxy*-compound, m. p. 186°; *sulphonyloxy*-compound, m. p. 114°; *benzoquinoneanil*, m. p. 115°), and 2 : 2′ : 4′-*trichloro*-5 : 6′-*dibromo-4-hydroxydiphenylamine*, m. p. 189° (*benzoquinoneanil*, m. p. 133°), which could not be sulphonylated or benzoylated, are obtained by bromination of the trichloro-compound in boiling chloroform solution. 2 : 2′ : 4′-*Trichloro*-3 : 5 : 6 : 6′-*tetrabromo*-4-*hydroxydiphenylamine*, m. p. 160° (*benzoyloxy*-compound, m. p. 163°), is obtained from the trichloro-compound by bromination in chloroform solution in sunlight and yields on oxidation 2 : 2′ : 4′-*trichloro*-3 : 5 : 6 : 6′-*tetrabromobenzoquinoneanil*, m. p. 136°, which is converted by hydrolysis into 2 : 4-dichloro-6-bromoaniline and chlorotribromobenzoquinone, m. p. 294°. The following corrected m. p. are given for substances described in previous papers: 3 : 5 : 2′ : 4′ : 6′-pentabromo-4-hydroxydiphenylamine, m. p. 157°; 3 : 5 : 2′ : 4′ : 6′-pentabromobenzoquinoneanil, m. p. 150·5°; 2 : 3 : 5 : 2′ : 4′ : 6′-hexabromo-4-hydroxydiphenylamine, m. p. 216°; 2 : 3 : 5 : 2′ : 4′ : 6′-hexabromobenzoquinoneanil, m. p. 171°.

G. A. C. Gough.

Polarity of the carbon–halogen linking. I. Determination of relative rates for the acid hydrolysis of positive halogens. II. Kinetics of the acid hydrolysis of halogenophenols and halogenonaphthols. J. R. Sampey (J. Amer. Chem. Soc., 1927, **49**, 2849—2852, 2855—2858).—I. The rates of dehalogenation of a number of bromo- and iodo-substituted phenols and naphthols were determined by heating known weights of these derivatives for varying periods with aqueous-alcoholic stannous chloride of known concentration at 70° in an atmosphere of nitrogen, and titrating the unused stannous chloride (cf. Nicolet, A., 1927, 869). The results obtained show the markedly positive nature of the halogens in the halogenonaphthols, but halogens in the 6- and 7-positions are not removed under the conditions applied. The latter observation supports the suggestion of Nicolet (*loc. cit.*) that quinones are formed intermediately in the removal of halogens by this method, especially in view of Vesely and Jakes' observation (A., 1923, i, 911) that the two most readily formed naphthaquinones possess one benzene nucleus intact.

II. The rate of dehalogenation of halogenophenols and halogenonaphthols under the conditions previously outlined increases markedly with increase in acidity of the system, but is independent of the concentration of the stannous chloride.

F. G. Willson.

Reaction of phenol with propyl alcohol at high temperatures and pressures. V. N. Ipatiev, N. Orlov, and A. Petrov (J. Russ. Phys. Chem. Soc., 1927, **59**, 541—544).—The reaction between phenol and propyl alcohol in the presence of a catalyst at high temperatures and pressures was investigated for comparison with the behaviour of methyl alcohol under similar conditions. Heating for 12 hrs. at 380—400° and 125—130 atm. gave a liquid mixture of phenyl propyl ether, propyl ether, alkylphenols (among them *o*-propylphenol) and their propyl ethers, and polymethylene hydrocarbons, together with a gas consisting of unsaturated and saturated hydrocarbons. At normal pressure, only a small quantity of phenyl propyl ether, together with propylene, was obtained.

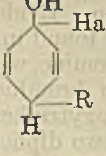
M. Zvegintzov.

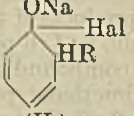
Migration of diphenylmethyl and benzyl groups in phenol. J. van Alphen (Rec. trav. chim., 1927, **46**, 799—812).—Diphenylchloromethane reacts with phenol at 110° either alone or in the presence of zinc chloride to give hydrogen chloride, 4-*hydroxytriphenylmethane*, m. p. 111°, 2 : 4-*dibenzhydrylphenol* (?), m. p. 128—129°, 2 : 4 : 6-*tribenzhydryl*)*phenol*, m. p. 168°, and *s*-tetraphenylethane, m. p. 211°. 4-Hydroxytriphenylmethane was also prepared by the action of zinc dust and acetic acid on 4-*hydroxytriphenylcarbinol*, m. p. 143°, which in turn was prepared from magnesium phenyl bromide and ethyl *p*-hydroxybenzoate. Similarly 2-hydroxytriphenylcarbinol, m. p. 143°, and 2-hydroxytriphenylmethane, m. p. 122° (cf. Baeyer, A., 1907, i, 759), were prepared; the latter compound, however, could not be found in the products of the reaction. Evidence of substitution in the 2 : 4 : 6-positions is found in the inert nature of that compound towards bromine, whilst 4-hydroxytriphenylmethane reacts with bromine in acetic acid to give 2 : 6-dibromo-4-hydroxytriphenylmethane, m. p. 130°. Moreover, only two diphenylmethyl groups can be introduced into *p*-hydroxybenzoic acid by heating it at 180° with diphenylchloromethane to give 4-*hydroxy*-3 : 5-*dibenzhydrylbenzoic acid*, m. p. 252° (Maquenne block), whilst *m*-chlorophenol reacts under similar conditions to give 3-*chloro*-2 : 4 : 6-*tribenzhydrylphenol*, m. p. 88—90°.

The suggestion that the first-mentioned reaction is preceded by the formation of diphenylmethyl ethers and their consequent isomerisation through an intermediate oxonium salt to the substituted ring compound is confirmed by the isolation of 2 : 4 : 6-tri- and 2 : 4-dibenzhydrylphenol from the product obtained by heating benzhydryl methyl ether at 160° in the presence of hydrogen chloride. In a similar way 4-hydroxydiphenylmethane may be obtained from phenyl benzyl ether or from benzyl chloride and phenol by heating at 100° and 160°, respectively, in the presence of zinc chloride. The hypothesis is extended to other substitution reactions of phenols and amines, *e.g.*, the production of 2 : 6-dinitrophenol from the nitration of *o*-nitrosalicylic acid and of 2-bromo-4 : 6-dinitrophenol by the bromination of 4-bromo-2 : 6-dinitrophenol. G. A. C. Gough.

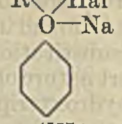
Alkylation of phenols. Introduction of diphenylmethyl. M. Busch and R. Knoll [with A. Leuze and A. Ruppert] (Ber., 1927, **60**, [*B*], 2243—2257; cf. Busch, Z. angew. Chem., 1925, **35**, 1145; Schorigin, A., 1927, 54).—Diphenylmethyl bromide and phenol in the presence or absence of solvent yield *p*-hydroxytriphenylmethane, whereas sodium phenoxide affords the corresponding *ortho*-compound. Benzhydryl aryl ethers are obtained by means of diphenyldiazomethane. Schorigin's observation that benzhydryl phenyl ether is formed by the action of diphenylmethyl bromide on sodium phenoxide dissolved in an excess of phenol (*p*-hydroxytriphenylmethane is also produced in almost equal yield) is explained by Claisen's generalisation that alkylation of phenols in dissociating media yields mainly ethers, whereas *C*-alkylation takes place in non-dissociating media. Nuclear alkylation is observed with a large number of phenols and their sodium compounds, whereas only the strongly acidic nitrophenols afford ethers. The presence of negative groups in the phenolic nucleus facilitates the entry of benzhydryl groups. If the *p*- and both *o*-positions are occupied, *C*-alkylation is rendered difficult, but the slight tendency towards *O*-alkylation is established by the observation that reaction occurs at most to a very limited extent and the effect cannot be attributed to steric hindrance. Reaction occurs with the formation of intermediate products some of which have been isolated, substances of the types I, II, and III being postulated in the alkylation of phenols (I), phenoxides (II), and phenoxides in dissociating media (II and III). The action of phenols on diphenyldiazomethane appears to afford a certain method for the preparation of ethers accompanied by only minute proportions of phenols (contrast Schorigin, *loc. cit.*); tetraphenylketazine is invariably produced also. Introduction of negative groups into the phenolic nucleus facilitates the production of *O*-compounds, the yields of which reach 95% under favourable conditions. Accumulation of alkyl groups hinders the reaction. Dihydric phenols do not yield ethers, but appear to accelerate the formation of ketazine, which may become almost explosive. Polyhydric phenols appear to behave in the tautomeric ketonic form.

(I.)





(II.)



(III.)

The following compounds are described: *p*-hydroxytriphenylmethane, m. p. 112° (also $+C_6H_6$, m. p. 81—82°); 2-*hydroxy*-5-*diphenylmethylazobenzene*, m. p. 148; 4-*nitro*-2′-*hydroxy*-5′-*diphenylmethylazobenzene*, m. p. 188—189°; *o*-hydroxytriphenylmethane, m. p. 125° (also $+C_6H_6$, m. p. 77·5°, and +EtOH, m. p. 76—80°); phenyl benzhydryl ether, m. p. 55°; 3-3-*benzhydryl*-p-*cresol*, m. p. 135°; 2-*hydroxy*-5-*methyl*-3-*diphenylmethylazobenzene*, m. p. 155°; 4-*nitro*-2′-*hydroxy*-5′-*methyl*-3′-*diphenylmethylazobenzene*, m. p. 252°; 3 : 5-*dibenzhydryl*-p-*cresol*, m. p. 190°, which does not couple with diazonium salts; 4-*nitro*-2 : 6-*dibenzhydrylphenol*, m. p. 256°; p-*nitrophenyl benzhydryl ether*, m. p. 156°; o-*nitrophenyl benzhydryl ether*, m. p. 107°; 4-*hydroxy*-3 : 5-*dibenzhydrylbenzaldehyde*, m. p. 230° [also $+C_6H_6$, m. p. (indef.) 200—205°], and the additive *compounds*, $C_{20}H_{16}O_2,CHPh_2Br$, m. p. 140° (decomp.); and $C_{20}H_{16}O_2,CHPh_2Cl$, m. p. (indef.) 180° (decomp.) after softening at 165°; unstable *phenylhydrazone* and p-*bromophenylhydrazone*, m. p. 184° (decomp.), of 4-hydroxy-3 : 5-dibenzhydrylbenzaldehyde; phenyl triphenylmethyl ether, m. p. 103°; *p*-hydroxytetraphenylmethane, m. p. 282°; p-*tolyl benzhydryl ether*, m. p. 77·5°, and the corresponding non-crystalline m-*tolyl* and o-*tolyl* compounds; 6-*chloro*-m-*tolyl benzhydryl ether*, m. p. 73°; 4 : 6-*dichloro*-m-*tolyl benzhydryl ether*, m. p. 106°; 3 : 4-*dimethylphenyl benzhydryl ether*, m. p. 87°, and the corresponding, non-crystalline compounds from *p*- and *m*-xylenol; 2 : 5-*dimethyl*-4-*benzhydrylphenyl benzhydryl ether*, m. p. 135°; m-*nitrophenyl benzhydryl ether*, m. p. 115°; *guaiacyl benzhydryl ether*, m. p. 86°; *thymyl benzhydryl ether*, m. p. 87°; β-*naphthyl benzhydryl ether*, m. p. 106°, and the non-crystalline α-*naphthyl benzhydryl ether*. H. Wren.

Direct introduction of substituents in aromatic mercaptans. T. van Hove (Bull. Soc. chim. Belg., 1927, **36**, 548—558).—See A., 1927, 555.

Measurement of the basicity of carbinols. K. Ziegler and E. Boye (Annalen, 1927, **458**, 229—247).—Previous measurements by the "titration method" (cf. Baeyer and Villiger, A., 1902, i, 769) have frequently been vitiated by (*a*) the difficulty of accurately observing the end-point, (*b*) the occurrence of "pseudo-halochromy," (*c*) differences in absolute colour-intensity of carbonium ions. Thus, under comparable conditions, the dilutions at which the colours of tri-*p*-diphenylyl-, phenyldi-*p*-diphenylyl-, and triphenyl-carbinol in acetic acid containing 5% of sulphuric acid become just imperceptible are in the ratio 100 : 10 : 1. "Pseudo-halochromy" is due to the presence of impurities which also yield coloured products with acids. For example, the titration basicity of diphenyl-α-naphthylcarbinol is approximately 1, the value 8·83 obtained by Skraup and Freundlich (A., 1922, i, 539) being due to the persistence of a yellow coloration after the disappearance of the true greenish-red halochromy. A rough measure of the basicity of a carbinol is afforded by the ease with which it is precipitated as perchlorate by adding a solution of perchloric acid in acetic anhydride to its ethereal solution. In this way it is shown that *p*-nitrotriphenylcarbinol is much less basic than triphenylcarbinol, the value 17·74 previously obtained (A., 1923, i, 667) being again due to pseudohalochromy. The concentration (*c*) of carbonium salt in solutions of carbinols in acetic acid containing 5% of sulphuric acid and 0—12% of water has been determined colorimetrically by a method similar to that of Lund (A., 1927, 661). Under these conditions the carbinol–carbonium salt equilibrium does not obey the simple dilution law, but the relative order of basicity of the carbinols is correctly given by the order of the " basicity curves " obtained by plotting *c* against the concentration of water. The following increasingly basic series of carbinols differs considerably from that obtained by the titration method: triphenyl-, diphenyldiphenylyl-, phenylbisdiphenylyl-, diphenyl-*p*-tolyl-, trisdiphenylyl-, diphenyl-*p*-anisyl-, phenyldi-*p*-anisyl-, tri-*p*-tolyl-, tri-*p*-anisyl-. The method is not applicable to very weakly basic carbinols, nor to those which form mono- and di-acid salts of different colours. In discussing the results it is pointed out (cf. Brand, A., 1925, i, 397) that Baeyer's law of powers (*loc. cit.*) is not applicable to phenylated triphenylcarbinols and that no simple relation exists between the basicity of a carbinol and either (*a*) the ability to ionise of the corresponding triarylmethyl chloride (cf. A., 1910, i, 236; 1922, i, 148), or (*b*) the tendency to association of the corresponding triarylmethyl. Determinations of the relative valency-demands of aryl radicals by the carbinol method (Skraup and Freundlich, *loc. cit.*) are, therefore, of no value. H. E. F. Notton.

Formation of triphenylmethyl peroxide from carbon dioxide and magnesium phenyl bromide. F. F. Blicke (J. Amer. Chem. Soc., 1927, **49**, 2843—2849).—When carbon dioxide is passed through a warm ethereal solution of magnesium phenyl bromide, the solution becomes deep orange. The colour is partly discharged by shaking the solution with air, and at the same time triphenylmethyl peroxide is precipitated, thus indicating the formation of triphenylmethyl in the Grignard solution (cf. Meyer and Tögel, A., 1906, i, 757). Improved methods for the preparation of α-bromonaphthalene, α-naphthoic acid, di-α-naphthyl ketone, and di-α-naphthylcarbinol are described. F. G. Willson.

" Tervalent " carbon. VI. *pp′p″*-Trinitrotriphenylmethyl. K. Ziegler and E. Boye (Annalen, 1927, **458**, 248—256).—The crystalline *aci*-sodium salt of *pp′p″*-trinitrotriphenylmethane (cf. Hantzsch and Hein, A., 1919, ii, 254) is less reactive than sodiotriphenylmethane, and is stable in absence of oxygen. With excess of bromine it gives pp′p″-*trinitrotriphenylmethyl bromide*, decomp. 191°, which reacts in pyridine with the above sodium salt, forming green pp′p″-*trinitrotriphenylmethyl* (cf. Gomberg, A., 1904, i, 489). This cannot be an *aci*-ester of trinitrotriphenylmethane, since the above sodium salt does not yield similar compounds with simple alkyl and aralkyl halides, whilst with triphenylmethyl bromide it gives a mixture of triphenylmethyl and the new radical. The latter is also formed together with metallic silver from the sodium salt and silver nitrate in pyridine. It combines slowly with bromine and affords a second example (cf. A., 1926, 57) of a radical which shows very little tendency to associate, being derived from a weakly basic carbinol. H. E. F. Notton.

Tolyl ethers and their reactions with metallic sodium. P. Schorigin (Ber., 1927, **60**, [*B*], 2369—2372; cf. A., 1927, 54).—p-*Tolyl triphenylmethyl ether*, m. p. 114°, prepared by the action of triphenylmethyl chloride on sodium *p*-tolyloxide, is decomposed by sodium in the presence of toluene at 100° into triphenylmethane and *p*-cresol. Similarly, m-*tolyl triphenylmethyl ether*, m. p. 101°, gives triphenylmethane and *m*-cresol. Phenolic transformation is not observed in either case. Phenyl allyl ether, b. p. 93—94°/26 mm., d_4^{15} 0·9832, and *o*-tolyl allyl ether, b. p. 104°/26 mm., d_4^{15} 0·9698, are decomposed by sodium with production of phenol and *o*-cresol, respectively. The compound described by van Alphen as *p*-tolyl triphenylmethyl ether is identified as triphenylmethyl ethyl ether, m. p. 82°. H. Wren.

Action of triphenylcarbinol on cresols. P. Schorigin (Ber., 1927, **60**, [*B*], 2373—2378).—Triphenylcarbinol is converted by *o*-cresol in the presence of glacial acetic and concentrated sulphuric acids at the atmospheric temperature into ααα-triphenyl-β-*o*-hydroxyphenylethane, m. p. 186°, in about 34% yield. Similarly, *m*-cresol gives 2-*hydroxy*-4-*methyltetraphenylmethane*, m. p. 213—214°, obtained also from triphenylmethyl chloride and sodium *m*-tolyloxide in xylene. Unexpectedly, *p*-cresol and triphenylcarbinol under like conditions give triphenylmethane in almost theoretical yield. Reaction does not occur in the absence of sulphuric acid and triphenylcarbinol does not yield triphenylmethane under the influence of sulphuric and acetic acids; the presence of *as*-*o*-xylenol but not of quinol causes production of triphenylmethane. At 100°, reaction occurs in the same manner as at the ordinary temperature. If the carbinol and cresol are used in the molecular proportion 1 : 0·5, a poorer yield of triphenylmethane is obtained. It appears therefore justifiable to assume that *p*-cresol acts as oxygen acceptor (ratio 1 : 1) in the reduction of triphenylcarbinol; it is probably converted into polymerised *p*-benzoquinonemethide. Triphenylcarbinol in the absence of *p*-cresol is converted by glacial acetic and sulphuric acids at 100° into triphenylmethane to a small extent, but mainly converted into products of higher m. p. which have not been closely examined. Triphenylmethyl chloride and sodium *p*-tolyloxide give ααα-*triphenyl*-β-p-*hydroxyphenylethane*, m. p. 182°. H. Wren.

Quinonoid and quinolide structure. A. Récsei (Ber., 1927, **60**, [*B*], 2378—2388).—The similarity of the absorption spectra of *p*-benzoquinonediethylsulphone, $O{:}C_6H_4(SO_2Et)_2$ (cf. A., 1927, 1079), and the salts of triphenylmethane and azobenzene establishes the quinolide structure for the latter substances. The absorption curves of quinonoid and quinolide compounds differ from one another in that the latter is displaced more towards the region of greater wave-length. In consequence of the greater absorption of quinolide compounds the first half period is deeper than that of the quinonoids. The quinolide curve slopes more steeply than the quinonoid, which resembles more closely the sine curve. The second, steeply rising period of the quinolide compounds always reaches a greater height than that of quinonoids. The differences may be regarded as characteristic of the curves of the two classes. Quinonoid compounds are usually yellow or colourless and auxochromes have not a bathochromic action. Quinolides, in the absence of auxochromes, are yellow or brown, whilst auxochromes have a strongly bathochromic effect. Transitions are observed between the quinonoid and quinolide structures. Thus dimethylaminofuchsone exhibits colours and absorption spectra differing with the solvent which can be arranged in a continuous series. Such a transition cannot be represented by fixed formulæ. H. Wren.

Colour and constitution. W. Dilthey (Helv. Chim. Acta, 1927, 10, 866–868).—Polemical against Kehrmann (A., 1927, 1184). H. Burton.

Purification of abietic acid from rosin, and preparation of some of its derivatives. C. C. Kesler, A. Lowy, and W. F. Faragher (J. Amer. Chem. Soc., 1927, 49, 2898—2903).—Pure abietic acid is obtained in 80% yield from "G" grade rosin (91% abietic acid) by the following procedure: the rosin is first isomerised, either by passing a current of dry hydrogen chloride through the molten material for 20 min., or by boiling the rosin with 3 parts of alcohol containing 1% of hydrogen chloride for 15 min. Aqueous or alcoholic sodium hydroxide is then added in amount sufficient to neutralise the hydrochloric acid and to neutralise also one fourth of the abietic acid present, when the *acid sodium* salt, $C_{19}H_{29}\cdot CO_2Na,3C_{20}H_{30}O_2$, m. p. 177°, separates in crystalline form, the resene being removed with filtrate and washings. Acidification of this salt with the calculated amount of mineral or acetic acid affords abietic acid, m. p. 166°. Treatment of (neutral) sodium abietate with ethyl sulphate at 100° affords *ethyl abietate*, b. p. 204—207°/4 mm., d_4^{15} 1·032, n 1·5265. The following esters were prepared similarly from the sodium salt and the appropriate alkyl *p*-toluenesulphonates: n-*propyl*, b. p. 237—240°/4 mm., d 1·015, n 1·5229; iso*propyl*, b. p. 214—217°/4 mm., d_4^{15} 1·010, n 1·5200; n-*butyl*, b. p. 247—250°/3 mm., d_4^{15} 1·014, n 1·5192; iso*butyl*, b. p. 222—225°/4 mm., d_4^{15} 1·008, n 1·5171; iso*amyl*, b. p. 254—257°/4 mm., d_4^{15} 1·001, n 5165; *allyl*, b. p. 282—285°/5 mm., d_4^{15} 1·024, n 1·5242; and *menthyl*, m. p. 77—83°. The following esters were obtained by treating equimolecular mixtures of dry, powdered sodium abietate and the sodium salt of the appropriate hydroxylic derivative with carbonyl chloride at the ordinary temperature: *phenyl*, b. p. 330—333°/4 mm., d_4^{15} 1·056, n 1·5354; cyclo*hexyl*, b. p. 299—302°/4 mm., d_4^{15} 1·061, n 1·535; m-*tolyl*, b. p. 310—313°/5 mm., d_4^{15} 1·039; *α-naphthyl*, b. p. 290°/2 mm. (decomp.), d_4^{15} 1·116; *terpineol*, b. p. 310°/2 mm. (decomp.), d_4^{15} 1·082, and *bornyl abietate*, m. p. 75—80°. *Benzyl abietate*, b. p. 294—297°/4 mm., d_4^{15} 1·036, n 1·551, is obtained by adding aqueous 40% sodium hydroxide (25 c.c.) and then water (25 c.c.) to abietic acid and benzyl chloride (0·25 mol. each) in carbon tetrachloride, and refluxing for 3 hrs. *Cholesteryl abietate*, m. p. 122—125°, is obtained by heating equivalents of cholesterol and abietic acid at 200° for 2 hrs. in presence of zinc, with subsequent dissolution in benzene, washing, and removal of solvent. *Cetyl abietate*, m. p. 42°, was prepared by heating cetyl iodide with sodium abietate at 150° for 6 hrs. Certain of the above esters can be used as plasticisers in cellulose nitrate lacquers. F. G. Willson.

Bile acids. L. Ruzicka and E. A. Rudolph (Helv. Chim. Acta, 1927, 10, 920—925).—Distillation of barium choloidanate with soda-lime at 300°/12 mm. gives a mixture of unsaturated hydrocarbons, b. p. 100°/720 mm. to 150—160°/1 mm. The fraction of b. p. 170—180°/720 mm., d_4^{20} 0·8792, n_D^{20} 1·4968, contains a *hydrocarbon*, probably $C_{11}H_{16}$, having either two or three double linkings. The fraction of b. p. 125—135°/12 mm., d_4^{21} 0·9441, n_D^{21} 1·5373, contains a dicyclic *hydrocarbon*, $C_{15}H_{20}$, having four double linkings, whilst the fraction of b p. 170—180°/12 mm., d_4^{22} 0·9707, n_D^{22} 1·5558, contains a dicyclic *hydrocarbon*, $C_{19}H_{26}$, having four or five double linkings. The results do not yield information as to the structure of the bile acids. H. Burton.

Calculation of general, alternating, and *ortho*-effects of substituents. C. F. van Duin (Rec. trav. chim., 1927, 46, 770—774).—Theoretical. A reply to Berger (A., 1927, 873). It is pointed out that in comparing the observed effect of the introduction of a *m*-methyl group into the benzoic acid molecule on the dissociation constant with the entry of that group into the hexahydrobenzoic acid molecule, the ratio of the differences from unity of each individual dissociation constant ratio should be taken and not, as Berger has done, the ratios themselves. When calculated thus a figure 3·75 [calculated from Højendahl's theory (A., 1924, ii, 122), 3·3] is obtained. G. A. C. Gough.

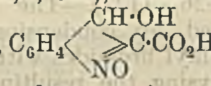
Calculation of general, alternating, and *ortho*-effects of substituents. G. Berger (Rec. trav. chim., 1927, 46, 855—857).—The assumption of van Duin that the general effect is entirely due to a direct influence of the substituents on the key-atom leads to the prediction that chlorine substitution in the δ-position of *n*-valeric acid should have a greater effect than substitution in the β- or the γ-position (owing to the stereo-proximity of the carboxyl group). Examination of the recorded data on dissociation constants, however, shows that δ-substitution actually has less effect. Unpublished data are quoted showing that the velocities of the reactions of the three toluoyl chlorides at 25° with an excess of *n*-butyl alcohol, with excess of benzyl alcohol, and with an equimolecular amount of benzyl alcohol in benzene are in the orders *o*->*m*->*p*-; *o*->*p*->*m*-; *o*->*m*->*p*-, respectively. The assumption of the additive nature of the effects gives a negative reaction velocity for the introduction of a *m*-nitro-group into some of the compounds studied by Olivier (A., 1923, i, 908). G. A. C. Gough.

Calculation of general, alternating, and *ortho*-effects of substituents. C. F. van Duin (Rec. trav. chim., 1927, **46**, 858—860).—In reply to Berger (preceding abstract) the work of Ruzicka and his co-workers (A., 1926, 727) is quoted to show that the ease of ring formation is not connected directly with the distance between the terminal carbon atoms and hence the application of this argument to substitution and dissociation constants is probably not justified. It is pointed out that neither the additive nor the multiplicative method of determining the total effect of substituents will predict the stability of *trans*-2 : 4-dimethoxycinnamic acid to bromine. G. A. C. Gough.

Reaction of *para*-substituted benzyl chlorides with sodium hydrogen sulphide. C. Barkenbus, E. B. Friedman, and R. K. Flege (J. Amer. Chem. Soc., 1927, **49**, 2549—2553).—Treatment of the sodium salt of 6-hydroxy-2-thio-4-methylpyrimidine with *p*-cyanobenzyl chloride in absolute alcohol affords 6-*hydroxy*-2-p-*cyanobenzylthiol*-4-*methylpyrimidine*, m. p. 240—241°, which on hydrolysis with hydrochloric acid yields p-*cyanobenzylmercaptan*, m. p. 37°, b. p. 135—138°/7 mm. Treatment of the sodium salt of the latter with *p*-cyanobenzyl chloride in absolute alcohol affords p-*cyanobenzyl sulphide*, m. p. 115°, whilst p-*cyanobenzyl disulphide*, yellow, m. p. 148°, is obtained by atmospheric oxidation of the mercaptan in aqueous-alcoholic ammonia. Treatment of *p*-cyanobenzyl chloride with alcoholic sodium hydrogen sulphide in a current of hydrogen sulphide affords *p*-cyanobenzyl sulphide (78·2%) and *p*-cyanobenzylmercaptan (10·2%). If the reaction is carried out with access of air, the sulphide and disulphide are the sole products. Treatment of ethyl ω-chlorotoluate with alcoholic sodium hydrogen sulphide affords *ethyl benzylmercaptan*-p-*carboxylate*, b. p. 140—141°/6 mm., together with the corresponding *sulphide*, m. p. 78°. The latter was also prepared from ethyl ω-chlorotoluate and alcoholic sodium sulphide. Hydrolysis of *p*-cyanobenzylmercaptan with hydrochloric acid yields *benzylmercaptan*-p-*carboxylic acid*, m. p. 176°. F. G. Willson.

Derivatives of δ-benzamidovaleric acid, and the synthesis of putrescine. S. J. Kanevskaia (J. Russ. Phys. Chem. Soc., 1927, **59**, 639—647).—Benzoylputrescine was synthesised by Hofmann's method from δ-benzamidovaleramide. The free acid and thionyl chloride gave δ-*benzamidovaleryl chloride*, an oil which decomposed on distillation in a vacuum. Reduction by Rosenmund's method (hydrogen in presence of palladium catalyst) gave, instead of the expected aldehyde, *N*-benzoylpiperidone, m. p. 112°. The same reaction takes place in a boiling inert solvent by the elimination of hydrochloric acid. The chloride gives an *anilide*, m. p. 170—171°, and an *amide*, m. p. 180—181°, which by the action of bromine and alkali yields *benzoylputrescine*, an oil which decomposes on distillation in a vacuum and forms a *hydrochloride*, m. p. 169—170°. By means of the Schotten–Baumann reaction, a characteristic *dibenzoyl* compound, m. p. 175—176°, is obtained, whilst prolonged boiling with concentrated hydrochloric acid gives putrescine hydrochloride. M. Zvegintzov.

Synthesis of benzoylcadaverine. S. J. Kanevskaia (J. Russ. Phys. Chem. Soc., 1927, **59**, 649—652; cf. preceding abstract).—Benzamidohexoamide, m. p. 140—141°, obtained by Gabriel's method from benzoylpiperidine *via* benzoylchloroamylamine by the action of phosphorus pentachloride, was treated with bromine in an excess of potassium hydroxide. *Benzoylcadaverine*, a strongly basic oil, which decomposed on distillation in a vacuum, was obtained. When treated with an alcoholic solution of hydrochloric acid it gave the *hydrochloride*, m. p. 159—160°, and on benzoylation, *dibenzoylcadaverine*, m. p. 135—135·5°. M. Zvegintzov.

Synthesis of *o*-nitrocinnamic acid and its photochemical behaviour. I. Tanasescu (Bull. Soc. chim., 1927, [iv], **41**, 1074—1077).—Thin layers of finely-powdered *o*-nitrocinnamic acid (improved method of preparation given) are exposed to sunlight, when a red substance, m. p. 120°, is produced (cf. Friedländer and Ostermayer, A., 1882, 201; Sachs and Hilpert, A., 1904, i, 876), which is probably hydroxyisatogenic acid,  $C_6H_4\left\langle\begin{matrix}CH\cdot OH\\NO\end{matrix}\right\rangle C\cdot CO_2H$. Prolonged exposure to sunlight does not increase the amount of coloured substance. H. Burton.

The two *o*-cyanocinnamic acids. W. Davies and H. G. Poole (J.C.S., 1927, 2661—2663).—Both *o*-cyanocinnamic acid, m. p. 256°, obtained in 36% yield by heating the sodium salt of 1-nitroso-β-naphthol in nitrobenzene, and *o*-cyano*allo*cinnamic acid, m. p. 137°, give on hydrolysis the same *o*-carboxycinnamic acid, m. p. 184°; which does not form a normal anhydride. Acetophenone-*o*-carboxylic acid (*oxime*, m. p. 156—157°; p-*nitrophenylhydrazone*, m. p. 211°; *phenylhydrazone*) was obtained as a by-product during a large-scale preparation of *o*-cyano*allo*cinnamic acid from nitroso-β-naphthol. The *allo*-acid, which is partly converted into its isomeride, m. p. 256°, on distillation, furnishes o-*cyano*allo-*cinnamoyl chloride*, m. p. 50°. S. Coffey.

Action of acetic anhydride and acetone in presence of pyridine on tyrosine and on phenylglycine. P. A. Levene and R. E. Steiger (J. Biol. Chem., 1927, **74**, 689—693).—Attempted acetylation of tyrosine with commercial acetic anhydride and pyridine gave a *substance*, $C_{14}H_{17}O_4N$, m. p. 122—123°, which, when boiled with dilute sodium hydroxide, lost an acetyl group to give a *compound*, $C_{12}H_{15}O_3N$, m. p. 163—166°; the compound $C_{14}H_{17}O_4N$ was formed more readily on addition of acetone to the reaction mixture, and is regarded as a condensation product of acetyltyrosine with acetone. Similar treatment of phenylglycine yielded carbon dioxide and a *substance*, $C_{11}H_{13}O_2N$, m. p. 100—101°. C. R. Harington.

Δ^2-*cyclo*Pentenylalkylacetic acids and their action towards *B. lepræ*. IX. J. A. Arvin and R. Adams (J. Amer. Chem. Soc., 1927, **49**, 2940—2942; cf. following abstract).—The following disubstituted malonic esters and acetic acids were prepared by methods analogous to those previously described (*loc. cit.*): *Ethyl* Δ^2-cyclo*pentenyl-alkylmalonates*: -n-*amyl*-, b. p. 133—136°/3 mm., d_4^{20}

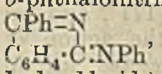
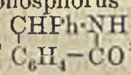
0·9981, n_D^{20} 1·4580; -n-*hexyl-*, b. p. 150—155°/4 mm., d_4^{20} 0·9867, n_D^{20} 1·4572; -n-*heptyl,-* b. p. 159—164°/3 mm., d_4^{20} 0·9791, n_D^{20} 1·4582; -n-*octyl-*, b. p. 169—174°/4 mm., d_4^{20} 0·9765, n_D^{20} 1·4591; and -n-*nonyl-*, b. p. 183—187°/5 mm., d_4^{20} 0·9756, n_D^{20} 1·4595. Δ^2-cyclo*Pentenyl-alkyl-acetic acids*: -n-*amyl-*, b. p. 142—145°/5 mm., d_4^{20} 0·9629, n_D^{20} 1·4659; -n-*hexyl-*, b. p. 150—155°/5 mm., d_4^{20} 0·9573, n_D^{20} 1·4671; -n-*heptyl-*, b. p. 162—165°/4 mm., d_4^{20} 0·9499, n_D^{20} 1·4683; -n-*octyl-*, b. p. 170—173°/4 mm., d_4^{20} 0·9452, n_D^{20} 1·4687; and -n-*nonyl-*, b. p. 173—176°/3 mm., d_4^{20} 0·9436, n_D^{20} 1·4690 (cf. Perkins and Cruz, A., 1927, 359). Amongst the substituted acetic acids, the bactericidal effect increases with increasing mol. wt., and the sodium salt of the nonyl derivative is fatal to *B. lepræ* at a dilution of 1 : 150,000.

F. G. Willson.

ω-*cyclo*Hexylalkylalkylacetic acids and their action towards *B. lepræ*. VIII. R. Adams, W. M. Stanley, S. G. Ford, and W. R. Peterson (J. Amer. Chem. Soc., 1927, **49**, 2934—2940; cf. A., 1926, 1137).—The following compounds were prepared by condensing the appropriate ω-*cyclo*hexylalkyl bromides with ethyl sodioalkylmalonates, hydrolysing the resulting substituted ethyl malonates, and eliminating carbon dioxide in the usual manner: *Ethyl* β-cyclo*hexylethyl-alkyl-malonates*: -*ethyl-*, b. p. 146—148°/2 mm., d_4^{25} 0·9907, n_D^{25} 1·4502; -n-*propyl-*, b. p. 153—156°/6 mm., d_4^{25} 0·9813, n_D^{25} 1·4518; -n-*butyl-*, b. p. 144—147°/4 mm., d_4^{25} 0·9714, n_D^{25} 1·4531; -n-*amyl-*, b. p. 174—176°/5 mm., d_4^{25} 0·9644, n_D^{25} 1·4537; -n-*hexyl-*, b. p. 188—191°/5 mm., d_4^{25} 0·9569, n_D^{25} 1·4539; -n-*heptyl-*, b. p. 171—173°/3 mm., d_4^{25} 0·9527, n_D^{25} 1·4545; -n-*octyl-*, b. p. 213—216°/7 mm., d_4^{25} 0·9449, n_D^{25} 1·4550; and -*allyl-*, b. p. 142—145°/2 mm., d_4^{25} 0·9915, n_D^{25} 1·4563. *Ethyl* γ-cyclo*hexylpropyl-alkyl-malonates*: -*ethyl-*, b. p. 149—151°/4 mm., d_4^{25} 0·9797, n_D^{25} 1·4528; -n-*propyl-*, b. p. 155—156°/4 mm., d_4^{25} 0·9743, n_D^{25} 1·4531; -n-*butyl-*, b. p. 160—161°/4 mm., d_4^{25} 0·9620, n_D^{25} 1·4534; -n-*amyl-*, b. p. 178—180°/4 mm., d_4^{25} 0·9603, n_D^{25} 1·4549; -n-*hexyl-*, b. p. 180—191°/4 mm., d_4^{25} 0·9501, n_D^{25} 1·4551; -n-*heptyl-*, b. p. 209—210°/5 mm., d_4^{25} 0·9471, n_D^{25} 1·4554, and -*allyl-*, b. p. 170—172°/5 mm., d_4^{25} 0·9837, n_D^{25} 1·4569. *Ethyl* δ-cyclo*hexylbutyl-alkyl-malonates*: -*ethyl-*, b. p. 165—167°/4 mm., d_4^{25} 0·9704, n_D^{25} 1·4536; -n-*propyl-*, b. p. 173—175°/4 mm., d_4^{25} 0·9695, n_D^{25} 1·4538; -n-*butyl-*, b. p. 175—177°/4 mm., d_4^{25} 0·9563, n_D^{25} 1·4546; -n-*amyl-*, b. p. 191—193°/5 mm., d_4^{25} 0·9530, n_D^{25} 1·4559; -n-*hexyl-*, b. p. 194—196°/4 mm., d_4^{25} 0·9514, n_D^{25} 1·4572; and -*allyl-*, b. p. 168—170°/4 mm., d_4^{25} 0·9742, n_D^{25} 1·4565. β-cyclo*Hexylethyl-alkyl-malonic acids*: -*ethyl-*, m. p. 114—115°; -n-*propyl-*, m. p. 132—133°; -n-*butyl-*, m. p. 135—136°; -n-*amyl-*, m. p. 125—126°; -n-*octyl-*, m. p. 108—109°; and -*allyl-*, m. p. 95—96°. γ-cyclo*Hexylpropyl-alkyl-malonic acids*: -*ethyl-*, m. p. 143°; -n-*propyl-*, m. p. 130°; -n-*butyl-*, m. p. 138°; -n-*amyl-*, m. p. 148°; -n-*hexyl-*, m. p. 134°; and -n-*heptyl-*, m. p. 99°. δ-cyclo*Hexylbutyl-alkyl-malonic acids*: -*ethyl-*, m. p. 136°; -n-*propyl-*, m. p. 140°; -n-*butyl-*, m. p. 113°; -n-*amyl-*, m. p. 64°; and -*allyl-*, m. p. 143°. β-cyclo*Hexylethyl-alkyl-acetic acids*: -*ethyl-*, b. p. 121—124°/3 mm., d_4^{25} 0·9619, n_D^{25} 1·4613; -n-*propyl-*, b. p. 122—125°/2 mm., d_4^{25} 0·9486, n_D^{25} 1·4623; -n-*butyl-*, b. p. 139—142°/4 mm., d_4^{25} 0·9410, n_D^{25} 1·4624; -n-*amyl-*, b. p. 182—185°/5 mm., d_4^{25} 0·9350, n_D^{25} 1·4626; -n-*hexyl-*, b. p. 174—177°/2 mm., d_4^{25} 0·9283, n_D^{25} 1·4628; -n-*heptyl-*, b. p. 162—185°/2 mm., d_4^{25} 0·9222, n_D^{25} 1·4631; -n-*octyl-*, b. p. 193—196°/4 mm., d_4^{25} 0·9193, n_D^{25} 1·4640; and -*allyl-*, b. p. 125—128°/2 mm., d_4^{25} 0·9714, n_D^{25} 1·4672. γ-cyclo*Hexylpropyl-alkyl-acetic acids*: -*ethyl-*, b. p. 146—147°/2 mm., d_4^{25} 0·9509, n_D^{25} 1·4622; -n-*propyl-*, b. p. 148—150°/2 mm., d_4^{25} 0·9419, n_D^{25} 1·4627; -n-*butyl-*, b. p. 153—154°/2 mm., d_4^{25} 0·9317, n_D^{25} 1·4630; -n-*amyl-*, b. p. 188—192°/5 mm., d_4^{25} 0·9266, n_D^{25} 1·4634; -n-*hexyl-*, b. p. 208—211°/8 mm., d_4^{25} 0·9221, n_D^{25} 1·4638; -n-*heptyl-*, b. p. 199—203°/2 mm., d_4^{25} 0·9137, n_D^{25} 1·4642; and -*allyl-*, b. p. 147—150°/2 mm., d_4^{25} 0·9552, n_D^{25} 1·4708. δ-cyclo*Hexylbutyl-alkyl-acetic acids*: -*ethyl-*, b. p. 173—175°/3 mm., d_4^{25} 0·9447, n_D^{25} 1·4622; -n-*propyl-*, b. p. 156—158°/1 mm., d_4^{25} 0·9408, n_D^{25} 1·4627; -n-*butyl-*, b. p. 178—180°/4 mm., d_4^{25} 0·9300, n_D^{25} 1·4631; -n-*amyl-*, b. p. 207—209°/8 mm., d_4^{25} 0·9254, n_D^{25} 1·4633; -n-*hexyl-*, b. p. 187—189°/1 mm., d_4^{25} 0·9191, n_D^{25} 1·4638; and -*allyl-*, b. p. 174—176°/6 mm., d_4^{25} 0·9531, n_D^{25} 1·4687. Amongst the above substituted acetic acids, increase in mol. wt. is accompanied by increasing toxicity to acid-fast bacteria, sodium salts of the acids of highest mol. wt. being much more effective against *B. lepræ* than those of chaulmoogric or hydnocarpic acids, or of any of the mixed acids from natural oils containing these.

F. G. Willson.

Complex salts of *o*-dinitriles with copper and pyridine. H. De Diesbach and E. von der Weid (Helv. Chim. Acta, 1927, **10**, 886—888).—*o*-Dibromobenzene when heated with a mixture of cuprous cyanide and pyridine for 8 hrs. at 200° in a sealed tube yields a small amount of phthalimide and a blue *compound*, $[C_6H_4(CN)_2,C_5H_5N]_2Cu$, also formed by the action of cuprous bromide and pyridine on *o*-phthalonitrile. From 4 : 5-dibromo-*o*-xylene are obtained similarly a blue *compound*, $[C_6H_2Me_2(CN)_2,C_5H_5N]_2Cu$, together with 4 : 5-*dimethylphthalimide*, m. p. 240—241°, hydrolysed by potassium hydroxide solution to 4 : 5-dimethylphthalic acid, m. p. 201° (cf. Korczynski, A., 1902, i, 274). 1 : 2-Dibromonaphthalene furnishes a dark green *compound*, $[C_{10}H_6(CN)_2,C_5H_5N]_2Cu$ (10%), together with naphthalene-1 : 2-dicarboximide (65%). These complex compounds are unaffected by warm, concentrated sulphuric acid and by concentrated alkalis, but are decomposed by hot, moderately concentrated nitric acid. H. Burton.

Action of organo-magnesium compounds on *o*-phthalonitrile. II. R. Weiss and G. Schlesinger (Monatsh., 1927, **48**, 451—457; cf. A., 1925, i, 139).—The action of magnesium phenyl bromide on *o*-phthalonitrile yields *phenyl*iso*indoloneanil*,  $\begin{array}{l}CPh{=}N\\ C_6H_4{\cdot}C{:}NPh\end{array}$, m. p. 234—236° (*perchlorate*; unstable *hydrochloride*), *o*-benzoylbenzamide, and a *compound*, $C_{14}H_{16}N_2O_3$, m. p. 169° (decomp.). Hydrolysis and simultaneous reduction of the anil by heating with hydriodic acid and red phosphorus under reflux for 0·75 hr. yields the lactam,  $\begin{array}{l}CHPh{\cdot}NH\\ C_6H_4{-}CO\end{array}$, identical with a synthetic specimen prepared by the method of Rose (A., 1911, i, 372), the reduction occurring thus: $C_{20}H_{14}N_2+H_2O+H_2=C_{14}H_{11}ON+NH_2Ph$.

J. W. Baker.

Substituted diaryl ethers. II. Friedel–Crafts reaction applied to di-*p*-tolyl ether. J. Reilly and P. J. Drumm (J.C.S., 1927, 2814—2819).—2-o-*Carboxybenzoyldi*-p-*tolyl ether* (I), m. p. 155° (*silver* salt described), obtained by the condensation of phthalic anhydride and di-*p*-tolyl ether by the Friedel–Crafts method, yields di-*p*-tolyl ether and potassium phthalate on fusion with potassium hydroxide. The constitution is confirmed by the alternative preparation from *p*-bromotoluene and the dipotassium derivative of 2-hydroxy-5-methylbenzophenone-2′-carboxylic acid in the presence of copper powder and alcohol at 200°. The substance (I) does not combine with hydroxylamine hydrochloride and yields with difficulty the *phenylhydrazone*, m. p. 156°. When heated at 100° with concentrated sulphuric acid, or when boiled with benzene, phosphorus pentachloride, and aluminium chloride, it affords 2 : 7-dimethylfluoran, m. p. 254°. Since 2-*o*-carboxybenzoyldi-*p*-tolyl ether may also be prepared by condensation of *p*-cresol with 2-chloro-4-methylbenzophenone-2′-carboxylic acid, the last-named substance must have the constitution here assigned and not the 3-chloro-6-methyl constitution as indicated by Heller and Schülke (A., 1908, i, 994), who prepared it from *p*-chlorotoluene and phthalic anhydride.

2-*Benzoyldi*-p-*tolyl ether*, m. p. 185—186°, prepared from benzoyl chloride, di-*p*-tolyl ether, and aluminium chloride, is converted into 9-phenyl-2 : 7-dimethylxanthen by boiling with acetic acid or by heating with phenylhydrazine at 160°. 2-Hydroxy-5-methylbenzophenone, m. p. 84·5°, and 2-*p*-tolyl-5-methylacetophenone, m. p. 168°, are best prepared by the Friedel–Crafts reaction, using *s*-tetrachloroethane as the medium. G. A. C. Gough.

Dehydrogenation with sulphur and dehydrogenating disruption with manganese dioxide and sulphuric acid. L. Ruzicka and E. A. Rudolph (Helv. Chim. Acta, 1927, 10, 915—920).—Irone (Tiemann and Krüger, A., 1894, i, 81) when heated with sulphur at 180—250° yields 1 : 6-dimethylnaphthalene (10%) (*picrate*, m. p. 109°), a methyl group being eliminated during the dehydrogenation. Oxidation of 1 : 6-dimethylnaphthalene with alkaline potassium ferricyanide at 80° yields *naphthalene*-1 : 6-*dicarboxylic acid*, m. p. 305° (decomp.) after sintering at 290° (cf. A., 1927, 60). Tetrahydronaphthalene is dehydrogenated by heating with sulphur to naphthalene (70%). Oxidation of menthene with manganese dioxide and sulphuric acid (cf. A., 1924, i, 171), and conversion of the resulting acids into their methyl esters, gives methyl benzenepentacarboxylate, m. p. 147—148°, and methyl terephthalate, m. p. 140°. Similar oxidation of ethyl 2-methyl-5-*iso*propylphenylacetate yields trimellitic acid, m. p. 224—225°. H. Burton.

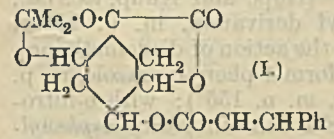
Stereochemistry of aromatic compounds. V. Racemisation of optically active diphenic acids. R. Kuhn and O. Albrecht (Annalen, 1927, 458, 221—229).—Contrary to the statement of Christie and Kenner (J.C.S., 1922, **121**, 614), it has not been found possible to racemise *d*-4 : 6 : 4′ : 6′-tetranitrodiphenic acid, m. p. 258—259°, sintering (decomp.) from 220°, $[\alpha]_D^{22}$ +100·7° in 2*N*-sodium hydroxide, prepared from the brucine salt, $[\alpha]_D^{20}$ +9° in 10·4*N*-acetic acid. The optical activity of the acid is not changed by heating it in xylene vapour at 125°, with aluminium chloride at 160—170°, or with 2*N*-sodium hydroxide at 100°. 4 : 6 : 4′-Trinitrodiphenic acid has been resolved through its brucine salt into a *l*-form, m. p. 281—282° (decomp.), $[\alpha]_D^{22}$ −37·8° in 2*N*-sodium hydroxide, and a *d*-form, m. p. 279—280°, $[\alpha]_D^{20}$ +33·3° (cf. J.C.S., 1923, **123**, 779). The velocities of racemisation of the *l*-acid at 74·6° and 98·6° in 2*N*-sodium hydroxide are lower than the corresponding values for *l*-4 : 6′-dinitrodiphenic acid (A., 1927, 876). The reaction is unimolecular and the heat of activation of the free anion calculated from the temperature coefficient, $(k_{t+10})/k_t=3{\cdot}4$, is 22,400 g.-cal./mol. These results further illustrate the stabilising effect of introducing 6-nitro-groups into optically active diphenic acids. H. E. F. Notton.

Manufacture of dinaphthyldicarboxylic acids. I. G. Farbenind. A.-G.—See B., 1927, 902.

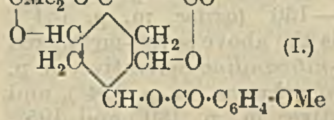
Synthesis of hydrastic acid. T. S. Stevens and M. C. Robertson (J.C.S., 1927, 2790—2792).—The lactone of 6-hydroxymethylhomopiperonylic acid (A., 1927, 265) condenses with benzaldehyde at 120° in the presence of piperidine to give α-(6-*hydroxymethylpiperonyl*)*cinnamolactone*, m. p. 190—192°, which on oxidation with potassium permanganate in acetone solution affords 4 : 5-methylenedioxyphthalide, m. p. 188—189° [6-*hydroxymethylpiperonylic acid*, m. p. 140—150° (indef.; solidifying and remelting as the lactone; *silver* salt described)]. Oxidation of the phthalide with alkaline potassium permanganate gives hydrastic acid, m. p. 228°.

G. A. C. Gough.

Monoacyl derivatives of quinic acid. K. Josephson (Ber., 1927, **60**, [*B*], 2270—2272).—The *iso*propylidene ether of quinic acid lactone (cf. Freudenberg, A., 1920, i, 322) is converted by cinnamoyl chloride in the presence of pyridine into *cinnamoyl*iso*propylidenequinide* (I), m. p. 189° (corr.), [α] +10·6° in chloroform. H. Wren.



Acyl derivatives of quinic acid. P. Karrer and K. P. Link (Helv. Chim. Acta, 1927, **10**, 794—799; cf. A., 1925, i, 673).—*iso*Propylidenequinide (cf. Fischer, A., 1921, i, 419) on anisoylation yields 4-*anisoyl*iso*propylidenequinide* (I), m. p. 126·5—127°, $[\alpha]_D^{18}$ −3·1° in acetone, which is hydrolysed by dilute sulphuric acid to 4-*anisoylquinide*, m. p. 155°, $[\alpha]_D^{18}$ −2·65° in acetone. This last compound when treated with sodium hydroxide solution yields 4-*anisoylquinic acid*, m. p. 193°, $[\alpha]_D^{18}$ +1·7° in acetone, which when treated with acetone containing 2% of hydrogen chloride regenerates



(I). 4-p-*Hydroxybenzoyl*iso*propylidenequinide*, m. p. 179—180°, is obtained by hydrolysis of its *acetyl* derivative, m. p. 165—166°. H. BURTON.

Reduction of acid chlorides under reduced pressure. Preparation of aldehydes. V. GRIGNARD and G. MINGASSON (Compt. rend., 1927, **185**, 1173—1176).—Working at 200—225°/140—400 mm., with platinum oxide as catalyst, benzoyl chloride (60%), phenylacetyl chloride (50%), and phenylpropionyl chloride (20%) were hydrogenated to the corresponding aldehydes with the yields indicated, without any formation of the by-products which occur under normal pressure. In the aliphatic series, also, reduction to the aldehyde only takes place, but the aldehydes were carried away with the hydrogen chloride evolved. Under reduced pressure at 300°, using nickel as a catalyst, 60% of benzaldehyde was obtained from benzoyl chloride, but poor results were obtained with aliphatic acid chlorides.

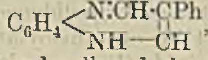
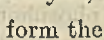
B. W. ANDERSON.

Constitution of *o*-nitrobenzaldehyde and the interference of nitro- and nitroso-groups on the Zerewitinoff method for the determination of active hydrogen. H. GILMAN and R. E. FOTHERGILL (J. Amer. Chem. Soc., 1927, **49**, 2815—2818).—Nitrobenzene, *s*-trinitrobenzene, nitrosobenzene, *o*- and *p*-nitrotoluenes, and *p*-nitrosodimethylaniline all evolve gas when treated with magnesium alkyl halides of low mol. wt., thereby indicating the presence of " active hydrogen " (cf. Zerewitinoff, B., 1926, 720). The evolution of gas under similar conditions from *o*-nitrobenzaldehyde does not therefore support the cyclic formula suggested for this substance by Tanasescu (A., 1926, 726).

F. G. WILLSON.

Hydroxymethylene-aldehydes. II. Condensations with hydroxymethylenephenylacetaldehyde. H. RUPE and A. HUBER (Helv. Chim. Acta, 1927, **10**, 846—858; cf. Rupe and Knup, A., 1927, 564).—Hydroxymethylenephenylacetaldehyde [*benzoyl* derivative, m. p. 72° (Rupe and Knup, *loc. cit.*, describe another benzoyl derivative, m. p. 115°); *methyl ether*, obtained by the action of diazomethane], reacts with hydrazine to form 4-phenylpyrazole, m. p. 230° (*silver* salt; *picrate*, m. p. 155°); with *o*-nitrophenylhydrazine, to yield 1-o-*nitrophenyl*-4-*phenylpyrazole*, m. p. 170°, and a *compound*,

$NO_2·C_6H_4·NH·N:CH·CPh:CH·NH·NH·C_6H_4·NO_2$,

m. p. 194°, formed by interaction with 2 mols. of the phenylhydrazine. The aldehyde condenses with *o*-phenylenediamine in alcohol solution to form the *compound*  $C_6H_4<\begin{matrix}N:CH·CPh\\ NH—CH\end{matrix}$, vermilion, m. p. 250° (dark blue and yellow *hydrochlorides*). With *o*-nitroaniline there is formed o-*nitroanilinomethylenephenylacetaldehyde*, m. p. 112—130° (*oxime*, m. p. 154°), which on reduction forms the above seven-membered ring compound. The m-*nitroanilino*-derivative, m. p. 152° and 165—166° (*semicarbazone*, m. p. 194°), and the p-*nitroanilino*-derivative, m. p. 180° and 195°, are described. When the *p*-nitroanilino-derivative is treated with ammoniacal silver nitrate solution, a dark blue *compound*, $C_{15}H_{14}O_3N_3Ag$, m. p. 154° (decomp.), is formed. To this is assigned the structure $[O·NO:C_6H_4:N·CH:CPh·CHO]AgNH_3$. *aci*-Quinonoid structures are allocated to the *o*- and *p*-nitroanilino-derivatives, since they give dark red colours with alcoholic potassium hydroxide. Reduction of the *p*-nitroanilino-compound with tin and acetic-hydrochloric acids furnishes p-*aminoanilinomethylenephenylacetaldehyde*, m. p. 95° [*hydrochloride*, m. p. 240° (decomp.)]. Methoxymethylenephenylacetaldehyde reacts with 2 mols. of aniline and *m*- and *p*-nitroanilines, yielding *anilinomethylenephenylacetaldehydeanil*, m. p. 137—139°, m-*nitroanilinomethylenephenylacetaldehyde*-m-*nitroanil*, m. p. 174°, and p-*nitroanilinomethylenephenylacetaldehyde*-p-*nitroanil*, m. p. 258—260°; with semicarbazide, to form 4-*phenylpyrazole*-2-*carboxylamide*, m. p. 166°, and with guanidine, to yield 2-*amino*-5-*phenylpyrimidine*, m. p. 162°. In all these reactions the methyl group is eliminated. Magnesium ethyl bromide reacts with the benzoyl derivative or the methyl ether of the hydroxy-aldehyde, eliminating benzoic acid or methyl alcohol, to form the *oxide*,  $\begin{matrix}CPh·CHEt\\ CH—O\end{matrix}$, b. p. 98—100°/11 mm.

H. BURTON.

Isomerisation of hydroxy-aldehydes. I. Transformation of diphenylglycollaldehyde into benzoin. S. DANILOV (Ber., 1927, **60**, [*B*], 2390—2401).—The transformation of diphenylglycollaldehyde into benzoin is due to the conversion of the hydroxy-aldehydic to the hydroxy-ketonic arrangement and to rearrangement of the skeleton with disappearance of tertiary carbon atoms. The second condition excludes change in the reverse direction. The transformation is effected by boiling an alcoholic solution of the hydroxy-aldehyde with a few drops of sulphuric acid; ethylbenzoin and possibly benzophenone are obtained as by-products. Isomerisation cannot be effected in pyridine even in the presence of mineral acid. Oxidation of diphenylglycollaldehyde by copper sulphate in the presence of potassium hydroxide affords considerable amounts of benzil, reaction occurring also in this direction when the alcoholic solution of the aldehyde is heated with mercuric chloride.

Hydrobenzoin is obtained in 70% yield by reduction of an alcoholic solution of benzaldehyde by zinc and hydrochloric acid under definite conditions; the glycol is transformed into diphenylacetaldehyde, b. p. 157·5°/7 mm., when heated with crystalline oxalic acid. Cautious bromination of the aldehyde dissolved in carbon disulphide affords the non-crystalline *bromodiphenylacetaldehyde*, converted by freshly-precipitated barium carbonate at 100° into *diphenylglycollaldehyde*, which appears to exist in a liquid form and a solid variety, m. p. (indef.) 162° (also $+C_6H_6$). The relationship of the two forms is not definitely established. Either variety is readily converted into *diphenylglycollaldoxime*, m. p. 124°, which is unimolecular in boiling benzene and *diphenylglycollaldehydesemicarbazone*, m. p. 243° (decomp.). Reduction of the aldehyde by magnesium *tert.*-butyl chloride affords *as*-diphenylethylene glycol, m. p. 122°. Oxidation with silver oxide converts it into benzophenone, whereas with permanganate in pyridine it yields benzilic acid. H. WREN.

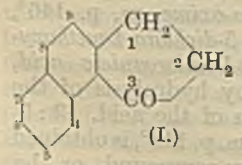
Constitution of the monomethyl ether of phloroglucylaldehyde. P. Karrer and A. Helfenstein (Helv. Chim. Acta, 1927, **10**, 789—794; cf. A., 1927, 564).—*p*-Toluenesulphonylation of phloroglucylaldehyde monomethyl ether (2 : 4-dihydroxy-6-methoxybenzaldehyde), m. p. 203° (Herzig and Wenzel, A., 1904, i, 251; 4-*benzoyl* derivative, m. p. 85°; *dibenzoyl* derivative, m. p. 131°), yields 2-*hydroxy*-4-p-*toluenesulphonyloxy*-6-*methoxybenzaldehyde*, m. p. 104°. Methylation of this compound yields 4-p-*toluenesulphonyloxy*-2 : 6-*dimethoxybenzaldehyde*, m. p. 137° after sintering at 118°, which is hydrolysed by alcoholic sodium hydroxide to 4-4-*hydroxy*-2 : 6-*dimethoxybenzaldehyde*, m. p. 224° after previous sintering. 6-p-*Toluenesulphonyloxy*-2 : 4-*dimethoxybenzaldehyde* has m. p. 144°. The dihydroxymethoxybenzaldehyde of m. p. 139° (A., 1927, 564) is 2 : 6-dihydroxy-4-methoxybenzaldehyde.

H. Burton.

Derivatives in the *cyclo*-octane series. M. Godchot and (Mlle.) Cauquil (Compt. rend., 1927, **185**, 1202—1203).—*cyclo*-Octanone when oxidised by chromic acid forms suberic acid. In ethereal solution the ketone is reduced by sodium in presence of a saturated solution of sodium hydrogen carbonate, yielding cyclo-*octanol*, m. p. 14—15°, b. p. 106—108°/22 mm., d^{17} 0·9663, n_D^{17} 1·4844 (*phenylurethane*, m. p. 62°), and a little "*azelaylpinacone*," $C_{16}H_{30}O_2$, m. p. 84—85°. By the dehydration of *cyclo*-octanol with boiling phthalic anhydride, *cyclo*-octene and a small quantity of a polymeride, $(C_8H_{14})_n$, are obtained. Magnesium methyl bromide reacts with *cyclo*-octanone, but the tertiary alcohol thus formed loses 1 mol. of water during distillation, giving Δ^1-*methyl*cyclo-*octene*, b. p. 158—160°, d^{15} 0·8515, n_D^{15} 1·4673 (*nitrosochloride*, m. p. 107—108°).

B. W. Anderson.

Synthesis of α-indanones. F. Mayer and P. Müller (Ber., 1927, **60**, [*B*], 2278—2283; cf. van Zütphen, Diss., Frankfurt, 1923).—1-Methylnaphthalene is converted by β-chloropropionyl chloride into 4-β-chloropropionyl-1-methylnaphthalene, transformed by concentrated sulphuric acid into 8-methyl-2-naphthindan-3-one (I). 1-Methylnaphthalene can be replaced by naphthalene or its 1-chloro-, 1-bromo-, or 2 : 6-dimethyl derivatives and β-chloropropionyl chloride by β-chloro-*n*-butyryl chloride. Ring closure could not be effected with the ketones from 1-methoxynaphthalene, acenaphthene, or tetrahydronaphthalene or from 4-chloroacetyl-1-methylnaphthalene. The presence of two substituents in the nucleus appears necessary for ring closure of benzenoid ketones prepared with β-chloropropionyl chloride, whereas those derived from β-chloro-*n*-butyryl chloride give unsaturated compounds in place of the expected indanones. The course of the change therefore consists in initial loss of hydrogen chloride exclusively in the side-chain followed by transformation of the unsaturated ketone into the indanone. This view is supported by the direct production of indanones from crotonyl chloride and hydrocarbons and the inability of α-ketones from chloroacetyl chloride and naphthalene derivatives to pass into acenaphthenones. The following ketones are derived from naphthalene: 1-β-*chloropropionyl*- (whence 1-*phenyl*-3-α-*naphthyl*-*pyrazoline*, m. p. 167—168°); 1-β-*chloro*-n-*butyryl*-; 4-β-*chloropropionyl*-1-*methyl*-, m. p. 60°; 4-β-*chloro*-n-*butyryl*-1-*methyl*-, m. p. 48—49°; 4-*chloro*-1-β-*chloropropionyl*-, m. p. 47°; 4-*chloro*-1-β-*chloro*-n-*butyryl*-, 4-*bromo*-1-β-*chloropropionyl*-, m. p. 63°; 4-*bromo*-1-β-*chloro*-n-*butyryl*-; 1 : 6-dimethyl-4-β-chloropropionyl-, m. p. 58°; 4-*methoxy*-1-β-*chloropropionyl*-, m. p. 77—78°; 4-*chloroacetyl*-1-*methylnaphthalene*, b. p. 182—184°/15 mm. p-β-*Chloropropionyldiphenyl*, m. p. 120°, 5-β-*chloropropionyldiphenylene oxide*, m. p. 158°, 5-β-chloropropionylacenaphthene, m. p. 81°, β-*bromo*-p-*methylpropiophenone*, m. p. 90°, 6-*chloro*-3-β-*chloropropionyltoluene*, m. p. 46°, 5-*chloro*-2-β-*chloropropionyltoluene*, 5-*chloro*-2-β-*chloro*-n-*butyryltoluene*, 4-*chloro*-3-β-*chloropropionyltoluene* (1-*phenyl*-3 : 2′-*chloro*-m-*tolylpyrazoline*, m. p. 123°), 2-β-*chloropropionyl*-p-*xylene* (1-phenyl-3-p-xylylpyrazoline, m. p. 117°), and 2-β-*chloro*-n-*butyryl*-p-*xylene* are described. The following unsaturated ketones are derived from naphthalene: 4-*crotonyl*-1-*methyl*-, b. p. 205—206°/14 mm. (*dibromide*, m. p. 109°); 4-*acrylyl*-1-*methyl*-, b. p. 180—190°/14 mm. (*dibromide*, m. p. 89°); 4-*chloro*-1-*acrylyl*-, b. p. 180—192°/12 mm., (*dibromide*, m. p. 89°); 4-*chloro*-1-*crotonyl*-, b. p. 105—206° (*sic*)/14 mm. (*dibromide*, m. p. 135°); 4-*bromo*-1-*acrylyl*-, b. p. 210—215°/15 mm. (*dibromide*, m. p. 106°); 4-*bromo*-1-*crotonyl*-, b. p. 210—212°/14 mm. (dibromide, m. p. 137°); 1-*crotonylnaphthalene*, b. p. 194—196°/14 mm. (dibromide, m. p. 99°). 5-*Chloro*-2-*crotonyltoluene*, b. p. 151—153°/22 mm. and 2-*crotonyl*-p-*xylene*, b. p. 152—153°/22 mm., have been prepared. The following α-naphthindan-3-ones are described: 1 : 8-*dimethyl*-, m. p. 70°; 8-*methyl*-, m. p. 133°; 8-*chloro*-, m. p. 143°; 8-*chloro*-1-*methyl*-, m. p. 81°; 8-*bromo*-, m. p. 138°; 8-*bromo*-1-*methyl*-, m. p. 94°; 1-*methyl*-, m. p. 99°; 5 : 8-*dimethyl*-, m. p. 91°; the parent *substance* has m. p. 103°. The following indan-3-ones have been prepared: 6-*chloro*-5(7)-*methyl*-, b. p. 188—190°/14 mm.; 6-*chloro*-4-*methyl*-, m. p. 71°; 4-*chloro*-7-*methyl*-, m. p. 128°; 4 : 7-*dimethyl*-, m. p. 78°.



(I.)

H. Wren.

Distyryl ketone and triphenylmethane. XIII. Coloured compounds of unsaturated ketones with acids. F. Strauss [with W. Heyn] (Annalen, 1927, **458**, 256—310).—Further evidence in favour of analogous general formulæ of the types (I) $[\overset{+}{C}R'R''{\cdot}OMe]Cl,HgCl_2$ and (II) $[\overset{+}{C}R'R''{\cdot}OH]Cl,HgCl_2$ for the complex salts of the methochlorides and hydrochlorides, respectively, of unsaturated ketones is furnished (*a*) by the preparation from distyryl ketones of compounds of type (I) which closely resemble the corresponding compounds of type (II), and (*b*) by the conversion of (II) into (I) by methylation. *pp*′-Dimethoxycinnamylideneacetophenone [(*c*) cf. A., 1925, i, 1430], prepared from *p*-methoxycinnamaldehyde and *p*-methoxyacetophenone, yields a *dihydrochloride* and *mercurichloride* (type II), m. p. 144—146° (decomp.), which resemble the *hydrochloride*, decomp. 64—70°, and *mercurichloride* (type I), m. p. 138—142° (decomp.), of its methochloride.

γ-Chloro-α-methoxy-αε-di-*p*-anisyl-$\Delta^{\beta\delta}$-pentadiene (III), m. p. 86—88° (cf. A., 1910, i, 563), is converted by hydrogen chloride into αγ-dichloro-αε-dianisyl-$\Delta^{\beta\delta}$-pentadiene, but in presence of methyl alcohol it gives the methochloride (IV) of *pp*′-dimethoxydistyryl ketone (γ-chloro-γ-methoxy-αε-di-*p*-anisyl-$\Delta^{\alpha\delta}$-pentadiene). This cannot be isolated, but its *hydrochloride*, decomp. 75—80°, and *mercurichloride* (I), decomp. 175—178°, closely resemble the dihydrochloride and *mercurichloride* (II), decomp. 177—178°, of *pp*′-dimethoxydistyryl ketone. The transformation (III)$\longrightarrow$(IV), which takes place less readily in the distyryl than in the phenyl styryl ketones (*c*), must therefore consist in the migration of a methoxyl group. It is shown that hydrogen chloride probably combines with this group, forming an active polar molecule, which then yields mainly one or the other of the above products according to the conditions. The ketone methochloride is an intermediate product in the conversion of the abnormal ketone chlorides into the ketones in methyl alcohol. This reaction (A., 1906, i, 859) does not take place in anhydrous methyl alcohol; instead, αγ-dichloro-αε-diphenyl-$\Delta^{\beta\delta}$-pentadiene yields mainly a bimolecular chlorine-free *substance* of high m. p., which is also formed directly from the ketone and methyl-alcoholic hydrogen chloride. The coloured by-product obtained in the decomposition of γγ-chloromethoxy-αγ-dianisylpropylene (*c*) is 2 : 4 : 6-trianisylpyrylium chloride. The methochloride (IV) is converted by sodium methoxide into the dimethylacetal of *pp*′-dimethoxydistyryl ketone (*γγ-dimethoxy-αε-dianisyl-*$\Delta^{\alpha\delta}$*-pentadiene*), b. p. 222—224°/0·2—0·4 mm. (decomp.). When the abnormal ketonic chloride of distyryl ketone is warmed in ether with methyl alcohol and mercuric chloride it gives first γ-chloro-α-methoxy-αε-diphenyl-$\Delta^{\beta\delta}$-pentadiene (*c*), and then the *mercurichloride* (I), m. p. 134—136°, of distyryl ketone methochloride (*hydrochloride*). This last is converted by sodium methoxide into *γγ-dimethoxy-αε-diphenyl-*$\Delta^{\alpha\delta}$*-pentadiene*, m. p. 56—57°, b. p. 178—179°/0·4 mm., identified by hydrogenation to γγ-dimethoxy-αε-diphenylpentane. The complex salts of cinnamylideneacetophenone (*mercurichloride*) and of its methochloride (*hydrochloride*) are very soluble and much less stable than those of the isomeric distyryl ketone derivatives. Such weakly basic ketones tend to form complex salts with more than 1 mol. of mercuric chloride.

The above ketone methochloride derivatives are more simply prepared by treating a suitable complex salt (*e.g.*, the dihydrochloride of *pp*′-dimethoxydistyryl ketone and the ferrichloride of distyryl ketone or cinnamylideneacetophenone) of the ketone in ether with 5—8 mols. of anhydrous methyl alcohol. The isolation of the complex salt is not necessary and the product may be directly converted into the ketone dimethylacetal. The yield of the latter depends on the solubility of the intermediate methochloride complex and on the degree to which it is hydrolysed by the water formed in the reaction. Since the ketones do not appear to unite directly with methyl halides the reversible formation from the highly coloured ketone methochlorides and their complex salts of nearly or quite colourless ethereal solutions indicates that they are in equilibrium with non-ionised ψ-forms, CR′R″Cl·OMe.

Comparison of the absorption spectrum of the halochromic solution of distyryl or phenyl styryl ketone in 100% sulphuric acid with that of an equivalent solution of the corresponding abnormal ketochloride indicates that, contrary to the statement of Hantzsch (*loc. cit.*), the two solutions cannot contain the same complex salt. Further, the ketochlorides are rapidly changed under these conditions into water-soluble products, whilst the ketones are quantitatively regenerated from their solutions by water even when the sulphuric acid contains hydrogen chloride. By analogy with the ketone methochlorides it is suggested that the carbonium atom in the complex salts derived from the ketochlorides is that to which the methoxyl group becomes attached on methoxylation, *i.e.*, the α-carbon atom, and salts from the abnormal chloride of distyryl ketone are formulated,

$[\mathrm{CHPh{:}CH{\cdot}CCl{:}CH{\cdot}\overset{+}{C}HPh}]\mathrm{X}$. Wizinger's classification of chlorine as a negative auxochrome (A., 1927, 764) is not in accordance with results obtained with abnormal ketochlorides and triphenylmethyl chloride derivatives (cf. A., 1922, i, 148). H. E. F. NOTTON.

Substitution products of 4-hydroxybenzophenone and its methyl ether. W. BLAKEY, W. I. JONES, and H. A. SCARBOROUGH (J.C.S., 1927, 2865—2872).—Halogeno- and nitro-substituents enter first the positions adjacent to the hydroxyl group of 4-hydroxybenzophenone and further substitution takes place in the opposite nucleus. Conversion of the hydroxyl group into methoxyl lessens its directive power and generally only one of the adjacent positions is substituted, the second substituent entering the opposite nucleus and the third the nucleus containing the methoxyl group. 3-*Chloro*-4-*methoxybenzophenone*, m. p. 98°, obtained by chlorination of the methoxy-compound in glacial acetic acid, yields on further chlorination 3 : 5-*dichloro*-4-*methoxybenzophenone*, m. p. 74° (also prepared by chlorination of the methoxy-compound in acetic acid containing sodium acetate). The latter gives an *α-oxime*, m. p. 146°, which is transformed into 3 : 5-*dichloro*-4-*methoxybenzanilide*, m. p. 154°. 3 : 5-*Dichloroanisic acid*, m. p. 202°, may be obtained by hydrolysis of the anilide or by direct chlorination of the acid. 3 : 5-*Dichloro*-4-*hydroxybenzophenone*, m. p. 148°, is obtained by hydrolysis of the methoxy-compound or by chlorination of 4-hydroxybenzophenone. 3-*Bromo*-4-*methoxybenzophenone*, m. p. 94°, gives an *α-oxime*, m. p. 164°, which is transformed into 3-*bromo*-4-*methoxybenzanilide*, m. p. 170°, and a *β-oxime*, m. p. 111·5°, which is transformed into *benz*-3-*bromo*-4-*methoxyanilide*, m. p. 156°. 3-*Chloro*-5-*bromo*-4-*methoxybenzophenone*, m. p. 92°, is obtained by chlorination of the corresponding bromo-compound. 3-*Iodo*-4-*methoxybenzophenone*, m. p. 81°, prepared by the action of an acetic acid solution of iodine monochloride on the hydroxy-compound, yields an *α-oxime*, m. p. 182°, giving 3-*iodo*-4-*methoxybenzanilide*, m. p. 206°. The *β-oxime*, m. p. 135°, is transformed into *benz*-3-*iodo*-4-*methoxyanilide*, m. p. 164°. 3-*Iodo*-4-*hydroxybenzophenone*, m. p. 184°, is obtained by hydrolysis of the corresponding methoxy-compound or by iodination of the hydroxy-compound with a 5% solution of iodine in potassium iodide. 3 : 5-*Di-iodo*-4-*hydroxybenzophenone*, m. p. 145°, is obtained by iodination of the hydroxy-compound with an acetic acid solution of iodine monochloride containing sodium acetate. 3-*Nitro*-4-*methoxybenzophenone*, m. p. 105°, prepared by the action of an excess of nitric acid (*d* 1·5), yields an α-*oxime*, m. p. 179°, giving 3-*nitro*-4-*methoxybenzanilide*, m. p. 163°. 3 : 5-*Dinitro*-4-*methoxybenzophenone*, m. p. 105°, is obtained by the action of a methyl-alcoholic solution of sodium methoxide on 4 - chloro - 3 : 5 - dinitrobenzophenone (Ullmann, A., 1909, i, 473). Nitration of 4-hydroxybenzophenone with an excess of nitric acid (*d* 1·4) gives 3 : 5-*dinitro*-4-*hydroxybenzophenone*, m. p. 138° (cf. Ullmann, *loc. cit.*), together with unidentified substances. 3′-*Nitro*-4-*methoxybenzophenone*, m. p. 95°, is prepared by the interaction of *m*-nitrobenzoyl chloride, anisole, and aluminium chloride in carbon disulphide. 3 : 3′ - *Dinitro* - 4 - *methoxybenzophenone*, m. p. 143° (*hydroxy*-compound, m. p. 165°), is prepared by the action of a solution of nitric acid (*d* 1·5) in glacial acetic and sulphuric acids at —10°; some 2′(?) : 3-*dinitro*-4-*methoxybenzophenone*, m. p. 125°, is concurrently formed. Nitration of 4′-nitro-4-methoxybenzophenone with nitric acid (*d* 1·5) alone yields 3 : 4′-*dinitro*-4-*methoxybenzophenone*, m. p. 174°. Nitration of 4-methoxybenzophenone yields 3 : 3′ : 5-*trinitro*-4-*methoxybenzophenone*, m. p. 184°, which is also obtained by nitration of the 3 : 3′- or the 3 : 5-dinitro-compounds. The structure follows from the fact that it gives some *m*-nitrobenzoic acid on oxidation and that no isomerides are formed in the second method of preparation. 2′(?) : 3 : 5 - *Trinitro* - 4 - *methoxybenzophenone*, m. p. 142°, was separated from the nitration products of 4-methoxybenzophenone and of 3 : 5-dinitro-4-methoxybenzophenone.

G. A. C. Gough.

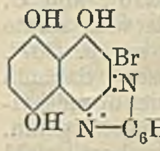
Organic compounds of sulphur. VIII. Action of $Mg+MgI_2$ on aromatic thioketones. A. Schönberg and O. Schütz [with W. Marschner] (Ber., 1927, 60, [*B*], 2351—2353).—4 : 4′-Dimethoxythiobenzophenone is converted by magnesium subiodide into tetra-amylethylene sulphide (cf. A., 1927, 667) and tetra-anisylethylene. In reactions of this type it is probable that additive compounds $[MgI{\cdot}S{\cdot}CAr_2]_2$ are intermediately produced and that they are also formed when thioketones react with Grignard reagents.

H. Wren.

Parachor and chemical constitution. VI. Cases of supposed ring–chain tautomerism. F. B. Garner and S. Sugden (J.C.S., 1927, 2877—2883).—Determinations of the parachor have been made to obtain evidence as to the structure of quinones, dibasic acid chlorides, and diketones. The parachors of quinones and diketones show that little or none of the peroxide form exists in them, whilst the parachors of the symmetrical and the unsymmetrical forms of phthalyl chloride are in agreement with the deductions made from purely chemical evidence. The following determinations are made: *p*-benzoquinone, 236·8 (calc. for the diketone, 236·1; for peroxide, 219·0); toluquinone, 272·0 (calc. for diketone, 275·1; for peroxide, 258·0); phthalyl chloride, m. p. 13°, 373·9; m. p. 88·5°, 367·8 (calc. for the *s*-form, 377·5; for the *as*-, 362·8); succinyl chloride, m. p. 18·5° (corr.), 282·6 (calc. for *s*-form, 282·6; for *as*-, 267·9); benzil, 480·8 (calc. for diketone, 476·0; for peroxide, 464·4); 2 : 2′-dimethoxybenzil, 596·8 (calc., for the diketone, 594·0; for the peroxide, 582·4). The high value for the parachor of the phthalyl chloride of m. p. 88·5° is probably due to partial conversion into the lower-melting form at the temperature at which the density determinations were made.

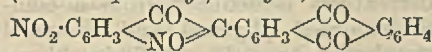
G. A. C. Gough.

Hydroxynaphthaquinone. VII. Bromination of naphthazarin. A. S. Wheeler and B. G. Carson (J. Amer. Chem. Soc., 1927, 49, 2825—2829; cf. A., 1923, i, 1020).—Bromination of naphthazarin (5 : 8-dihydroxy-1 : 4-naphthaquinone; cf. Dimroth and Ruck, A., 1926, 297) in boiling glacial acetic acid affords 2 : 3 : 6 : 7-*tetrabromonaphthazarin*, bronze-coloured, m. p. 300° (*diacetate*, yellow, m. p. 262°), which when boiled with alcoholic aniline yields a *dibromodianilinonaphthazarin*, bronze-coloured, m. p. 251°. Prolonged treatment of naphthazarin with bromine in acetic acid at the ordinary temperature affords 2 : 3 : 6 : 7 - *tetrabromo* - 1 : 4 : 5 : 8 - *naphthadiquinone*, yellow, subliming at 275—280°, which is converted, as above, into a *dibromodianilino*-derivative, brown, subliming at 220—225°. 2 : 3-Naphthazarin dichloride (cf. Zincke and Schmidt, A., 1895, i, 613) is obtained by treating 1 : 4 : 5 : 8-tetrahydroxynaphthalene with chlorine in chloroform. 2 : 3-Dibromonaphthazarin, obtained by treating naphthazarin in glacial acetic acid with 1·5 mols. of bromine (cf. Wheeler and Edwards, A., 1918, i, 75), condenses with *o*-phenylenediamine in alcohol, with formation of a purplish-blue *compound*, decomp. about 225°, presumably of the annexed formula.

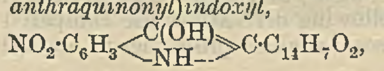


F. G. Willson.

Anthraquinonylisatogen and other condensation products of anthraquinone-2-aldehyde. P. Ruggli and A. Disler (Helv. Chim. Acta, 1927, 10, 938—947; cf. A., 1921, i, 811; 1925, i, 561).—Anthraquinone-2-aldehyde condenses with 2 : 4-dinitrotoluene in nitrobenzene–piperidine solution to form β - (2 : 4 - *dinitrophenyl*) - α - (2 - *anthraquinonyl*) - *ethylene*, m. p. 281° (*dichloride*, m. p. 250°; *dibromide*, m. p. 252°). The dibromide when treated with pyridine or alcoholic potassium hydroxide regenerates the stilbene derivative, whilst the dichloride is converted by pyridine into α-*chloro*-β-(2 : 4-*dinitrophenyl*)-α-(2-*anthraquinonyl*)*ethylene*, (I), m. p. 218°. Treatment of this last substance with pyridine–alcoholic potassium hydroxide furnishes β-(2 : 4-*dinitrophenyl*)-α-(2-*anthraquinonyl*)*acetylene* (II) (10—15% yield), m. p. 272—273° (*dichloride*, m. p. 246°; *dibromide*, m. p. 238°). When a solution of (I) or (II) in pyridine is exposed to sunlight there is produced 6-*nitro*-2-(2-*anthraquinonyl*)*isatogen*,



$NO_2{\cdot}C_6H_3{<}\begin{smallmatrix}CO\\NO\end{smallmatrix}{\gg}C{\cdot}C_6H_3{<}\begin{smallmatrix}CO\\CO\end{smallmatrix}{>}C_6H_4$, m. p. 282°, converted by phenylhydrazine into 6-*nitro*-2-(2-*anthraquinonyl*)*indoxyl*,



$NO_2{\cdot}C_6H_3{<}\begin{smallmatrix}C(OH)\\NH\text{--}\end{smallmatrix}{\gg}C{\cdot}C_{11}H_7O_2$, m. p. 328—334°

(*acetyl* derivative, m. p. 295° with previous decomp.).

Anthraquinone-2-aldehyde (1-*phenyl*-3-*methylpyrazolone* derivative, m. p. 243°; α-*ketodihydrothionaphthen* derivative, m. p. 334—336°) condenses with ethyl malonate, ethyl acetoacetate, benzoylacetone, α-picoline, and 2-methylquinoline, in presence of piperidine, to give the following derivatives of α-(2-anthraquinonyl)ethylene: ββ-*dicarbethoxy*-, m. p. 223°; β-*acetyl*-β-*carbethoxy*-, m. p. 180°; β-*benzoyl*-β-*acetyl*-, m. p. 243°; β-α-*pyridyl*-, m. p. 175°, and β-α-*quinolyl*-, m. p. 174°, respectively.

H. BURTON.

Anthraquinone derivatives (diurethano-1 : 1′-dianthraquinonyls). W. SMITH, J. THOMAS, and SCOTTISH DYES, LTD.—See B., 1927, 902.

Manufacture of dibenzanthronyls. I. G. FARBENIND. A.-G.—See B., 1927, 903.

Saponins and related substances. XVIII. Sugar-beet sapogenin. XIX. Identity of beet saponin with oleanol, the phytosterol-like substance from olive leaves, and with caryophyllin from cloves. A. W. VAN DER HAAR (Rec. trav. chim., 1927, 46, 775—792, 793—798).—XVIII. By the addition of ether and light petroleum to an alcoholic solution of the alkali-soluble portion of the scum obtained when beet-sugar liquors are treated with lime, a saponin (*A*), blackening at 214—216°, is obtained. From the mother-liquors two other fractions are obtained: *B*, m. p. 214—216°, and *C*, m. p. 206°. Saponin *B*, on hydrolysis with dilute sulphuric acid, affords a sapogenin, m. p. 307°, together with pentoses and methylpentoses. Saponin *C* similarly gives pentoses, small amounts of methylpentoses, and the same sapogenin. This sapogenin, which was also obtained directly from beet (yield 0·0025%), was prepared in quantity from the scum by Kobert's method. It is concluded that the formula is actually $C_{31}H_{50}O_3$ (see also below) and not $C_{22}H_{36}O_2$ (Andrlík and Votoček, A., 1899, i, 157). The sapogenin gives Liebermann's cholesterol reaction and Kahlenberg's reaction with a chloroform solution of antimony pentachloride. The *potassium* salt, $OH\cdot C_{30}H_{48}\cdot CO_2K$, the *methyl* ester, m. p. 199—200° (*acetyl* derivative, m. p. 223°), and the *diphenylcarbamide*, m. p. 137—138°, are described. Acetic anhydride converts the sapogenin into *diacetylsapogenin anhydride*, m. p. 315°. When crystallising with a molecule of acetic anhydride it has m. p. 215° (solidifying and re-melting at 315°) and is evidently identical with diacetyloleanol (Power and Tutin, J.C.S., 1908, 93, 897) and with diacetylcaryophyllin (Dodge, A., 1919, i, 91). *Monoacetylsapogenin*, m. p. 260° (corresponding with analogous derivatives obtained by the above authors), is prepared by the action of ethyl or methyl alcohol on the diacetyl anhydride.

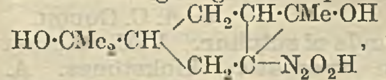
XIX. The identity of these substances and their corresponding derivatives is deduced from a comparison of their recorded physical and chemical properties. Caryophyllin has $[\alpha]_D^{15}$ +79·7° in chloroform (Dodge gives +54·5°) and yields a *methyl* ester, m. p. 198°. The following derivatives are compared and found to possess similar properties: methyl esters, acetyl derivatives of the methyl esters, diacetyl anhydrides, monoacetyl derivatives, and diphenylcarbamides. A table giving the colours obtained by Kahlenberg's reagent with various sterols and sapogenin derivatives is also included.

G. A. C. GOUGH.

Chemical nature of glycyrrhizin. M. GALASSI (Arch. Farm. sperim., 1927, 26, 231—240).—In the pure crystalline form, neither glycyrrhizin nor glycyrrhizic acid reduces Fehling's solution, and the acid contains no nitrogen. Hydrolysis of the acid yields, not glycuronic acid, as stated by Tschirch and Gauchmann (A., 1908, i, 898), but gluconic acid (2 mols.) and glycyrrhetic acid (1 mol.), so that glycyrrhizic acid is a gluconic ester of glycyrrhetic acid.

T. H. POPE.

Action of cold concentrated sulphuric acid on pernitrosoketocineole. A. D'AMBROSIO (Gazzetta, 1927, 57, 717—726).—When pernitrosoketocineole is treated with cold concentrated sulphuric acid under the conditions employed for the conversion of pernitrosocamphor into *iso*pinolone, nitrous oxide is evolved and 1-*acetyl*-3-iso*propylidene*-Δ^1-cyclo*pentene* (I), m. p. 90—91°, d^{27} 1·0857, n_D^{27} 1·59329, is obtained. The ketone forms an *oxime*, m. p. 167°, and a *semicarbazone*, m. p. 240° (decomp.); on catalytic hydrogenation, six atoms of hydrogen are taken up simultaneously (indicating the presence of a conjugated system) to give 1-β-*ethanol*-3-iso*propyl*cyclo*pentane*, b. p. 214—215°, which with alkaline potassium permanganate gives inactive dihydropinolone (1-acetyl-3-*iso*propyl*cyclo*pentane) (*semicarbazone*, m. p. 158°). The ketone (I) is oxidised by hydrogen peroxide to acetone and succinic acid. It is considered that in the formation of the ketone, water is added first to the pernitroso-group, then to the ether linking; ring closure then giving the compound



, there would be obtained on loss of nitrous oxide and opening of the *cyclo*propane ring the trihydrated form of the ketone (I).

E. W. WIGNALL.

Action of diazonium salts on α-terpineolhydroxylamineoxime. A. D'AMBROSIO (Gazzetta, 1927, 57, 726—731).—α-Terpineolhydroxylamineoxime, prepared by the method of Cusmano (A., 1912, i, 272), reacts with benzenediazonium chloride to give a *benzeneazo*-compound, m. p. 199—200°, in which the ·NH·OH group has been replaced by ·N(OH)·N:NPh. The product forms a *copper* salt, m. p. 163°, and is decomposed by hydrochloric acid with evolution of nitrogen. Of the toluenediazonium chlorides, the *ortho*-compound gives an unstable product, the *meta*- does not react, and the *para*- gives a p-*tolueneazo*-compound, m. p. 71° (*copper* salt, m. p. 135°); the p-*phenetoleazo*-compound, m. p. 160°, forms a *copper* salt, m. p. 163°. The benzeneazo-compound is reduced to a *hydrazo*-compound, m. p. 201° (decomp.) (*copper* salt, m. p. 151° decomp.).

E. W. WIGNALL.

Catalytic dehydrogenation of hydroaromatic compounds. W. TREIBS and H. SCHMIDT (Ber., 1927, 60, [*B*], 2335—2341).—Hydroaromatic hydroxy-and keto-compounds can be dehydrogenated in the presence of a copper or nickel catalyst at temperatures (about 200°) below the b. p. of the liquids. Since the catalysts possess hydrogenating powers at this temperature the products are mixed with varying amounts of hydrogenated substances, the proportion of which can be diminished by dilution or removal of hydrogen by admixture with an indifferent gas. Dehydrogenation occurs more readily with unsaturated than with saturated compounds. The nickel catalyst is prepared by passing hydrogen over a mixture of pumice with nickel formate or freshly-precipitated nickel carbonate at 200—280° until water ceases to be formed; the copper catalyst is obtained by precipitating copper acetate with an excess of hot, concentrated sodium hydroxide and reducing the washed copper hydroxide deposited on copper gauze, pumice, or asbestos by hydrogen at 280°. The vapours of the substance are passed over the catalyst heated in glass tubes in a Heraeus furnace or, in some cases, the liquid is simply heated at its b. p. with the catalyst. The following examples are cited: piperitone and pulegone to thymol and menthone at 200°, whereas menthone and thujone are almost unaffected at this temperature; menthol and *neo*menthol at 280° mainly to menthone and thymol, the proportion of ketone increasing with decreasing temperature; fenchyl alcohol exclusively to fenchone; sabinol to thujone; pinocarveol to pinocamphone; carveol and dihydrocarveol to tetrahydrocarvone and carvacrol; *iso*pulegol to menthone and thymol; geraniol to citronellal; citronellol to citronellal; limonene and phellandrene to cymene and menthane; pinene to cymene and pinane.

H. Wren.

Hydration of nopinene. IV. Comparison of terpene alcohols obtained by hydration of nopinene and pinene. G. Austerweil (Bull. Soc. chim., 1927, [iv], 41, 1507—1511; cf. A., 1927, 60).—Pure nopinene is converted by 2 mols. of benzoic acid at 138—143° into a mixture of 16·2% of *iso*borneol and 83·8% of borneol. Under similar conditions pure *l*-pinene affords practically pure borneol. With salicylic acid similar results are obtained, but in each case the rotatory power of the terpene alcohol is lower than with the stronger benzoic acid. From these results it is inferred that nopinene is the source of camphene found in a specimen of turpentine or in the products of the action of an organic acid on the pinene fraction of a terpene. R. Brightman.

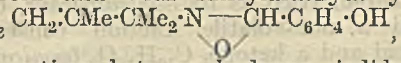
Formation of camphene from pinene hydrochloride [bornyl chloride]. T. Ikeda (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, 7, 62—73).—The formation of camphene when bornyl chloride vapour is passed over heated metallic oxides has been investigated. Of the oxides examined, lead oxide and barium oxide gave the best yield, the optimum temperatures being 250° and 300°, respectively. The oxides of zinc, magnesium, calcium, iron, and manganese gave relatively poor yields, other terpenes and polyterpenes also being formed. Ferric and zinc chlorides apparently effect the removal of hydrogen chloride catalytically, with production of a mixture of hydrocarbons. R. Cuthill.

Dehydration of borneol. T. Ikeda (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, 7, 47—61).—By heating borneol with zinc chloride, an *ether*, $(C_{10}H_{17})_2O$, m. p. 43—44°, b. p. 317°/753 mm., was obtained. When an excess of zinc chloride was used, and the time of heating prolonged, a mixture of hydrocarbons was formed, the principal product being a *diterpene*, $C_{20}H_{32}$, b. p. 168—169°/10 mm., of uncertain structure. On reduction, this substance yielded a mixture of $C_{20}H_{51}$ hydrocarbons, one having m. p. 80—84°. A hydrocarbon $C_{20}H_{54}$, m. p. 88—89°, was also obtained by the action of magnesium on bornyl chloride in ethereal solution.

R. Cuthill.

6-Methylbornylene. L. J. Briusova (J. Russ. Phys. Chem. Soc., 1927, 59, 653—657).—The dehydration of 6-methylborneol and the behaviour of the product towards perbenzoic acid were investigated. Unlike other dicyclic alcohols, 6-methylborneol gives on dehydration only one hydrocarbon, viz., 6-*methylbornylene*, m. p. 118·5—119°, oxidised by potassium permanganate to 6-methylcamphoric acid, and completely oxidised by perbenzoic acid.

M. Zvegintzov.

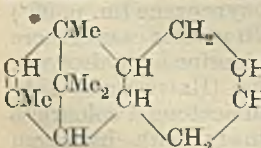
Action of hydrogen iodide on nitroso-compounds. J. C. Earl and J. Kenner (J.C.S., 1927, 2139—2145).—The action of hydrogen iodide on a variety of nitroso-compounds takes place with elimination of iodine and reduction of the nitroso- to the corresponding hydroxylamino-derivative (cf. Thiele, A., 1894, i, 217; Baeyer, A., 1894, i, 252). Baeyer's conclusion that the nitrosochloride of tetramethylethylene reacts in a different way with hydrogen bromide in acetic acid is shown to be incorrect, although the hydroxylamino-derivative first formed loses the elements of hydrogen chloride when liberated in the presence of alkali, and the product isolated is β-*hydroxylamino*-βγ-*dimethyl*-Δγ-*butene hydrochloride*, which reduces Fehling's solution in the cold and with salicylaldehyde yields the *substance*  $CH_2{:}CMe{\cdot}CMe_2{\cdot}\underset{\diagdown O \diagup}{N{-}{-}CH}{\cdot}C_6H_4{\cdot}OH$, m. p. 53°. In the reactions between hydrogen iodide and the nitrosochlorides of tetramethylethylene and γ-terpinyl acetate, the amount of iodine liberated corresponds approximately with the decrease of halogen ion present; hence in these instances the nitroso-group does not induce sufficient positive polarity in the chlorine atom to render it liable to displacement by hydrogen in the presence of hydrogen iodide. With *m*- and *p*-chloronitrosobenzene and hydrogen iodide reduction is immediately followed by the condensation of the hydroxylamino- with the nitroso-derivative, and, in presence of red phosphorus to remove the iodine as formed, 3 : 3′-dichloroazoxybenzene (m. p. 154°) or 4 : 4′-dichloroazoxybenzene (m. p. 96°) is produced in excellent yield. In neither case is there any evidence of the removal of chlorine by hydrolysis.

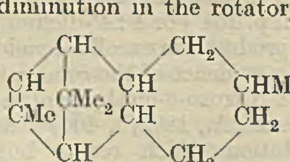
δ-Nitroso-δ-methylpentan-β-one (Harries and Jablonski, A., 1898, i, 400) yields in acetone a colourless solution which reacts but slowly with hydrogen iodide in the cold; on heating, however, the solution develops a blue colour, and on re-cooling is much more reactive. 8-Nitrosomenthone (Harries and Roeder, A., 1900, i, 182), although blue when prepared, tends to polymerise and therefore reacts comparatively slowly, whilst with 4-nitrosomenthone (Baeyer, A., 1895, i, 549), which is known to be a bis-compound, iodine is slowly liberated when a cold solution in acetone is treated with hydrogen iodide. The primary product of the reaction between nitrous acid itself and hydriodic acid is probably dihydroxyammonia, which reacts further with nitrous acid, forming nitric oxide and water. Ethyl ether reacts slowly with hydrogen iodide at the ordinary temperature. W. J. POWELL.

Mono- and sesqui-terpenes. [Caryophyllene, cedrene, and cadinene.] E. DEUSSEN [with F. WEISS, P. HACKER, and P. HILLE] (J. pr. Chem., 1927, [ii], **117**, 273—304; cf. A., 1926, 1252).—Treatment of caryophyllene dihydrochloride (1 mol.) with magnesium (2 atoms) in ether containing a small amount of ethyl bromide or bromobenzene yields an unsaturated *hydrocarbon*, $C_{15}H_{26}$, b. p. 131°/10 mm., d_4^{15} 0·8965, n_D^{18} 1·496, α —4·97°, R_L 66·9, which with aqueous mercuric acetate at 0°, and subsequent treatment with potassium iodide, furnishes a *compound*, $C_{15}H_{26}HgI{\cdot}OH$, m. p. 131—133°. γ-Caryophyllene condenses with ethyl diazoacetate in presence of copper powder at 165° to form *ethyl γ-caryophyllene*-cyclo*propanecarboxylate*, $C_{15}H_{24}{>}CH{\cdot}CO_2Et$, $[\alpha]_D^{18}$ +38·12°, R_L 86·44, which is reduced catalytically to a *dihydro*-derivative, $[\alpha]_D^{20}$ +13·43° in alcohol. This last compound on hydrolysis followed by oxidation with potassium permanganate yields *as*-dimethylsuccinic acid. By catalytic reduction of γ-caryophyllene there is obtained γ-dihydrocaryophyllene, b. p. 129—130°/14 mm., $[\alpha]_D^{19}$ —32·7° (cf. K. Meyer, Diss., Leipzig, 1912), which does not give a mercuric acetate additive compound. Ozonisation of γ-caryophyllene in chloroform solution yields an *ozonide*, $C_{15}H_{24}O_6$, $[\alpha]_D^{13}$ +23·4° in chloroform, which when decomposed with steam yields a volatile portion containing formaldehyde, formic acid, and a ketone, $C_8H_{14}O$, characterised as its *semicarbazone*, decomp. 207°, and a non-volatile fraction consisting of succinic acid and a ketone, $C_{10}H_{16}O_2$ (*semicarbazone*, decomp. 120°).

Magnesium phenyl bromide reacts with blue β-caryophyllene nitrosite (A., 1915, i, 274) to form a *base*, $C_{15}H_{26}O_2N{\cdot}NH_2$ (*sulphate*, m. p. 117°), also obtained from the nitrosite by treatment with hydrogen sulphide.

Reduction of cedrene with sodium and amyl alcohol gives a *dihydrocedrene*, $C_{15}H_{26}$, b. p. 118—124°/12 mm., d^{20} 0·9041, n_D^{20} 1·48719, α +33·1°, differing in physical constants from other described dihydrocedrenes (cf. Semmler and Mayer, A., 1912, i, 480). The effect of sulphuric acid of varying concentration on cedrene is to cause a diminution in the rotatory power. Cedrene is not dehydrogenated smoothly by sulphur at 260°, but oxidation with manganese dioxide and 50% sulphuric acid furnishes acetic acid, together with small quantities of cedreneketonic acid (A., 1907, i, 946) and phthalic acid. Cedrene is probably (I) or (II). The effect of oxygen in presence of various catalysts on the higher-boiling fraction of cedar-wood oil is to cause thickening, owing to the formation of a resin-like substance.


(I.)


(II.)

Magnesium reacts with *l*-cadinene dihydrochloride, m. p. 118—118·5° (cf. Deussen, A., 1912, ii, 510), to form a *hydrocarbon*, $C_{15}H_{26}$ (10%), together with a *terpene*, $C_{15}H_{24}$ (90%), which with hydrogen chloride affords about 20% of *l*-cadinene dihydrochloride. H. BURTON.

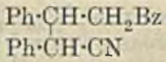
7-Hydroxy-3-phenylcoumarin. W. BAKER (J.C.S., 1927, 2898—2899).—Jacobson and Ghosh (A., 1915, i, 832; 1916, i, 281) describe the preparation of a compound, m. p. 131°, from ethyl α-formylphenylacetate and resorcinol, which they claim to be 7-hydroxy-3-phenylchromone. Since such condensations are known to give coumarins (cf. Baker and Robinson, A., 1925, i, 1299; Baker, A., 1926, 74; Bargellini, A., 1925, i, 1299) the original experiments have been repeated. 7-Hydroxy-3-phenylcoumarin, m. p. 207—208°, is always produced and no trace of *iso*flavone can be detected. Ethyl α-formylphenylacetate and phloroglucinol when condensed in the presence of phosphoric anhydride afford the *acetyl* derivative, m. p. 255—256°, of a phenolic *compound*, m. p. 308—310°, which is not identical with 5 : 7-dihydroxy-3-phenylcoumarin. S. COFFEY.

Methysticin. W. LAMPE, J. ZIELIŃSKA, and J. MAJEWSKA (Rocz. Chem., 1927, 7, 139—149).—The structural formula for methysticin proposed by Pomeranz (Monatsh., 1888, 9, 863) is in reality that of ψ-methysticin, as is shown by the following synthesis. *Methyl α-piperoylacetoacetate*, m. p. 166—167°, prepared from piperic acid, is converted into *piperoylacetone*, m. p. 119—120°, by heating with water under pressure, or into *methyl piperoylacetate*, m. p. 132—134°, identical with ψ-methysticin, by boiling with 75% acetic acid.

ψ-Methysticin yields 3 : 4-methylenedioxycinnamylideneacetone on hydrolysis with 10% sulphuric acid; with soduim hydroxide methysticinic acid is produced, from which ψ-methysticin may be prepared by methylation. *Methysticin dibromide*, m. p. 156°, is produced by the action of bromine on methysticin, whilst ψ-methysticin yields a *monobromo*-derivative (*methyl α-bromopiperoylacetate*), m. p. 98°. The following compounds are described: *α-bromo-α-cinnamoylacetone*, m. p. 91—93°, *ethyl α-piperoylacetoacetate*, m. p. 92—94°, and *ethyl piperoylacetate*, m. p. 73—75°. The reactions given by methysticin indicate that it is a condensation product of ψ-methysticin, and is 2-(3′ : 4′-methylenedioxystyryl)-6-methoxy-2 : 3-dihydro-γ-pyrone. R. TRUSZKOWSKI.

Condensation of pyruvic acid with aromatic amines and aldehydes. S. WEIL and S. AUERBACHÓWNA (Rocz. Chem., 1927, 7, 357—361).—Ethyl *p*-aminobenzoate, benzaldehyde, and pyruvic acid condense with the production of 4 : 5-*diketo-2-phenyl-1-p-carbethoxyphenylpyrrolidine*, m. p. 154—155°. Under similar conditions pyruvic acid does not react with methyl 4-amino-2-hydroxybenzoate and piperonal, but the *piperonylidene* derivative of the amino-acid, m. p. 174—175°, is formed. *o*-Nitro-*p*-toluidine and *m*-nitroarsanilic acid do not condense with piperonal and pyruvic acid. The presence of nitro- or hydroxy-groups *ortho* to the amino-group appears to inhibit condensation. R. TRUSZKOWSKI.

Catalytic reduction of nitriles. H. RUPE and L. STERN (Helv. Chim. Acta, 1927, **10**, 859—866).—An improved method of obtaining α-camphomethylamine [*oxalate*; *benzoyl* derivative, m. p. 82°; *acetyl* derivative, m. p. 84°, and *dimethylamino*-derivative (*hydrochloride*, m. p. 165° after browning at 150°) described] from α-camphomethylaminomethylenecamphor (A., 1925, i, 275) is described. α-*Camphomethylcarbamide* has m. p. 145°.

Reduction of the two stereoisomeric γ-cyano-βγ-diphenylbutyrophenones (αβ-diphenyl-β-phenacylpropionitriles), m. p. 109° and 118° (Kohler and Allen, A., 1924, i, 855), under the same conditions (see A., 1923, i, 1199) shows that 75% of the form of higher m. p. is reduced, as is 75% of that of lower m. p. In the latter case, however, the remaining 25% of the nitrile rearranges to the less fusible form. The reduction product is 2 : 4 : 5-*triphenylpiperidine*, m. p. 72° (*hydrochloride*; *phenylthiocarbamide*, m. p. 165°; *nitroso*-derivative, m. p. 153°; *benzoyl* derivative, m. p. 155°). 2 : 4 : 5-*Triphenyl-1-ethylpiperidine* (*picrate*, m. p. 181°) has m. p. 121°, whilst 2 : 4 : 5-*triphenyl*-1-*methylpiperidine* (*methiodide*) has m. p. 141°. These results indicate that the nitrile of higher m. p. is  $\begin{array}{l}\mathrm{Ph{\cdot}CH{\cdot}CH_2Bz}\\ \mathrm{Ph{\cdot}CH{\cdot}CN}\end{array}$ and that of lower m. p.  $\begin{array}{l}\mathrm{Ph{\cdot}CH{\cdot}CH_2Bz}\\ \mathrm{CN{\cdot}CHPh}\end{array}$. H. BURTON.

Orienting influence of free and bound ionic charges on attached simple or conjugated unsaturated systems. II. Nitration of 1-benzylpiperidine and some related substances. A. POLLARD and R. ROBINSON (J.C.S., 1927, 2770—2780).—Comparatively simple considerations of electron displacement towards the nitrogen atom to explain substitution in benzylammonium salts (cf. A., 1926, 397, 1132) cannot be extended to benzylpiperidine, which furnishes a higher yield of *m*-nitro-derivative than the closely related open-chain tertiary bases (A., 1926, 946). New determinations, using the bromination method of Francis and Hill (A., 1925, ii, 163), prove that the reaction product contains 72% of *m*-nitrobenzylpiperidine. 1-β-*Phenylethylpiperidine*, b. p. 262—264°/760 mm. (*picrate*, m. p. 144—145°), prepared from magnesium benzyl chloride and 1-*iso*butoxymethylpiperidine, gives 22% of *m*-nitro-derivative under similar conditions, whilst γ-*phenylpropylpiperidine*, b. p. 150°/15 mm. (*picrate*, m. p. 99—100°), affords 6% of the *m*-nitro-derivative.

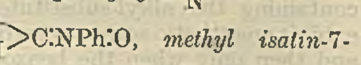
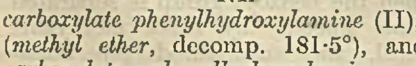
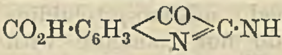
The proportion of *m*-nitrobenzylpiperidine is reduced by the addition of ammonium nitrate (to 56%), or the more soluble trimethylammonium nitrate (to 16%), or carbamide. The effect caused by the latter is due to Flürscheim's effect (cf. A., 1926, 830) and not to the removal of nitrous acid. This effect is attributed to the progressive electrostriction of the cations by nitrate ions. The proportion of the *m*-isomeride is related to the existence of constitutive factors that hinder or assist the electrostriction of the cations, which will be influenced as follows: The degree of electrostriction should be greater (1) the smaller the number of atoms directly attached to the central charged atom. Thus *benzylmethylpiperidinium nitrate*, from the corresponding *iodide*, m. p. 147°, furnishes more than 90% of *m*-nitro-isomeride, whilst benzylpyridinium perchlorate affords only 67%; (2) the greater the volume of the central charged atom. This involves the probability of diminishing *m*-substitution in ascending a group of the periodic table; (3) the smaller the space occupied by atoms or groups attached to the central charged atom, and (4) the greater the mobility of the groups surrounding the central charged atom. The latter affords an explanation of the nitration of benzylpiperidine. The nitration of benzylpiperidine is unaffected by the addition of nitromethane or ethyl malonate and addition of nitrobenzene lowers the proportion of *m*-isomeride to only 58%.

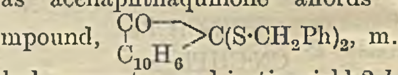
The following compounds are also described: o-*nitrobenzylmethylpiperidinium iodide*, m. p. 183—184°; m-*nitrobenzylmethylpiperidinium iodide*, m. p. 204° after blackening at 198°; p-*nitrobenzylmethylpiperidinium iodide*, m. p. 188° (decomp.). The above *o*- and *p*-compounds, unlike the *m*-compound, develop a brownish-yellow colour in boiling methyl-alcoholic potassium hydroxide, whilst with acetone and solid potassium hydroxide only the *m*-derivative gives an intense violet colour. o-, m-, and p-*Nitrobenzylpiperidinium perchlorates* have m. p. 155—156°, 176—177°, and 181—182°, respectively. The *o*- and *p*-compounds afford *o*- and *p*-nitrotoluenes when boiled with sodium hydroxide solution. S. COFFEY.

Piperidine derivatives. IV. Substituted piperidinoalkyl benzoates and *p*-aminobenzoates. S. M. MCELVAIN (J. Amer. Chem. Soc., 1927, 49, 2835—2840; cf. A., 1926, 1044).—The following piperidinoalkyl benzoate hydrochlorides were prepared by condensing substituted piperidines with the appropriate ω-chloroalkyl benzoates: γ-*piperidinopropyl*, m. p. 186—188°; γ-2-*methylpiperidinopropyl*, m. p. 167—169°; γ-2-*propylpiperidinopropyl*, m. p. 184—186°; γ-3-*methylpiperidinopropyl*, m. p. 178—180°; β-3-*methylpiperidinoethyl*, m. p. 134—136°, and γ-3-*carbethoxypiperidinopropyl benzoate hydrochloride*, m. p. 161—163°. The following were prepared by condensing piperidines with trimethylene chlorohydrin, esterifying the resulting γ-piperidinopropyl alcohols with *p*-nitrobenzoic acid, and finally reducing the nitro-group catalytically: γ-*piperidinopropyl* p-*nitrobenzoate*, m. p. 201—203°, and p-*aminobenzoate hydrochloride*, m. p. 214—216°; γ-3-*methylpiperidinopropyl* p-*nitrobenzoate*, m. p. 190—192°, and p-*aminobenzoate hydrochloride*, m. p. 158—160°; γ-3-*carbethoxypiperidinopropyl* p-*nitrobenzoate*, m. p. 177—179°, and p-*aminobenzoate hydrochloride*, m. p. 113—115°. Of the above derivatives, only those containing the alkyl-substituted piperidine nucleus exhibit anæsthetic action towards mucous membranes, and then only when the benzoyl group is separated from the piperidine nucleus by three methylene groups. In general, the substituted piperidino-derivatives are less toxic than those unsubstituted.

F. G. WILLSON.

Piperidine derivatives. V. Preparation and reduction of phenyl-substituted 3-carbethoxy-4-piperidones. 1-*cyclo*Hexyl- and 1-phenylethyl-3-carbethoxy-4-piperidyl *p*-aminobenzoates. J. R. Thayer and S. M. McElvain (J. Amer. Chem. Soc., 1927, 49, 2862—2869; cf. preceding abstract).—β-Carbethoxyethylaniline, obtained from aniline and ethyl β-bromopropionate, has b. p. 133—135°/2 mm., n_D^{20} 1·5315, d_{20}^{20} 1·0709 (*hydrochloride*, m. p. 98—99°) (cf. Harries and Loth, A., 1896, i, 321). Benzylamine affords similarly β-*carbethoxyethylbenzylamine*, b. p. 132—134°/2 mm., n_D^{20} 1·5059, d_{20}^{20} 1·9126 (*hydrochloride*, m. p. 147—149°). β-*Phenylethyl*-β-*carbethoxyethylamine*, b. p. 145—147°/2 mm., n_D^{20} 1·5040, d_{20}^{20} 1·0098 (*hydrochloride*, m. p. 161—163°), *phenyldi*-(β-*carbethoxyethyl*)*amine*, b. p. 182—184°/2 mm., n_D^{20} 1·5176, d_{20}^{20} 1·0948, *benzyldi*-(β-*carbethoxyethyl*)*amine*, b. p. 181—183°/2 mm., n_D^{20} 1·4942, d_{20}^{20} 1·0598, and β-*phenylethyldi*-(β-*carbethoxyethyl*)*amine*, b. p. 190—193°/2 mm., n_D^{20} 1·4990, d_{20}^{20} 1·0598, are obtained analogously. Treatment of the above dicarbethoxy-tertiary amines with sodium in boiling xylene (cf. A., 1926, 1044) affords, respectively, 1-*phenyl*- (I), m. p. 144—145°, 1-*benzyl*- (II), m. p. 170—172°, and 1-β-*phenylethyl*-3-*carbethoxy*-4-*piperidone hydrochloride* (III), m. p. 165—167°). Reduction of (I) with hydrogen in presence of platinum oxide in alcohol, with subsequent treatment of the product with *p*-nitrobenzoyl chloride, yields 1-cyclo*hexyl*-3-*carbethoxy*-4-*piperidyl* p-*nitrobenzoate hydrochloride*, m. p. 188—190°. Similarly (III) affords 1-β-*phenylethyl*-3-*carbethoxy*-4-*piperidyl* p-*nitrobenzoate hydrochloride*, m. p. 195—197°, but reduction of (II) could not be controlled to yield a crystalline product. Catalytic reduction of the nitrobenzoates yields, respectively, 1-cyclo*hexyl*- (IV), m. p. 220—222°, and 1-β-*phenylethyl*-3-*carbethoxy*-4-*piperidyl* p-*aminobenzoate dihydrochloride*, (V), m. p. 215—218°. The anæsthetic effect of (V) on the rabbit's cornea, and its toxicity to white mice, are both slightly greater than that of cocaine, whilst (V) is more than twice as effective an anæsthetic as cocaine under similar conditions, with approximately only one fifth of the toxicity of the latter. F. G. Willson.

Phenylhydroxylamine derivative of isatin-7-carboxylic acid. H. Rupe and G. A. Guggenbühl (Helv. Chim. Acta, 1927, **10**, 926—937).—Isatin-7-carboxylic acid (Sandmeyer, A., 1919, i, 318) (β-*phenylhydrazone*, decomp. 267°; α-*oxime*, decomp. 254°; β-*semicarbazone*, decomp. 261°) is difficult to esterify. The *methyl*, m. p. 192° (α-*oxime*, decomp. 228—229°; β-*phenylhydrazone*, m. p. 202°), and *ethyl* esters, m. p. 189—190°, are described. The acid and esters react with phenylhydroxylamine, yielding *isatin-7-carboxylic acid phenylhydroxylamine* (I), decomp. 221·5°, represented by either the lactim or pseudo-acid structure,  $CO_2H\cdot C_6H_3<\substack{CO\\ -N}\geqslant C\cdot NPh\cdot OH$  $\rightleftharpoons CO_2H\cdot C_6H_3<\substack{CO-\\ NH}>C:NPh:O$, *methyl isatin*-7-*carboxylate phenylhydroxylamine* (II), decomp. 187·5° (*methyl ether*, decomp. 181·5°), and *ethyl isatin*-7-*carboxylate phenylhydroxylamine*, decomp. 176·5°, respectively. Reduction of (I) with zinc dust and acetic acid furnishes *isatin-7-carboxylic acid-α-anil* (III),  $CO_2H\cdot C_6H_3<\substack{CO\\ -N}\geqslant C\cdot NHPh$ (*zinc* salt; *hydrochloride*, m. p. 173°; *methyl ester hydrochloride*, decomp. 141—143°), which is oxidised by ferric chloride to isatin-7-carboxylic acid and aniline. Treatment of (I) and (III) with phenylhydrazine and hydroxylamine furnishes respectively isatin-7-carboxylic acid-β-phenylhydrazone, and -α-oxime. Similarly (II) yields the β-phenylhydrazone and α-oxime of methyl isatin-7-carboxylate. Hydrolysis of (I) with 10% hydrochloric acid gives isatin-7-carboxylic acid and aniline, whilst with 10% sodium hydroxide there are obtained the acid, aniline, and azoxybenzene. H. Burton.

Organic compounds of sulphur. VII. Behaviour of mercaptans towards phenanthraquinone, isatin, and αβ-unsaturated ketones. A. Schönberg and O. Schütz [with G. Arend and J. Peter] (Ber., 1927, **60**, [*B*], 2344—2351).—Phenanthraquinone is readily converted by benzyl mercaptan into the *compound* $C_{21}H_{16}O_2S$, which decomposes into its components at about 115°. Since the colour of additive compounds of phenanthraquinone is generally equal to or darker than that of the quinone itself whereas the present compound is less intensely coloured, it is regarded as 10-*keto*-9-*hydroxy*-9-*benzylthiol*-9 : 10-*dihydrophenanthrene* ("*phenanthraquinone benzylsemimercaptol*"); the corresponding *phenyl*, decomp. about 100°, *ethyl*, and n-*butyl* compounds are described. Chrysoquinone yields an analogous *derivative*, $C_{25}H_{18}O_2S$, with benzyl mercaptan, whereas acenaphthaquinone affords the *dibenzylthiol* compound,  $\substack{CO-\\ |\\ C_{10}H_6}>C(S\cdot CH_2Ph)_2$, m. p. 104—105°. Ethyl mercaptan and isatin yield 2-*keto*-3-*hydroxy*-3-*ethylthiolindoline*; the corresponding *benzyl* compound is described. The possibility that the mercaptan is added at the nitrogen atom is excluded by the observation that *N*-acetylisatin gives the *acetyl* derivative of 2-*keto*-3-*hydroxy*-3-*benzylthiolindoline*. Addition of mercaptans to αβ-unsaturated ketones is realised in the case of 2 : 3-diphenylindone, which gives the corresponding 1 : 1-*diphenylthiol*-, m. p. (indef.) 134—136°, and *dibenzylthiol*-, m. p. 142—143°, derivatives; the latter compound is converted by sulphuric acid in glacial acetic acid into 2 : 3-diphenylindone. H. Wren.

New stereoisomeride (*trans*-) of hexahydrocarbazole. J. Gurney, W. H. Perkin, jun., and S. G. P. Plant (J.C.S., 1927, 2676—2679; cf. A., 1926, 410).—Reduction of tetrahydrocarbazole with tin and hydrochloric acid yields *cis*-hexahydrocarbazole, m. p. 99°, b. p. 280°/769 mm. (*picrate*, m. p. 166°), together with a small quantity (1—2%) of trans-*hexahydrocarbazole*, m. p. 127°, b. p. 286°/769 mm. (*picrate*, m. p. 179°; 9-*acetyl* derivative, m. p. 113°; 9-*benzoyl* derivative, m. p. 133°). The molecule of *trans*-hexahydrocarbazole is under considerable strain, accounting for its formation in small amount. The existence of these stereoisomerides is discussed in relation to the Sachse–Mohr theory of multiplanar rings. M. Clark.

Ammoniated iridodipyridino-salts. M. Delépine (Z. physikal. Chem., 1927, **130**, 222—232;

cf. A., 1923, i, 944).—The action of ammonia in the cold on iridium *trans*-dipyridino-tetrachloride, $Ir(C_5H_5N)_2Cl_4$, furnishes the *complexes*
$[Ir(C_5H_5N)_2Cl_4][Ir(C_5H_5N)_2(NH_3)_2Cl_2],2H_2O$,
red, triclinic, and
$[Ir(C_5H_5N)_2Cl_4]_2[Ir(C_5H_5N)_2(NH_3)_3Cl],5H_2O$, which can be separated by levigation, followed by recrystallisation from aqueous solution. Double decomposition of these complexes with pyridine hydrochloride gives rise to the *salts* $Cl[Ir(C_5H_5N)_2(NH_3)_2Cl_2]H_2O$ and $Cl_2[Ir(C_5H_5N)_2(NH_3)_3Cl],4H_2O$. The *iodide, bromide, sulphate,* and *hydrogen sulphate* corresponding with the first of these salts are also described. A carbonate, $CO_3[Ir(C_5H_5N)_2(NH_3)_2(H_2O)Cl],6H_2O$, has also been prepared by the action of silver oxide and carbon dioxide of the air on the monochloride. The *chloride,* $Cl_3[Ir(C_5H_5N)_2(NH_3)_4]$, and a basic salt derived from it are also described.

L. S. Theobald.

Synthesis of the "β-acid" (2 : 6-dihydroxyquinoline-4-carboxylic acid) obtained by hydrolysis of crude oryzanin. Y. Sahashi (Biochem. Z., 1927, 189, 208—215).—The author's view (A., 1926, 441, 846) that the β-acid of Suzuki, Shimamura, and Odake (A., 1912, ii, 980) obtained by hydrolysis of crude oryzanin is 2 : 6-dihydroxyquinoline-4-carboxylic acid is confirmed by synthesis. Quinic acid is converted by methyl iodide and sodium hydroxide into 2-hydroxy-6-methoxy-1-methylquinoline-4-carboxylic acid (ethyl ester, m. p. 166—167°), identical with the dimethyl derivative of the β-acid obtained by treatment with methyl sulphate. The same compound is also obtained synthetically (starting with a *p*-anisidine, diethylketomalonate condensation) and this compound on demethylation by Zeisel's method gave 2 : 6-hydroxyquinoline-4-carboxylic acid identical with the β-acid. P. W. Clutterbuck.

Synthesis of 2-carboxymethylquinoline-3-carboxylic acid and of certain of its derivatives. B. Bobrański and E. Sucharda (Rocz. Chem., 1927, 7, 192—203).—Condensation of *o*-aminobenzaldehyde with ethyl acetonedicarboxylate yields *ethyl 2-carbethoxymethylquinoline-3-carboxylate,* m. p. 62° (*hydrochloride,* m. p. 108°; *nitrate,* m. p. 111°), whence on alkaline hydrolysis is obtained the corresponding acid, which at the ordinary temperature rapidly loses carbon dioxide, yielding 2-methylquinoline-3-carboxylic acid. The *anhydride,* m. p. 255° (decomp.), the *monoamide,* m. p. 218—220° (*acetyl* derivative, m. p. 239°), and the *imide,* m. p. 375°, of 2-carboxymethylquinoline-3-carboxylic acid are prepared, the imide being identical with 1 : 3-dihydroxybenzo-2 : 5-naphthadiazine (Niementowski and Sucharda, A., 1919, i, 354).

R. Truszkowski.

Esters of α-phenylcinchoninic acid. S. Weil and A. Joskowiczówna (Rocz. Chem., 1927, 7, 362—368).—The following esters of α-phenylcinchoninic acid have been prepared: p-*chlorophenyl,* m. p. 117—118°, β-*phenylethyl,* m. p. 72°, *pyrocatechyl,* m. p. 178—179°, *guaiacyl,* m. p. 104—105°, *resorcinyl,* m. p. 195—196°, *pyrogallyl,* m. p. 170—171°, *thymyl,* m. p. 110—111°, and the *triphenylcinchoninyl ether of quinic anhydride,* m. p. 208°. R. Truszkowski.

Manufacture of insoluble azo dyes. I. G. Farbenind.—See B., 1927, 902.

[Nitro- and amino-acridines.] K. Lehmstedt (Ber., 1927, 60, [*B*], 2413; cf. A., 1927, 575).—A reply to Jensen (A., 1927, 1087). H. Wren.

Isolation of acridine derivatives etc. Preparation of acridine-9-carboxylonitrile. E. Wirth.—See B., 1927, 925.

Preparation of acridinic [quinoline-2 : 3-dicarboxylic] acid and derivatives. A. Konopnicki and E. Sucharda (Rocz. Chem., 1927, 7, 183—186).—Acridinic acid is produced in 70% yield by the action of concentrated nitric acid on 2 : 4-dihydroxyacridine. The *anhydride,* m. p. 223°, and *imide,* m. p. 316°, are described. R. Truszkowski.

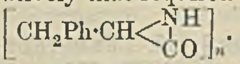
New type of acridone: *para*-acridones. I. Tanescu (Bull. Soc. chim., 1927, [iv], 41, 1511—1514).—When treated with sulphuric acid in cool benzene solution for 24 hrs. *p*-nitrobenzaldehyde affords mainly *p*-nitrotriphenylmethane, a little 4-nitrotriphenylmethane-2(?)-sulphonic acid, brick-red, m. p. 160°, and traces of a para-*acridone,* $C_{13}H_9ON$, m. p. above 300°. The latter is also obtained by internal condensation from 4-bromo-4′-aminobenzophenone, by heating in presence of copper powder, a little potassium iodide, and amyl alcohol in a sealed tube at 350°. The formation of *m*-nitrotriphenylmethane from *m*-nitrobenzaldehyde in the same way is accompanied by the formation of a little 3-nitrotriphenylmethane-6(?)-sulphonic acid, but no acridone is formed. R. Brightman.

Synthesis of the pyridine analogues of quinizarin. S. Niementowski, J. Frühling, and R. Joszt (Rocz. Chem., 1927, 7, 218—229).—By condensation of quinol dimethyl ether with quinolinic anhydride, 5 : 8-*dihydroxy-α-anthrapyridoquinone* ($+0{\cdot}5C_6H_6$), m. p. 230°, is produced; with cinchomeronic anhydride the corresponding β-*derivative,* m. p. 209° (*diacetyl* derivative, m. p. 187·5—189·5°; *tetra-acetyl* derivative, m. p. 283°), is obtained.

R. Truszkowski.

Manufacture of heterocyclic compounds [naphthaquinolines etc.]. I. G. Farbenind.—See B., 1927, 903.

α-Amino-*N*-carboxylic anhydrides. V. Side-reactions of the pyridine decomposition. F. Wessely and M. John (Z. physiol. Chem., 1927, **170**, 38—43; cf. A., 1926, 1235; 1927, 655).—From the ether-soluble portion of the product obtained by heating phenylalanine-*N*-carboxylic anhydride in pyridine there are isolated the two inactive forms of α-(5-benzyl-3-hydantoin)-β-phenylpropionic acid, m. p. 234—235° (corr.) and 170° (sintering 90—100°), respectively. Glycine-*N*-carboxylic anhydride gives in the same way a much smaller quantity of hydantoin-3-acetic acid. The hydantoins are probably the result of addition of the decarboxylated residue, $\cdot NH\cdot CHR\cdot CO\cdot$, to the carbimide, $CO{:}N\cdot CHR\cdot CO_2H$, formed by isomerisation of the anhydride. No such by-products are obtained when phenylalanine-*N*-carboxylic anhydride is heated with aniline or methylaniline, the evolution of carbon dioxide being quantitatively that required for formation of



$\left[\text{CH}_2\text{Ph}\cdot\text{CH}<\begin{matrix}\text{NH}\\ |\\ \text{CO}\end{matrix}\right]_n$. C. Hollins.

3 : 5-Hydantoin derivatives as anhydrides of amino-acid diureides. C. Gränacher and H. Landolt (Helv. Chim. Acta, 1927, **10**, 799—815).—The formation of 3 : 5-disubstituted hydantoins, $\overline{\text{CO}\cdot\text{CHR}'\cdot\text{NH}\cdot\text{CO}\cdot\text{N}}\cdot\text{CHR}''\cdot\text{CO}_2\text{H}$, from dipeptides of the type $\text{CO}_2\text{H}\cdot\text{CHR}'\cdot\text{NH}\cdot\text{CO}\cdot\text{NH}\cdot\text{CHR}''\cdot\text{CO}_2\text{H}$, by elimination of 1 mol. of water proceeds smoothly. Carbamidoglycylglycine ester, $\text{NH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}_2\text{Et}$, when heated at 180—190° in a vacuum, affords ammonia and *ethyl hydantoin-3-acetate*, m. p. 120°, which when treated with ammonia gives *carbamidodiacetamide*, $\text{CO}(\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{NH}_2)_2$, m. p. 226—228° (decomp.), also obtainable from ammonia and ethyl carbamidodiacetate. Hydrolysis of the above diacetamide with *N*-hydrochloric acid yields hydantoin-3-acetic acid, m. p. 196—198° (Johnson and Renfrew, A., 1925, i, 583, give m. p. 190—191°), also produced from the above diacetate by treatment with concentrated hydrochloric acid in ether. Hydantoin-3-acetic acid is unaffected by hot hydrochloric acid, but is hydrolysed by *N*-sodium hydroxide to carboxyglycylglycine. *Ethyl* 5-*benzylidenehydantoin*-3-*acetate*, m. p. 174° (free *acid*, m. p. 260°), is reduced by sodium amalgam and a trace of acetic acid in aqueous alcohol to *ethyl* 5-*benzylhydantoin*-3-*acetate*, m. p. 155° (free *acid*, m. p. 181—183°; *acid amide*, m. p. 216—218°). Similarly, *ethyl* 5-p-*anisylidenehydantoin*-3-*acetate*, m. p. 182—183° (free *acid*, m. p. 275°), gives *ethyl* 5-p-*methoxybenzylhydantoin*-3-*acetate*, m. p. 140°. Ethyl α-aminopropionate is converted by carbonyl chloride into *ethyl carbamidodi-α-propionate*, $\text{CO}(\text{NH}\cdot\text{CHMe}\cdot\text{CO}_2\text{Et})_2$, m. p. 152°, which when treated with concentrated hydrochloric acid in ether furnishes α-5-*methylhydantoin*-3-*propionic acid*, m. p. 187—189° after previous sintering. From ethyl carbonyldi-α-amino-γ-methylvalerate (Hugounenq and Morel, A., 1905, i, 178), by distillation at 225—230°/12 mm., there is obtained *ethyl* α-5-iso*butylhydantoin*-3-γ-*methylvalerate*, whilst treatment with hydrochloric acid in ether yields α-5-iso*butylhydantoin*-3-γ-*methylvaleric acid*, m. p. 148° after sintering at 140°.

H. Burton.

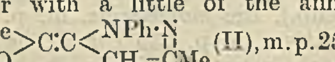
Action of light on the isomeric modifications of certain polypeptide-hydantoins. D. A. Hahn and J. Evans (J. Amer. Chem. Soc., 1927, **49**, 2877—2883).—*Methyl* 4-*benzylidene*-3-*methylhydantoin*-1-*acetate* exists in two stereoisomeric forms, m. p. 65·5—66·5° (I) and 98·5—99·5° (II), respectively. When (I) is exposed to daylight or ultra-violet light in presence of a trace of iodine, it is partly converted into (II) and a *polymeride*, m. p. 276—278° (III), whilst some decomposition takes place with formation of benzaldehyde; (II) yields similarly (I) and (III), the change being preceded by an induction period. 4-*Benzylidene*-3-*methylhydantoin*-1-*acetic acid* also exists in two stereoisomeric forms, m. p. 186·5—187·5° (IV) and 198·5—199·5° (V), respectively. Whilst (IV) does not yield measurable quantities of other products when exposed to light for 5 months, (V) is much more rapidly changed under similar conditions, with production of a small proportion of (IV) and a *polymeride*, m. p. 292—294°, which is also obtained by boiling (II) with hydrochloric acid in glacial acetic acid.

F. G. Willson.

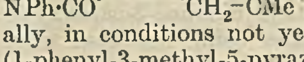
Action of tolylhydrazines on dihydroxytartaric acid. F. D. Chattaway and W. G. Humphrey (J.C.S., 1927, 2793—2796).—The action of *o*- and *p*-tolylhydrazines on dihydroxytartaric acid, unlike that of other hydrazines (A., 1927, 776), yields pure monohydrazones. When *diketosuccinic acid* o-*tolylhydrazone* (I), m. p. 192° (decomp.), is heated with acetic anhydride, the *anhydride* (II), m. p. 208° (decomp.), is obtained. Crystallisation of (II) from dilute acetic acid regenerates (I), whereas crystallisation from anhydrous alcohol yields the *ethyl hydrogen* ester, m. p. 115°, converted by prolonged boiling with alcohol saturated with hydrogen chloride into the *ethyl* ester (III), m. p. 90°. (III) is alternatively prepared by coupling diazotised *o*-toluidine with the potassium derivative of ethyl oxalacetate. *Diketosuccinic acid* p-*tolylhydrazone* [*anhydride*, m. p. 192° (decomp.); *ethyl hydrogen* ester, m. p. 112°] has m. p. 190° (decomp.). The monohydrazones of dihydroxytartaric acid cannot be converted into pyrazoline derivatives. *Diketosuccinic acid* o-*tolylosazone* (IV), m. p. 170° (decomp.), which cannot be crystallised unchanged, yields, with acetic anhydride, the *anhydride* (V), m. p. 198° (decomp.). Crystallisation of (IV) from acetic acid or acidification of its sodium salt yields 4 : 5-*diketo*-1-o-*tolylpyrazoline*-3-*carboxylic acid* 4-o-*tolylhydrazone* (VI), m. p. 229° (decomp.); (V) is also produced in the former case. The *ethyl* ester of (VI), m. p. 145°, is most easily obtained by boiling (IV) with alcohol containing hydrochloric acid. *Diketosuccinic acid* p-*tolylosazone* [*anhydride*, m. p. 230° (decomp.)] has m. p. 175° (decomp.). 4 : 5-*Diketo*-1-p-*tolylpyrazoline*-3-*carboxylic acid* 4-p-*tolylhydrazone* (*ethyl* ester, m. p. 143°) has m. p. 233° (decomp.).

M. Clark.

Autocondensation of 1-phenyl-3-methyl-5-pyrazolone. V. Ionescu and V. Georgescu (Bull. Soc. chim., 1927, (iv), **41**, 1514—1518).—When heated at 200° for 6 hrs. with alcohol and piperidine, 1-phenyl-3-methyl-5-pyrazolone yields the *bis*-derivative,



$\left(\begin{matrix}\text{N}{=}\text{CMe}\\ |\\ \text{NPh}\cdot\text{CO}\end{matrix}>\text{CH}\right)_2\text{C}<\begin{matrix}\text{NPh}\cdot\text{N}\\ \qquad\ \ ||\\ \text{CH}_2{-}\text{CMe}\end{matrix}$ (I), m. p. 262°, together with a little of the anhydro-derivative,



$\begin{matrix}\text{N}{=}\text{CMe}\\ |\\ \text{NPh}\cdot\text{CO}\end{matrix}>\text{C}{:}\text{C}<\begin{matrix}\text{NPh}\cdot\text{N}\\ \qquad\ \ ||\\ \text{CH}_2{-}\text{CMe}\end{matrix}$ (II), m. p. 258°, and occasionally, in conditions not yet determined, a little bis-(1-phenyl-3-methyl-5-pyrazolone), m. p. above 300°. When heated at 280° or treated with cold sulphuric acid (I) is converted into (II) and 1-phenyl-3-methyl-5-pyrazolone, a reaction which confirms the above structures (cf. Mohr, A., 1905, i, 676).

R. Brightman.

Asymmetric nitrogen atom. LIV. Activation of an asymmetric tertiary base in the form of its salts with optically active acids. E. Wedekind and K. A. Klatte (Ber., 1927, **60**, [*B*], 2325—2334).—The activation of derivatives of tervalent nitrogen includes the problems of the fission of nonquaternary salts containing an optically active acid, replacement of the active anion by an optically inactive anion, and final removal of the latter with the production of an optically active, asymmetric, tertiary base. The first of these problems has been partly realised in the 4-aminopyrazolone series. Thus the cautious crystallisation of 4-*methylethylamino*-1-*phenyl*-2 : 3-*dimethylpyrazol*-5-*one* d-*camphorsulphonate*, m. p. 142—143°, from ethyl acetate gives a series of fractions which show distinct progressive change in their molecular rotation in aqueous solution, the calculated values for the cation varying from +35·6° to −15·6°. Similar crystallisation of the corresponding d-*bromocamphor*-π-*sulphonate*, m. p. 187—188°, from a mixture of ethyl acetate and acetone gives a most sparingly soluble fraction the cation of which has $[M]_D$ +49°. In one (non-reproducible) instance, a fraction having $[M]_D$ −253° for the cation was produced from the camphorsulphonate; the rotation of this fraction increased to a maximum and then diminished to zero. Salts containing a lævorotatory cation exhibit a gradual change in rotation with time in the sense that the − sign passes to + or to ±, reaching in the first case a maximal value of +17° for the cation, whilst in the second case the observed rotation, +51°, corresponds with that of the camphorsulphonate ion. A case of racemisation of the optically active nitrogenous cation appears to be realised. The rotation of fractions with dextrorotatory cations is independent of the time and unchanged by hydrogen ions or more protracted exposure to relatively high temperature. The apparent stabilisation of the dextrorotatory basic group by the dextrorotatory acidic component is in harmony with the observations of Wedekind and Ney (A., 1912, i, 501), but an explanation of the mutual influence of the groups is rendered difficult by their presence as ions in the solution. Conversion of the head and tail fractions of the *d*-bromocamphor-π-sulphonate into the perchlorate gives a completely inactive *salt*, m. p. 189—191°. 4-Benzylethylamino-1-phenyl-2 : 3-dimethylpyrazol-5-one gives a d-*camphorsulphonate*, m. p. 132—133°, from which a fraction is derived by crystallisation from ethyl acetate having $[M]_D$ +24° for the active cation.

4-*Methylethylamino*-1-*phenyl*-2 : 3-*dimethylpyrazol*-5-*one*, m. p. 92°, is prepared by treating methylaminoantipyrine with ethyl iodide followed by 10% potassium hydroxide.

H. Wren.

Glyoxalones and glyoxalidones. II. C. Gränacher and G. Gulbas (Helv. Chim. Acta, 1927, 10, 819—826; cf. Gränacher and Mahler, A., 1927, 467).—Reduction of 2-phenyl-4-benzylideneglyoxal-5-one with sodium amalgam and acetic acid in presence of alcohol yields 2-*phenyl*-4-*benzylglyoxalid*-5-*one*, m. p. 145—146°, which when treated with hot *N*-hydrochloric acid gives benzaldehyde, phenylalanine, and phenylalanineamide. α-*Benzamidocinnamic acid ethylamide*, m. p. 187°, prepared from ethylamine and the lactimide of benzylidenehippuric acid in alcoholic solution, when heated at 190—200° in a vacuum affords 2-*phenyl*-4-*benzylidene*-1-*ethylglyoxal*-5-*one*, m. p. 110—112°. α-*Benzamidocinnamic acid benzylamide*, m. p. 173—174°, furnishes 2-*phenyl*-1-*benzyl*-4-*benzylideneglyoxal*-5-*one*, m. p. 143—144°. 1 : 2-*Diphenyl*-4-*benzylideneglyoxal*-5-*one* has m. p. 180°. α-*Benzamidocinnamic acid* iso*propylamide*, m. p. 159—160°, when heated in a vacuum does not give the glyoxalone, but yields the lactimide of benzylidenehippuric acid (cf. Gränacher and Mahler, *loc. cit.*). α-*Benzamido*-p-*methoxycinnamic acid methylamide*, m. p. 219°, gives 2-p-*methoxyphenyl*-4-*benzylidene*-1-*methylglyoxal*-5-*one*, m. p. 163° (the 1-*ethyl* compound, m. p. 103°, is obtained from the *ethylamide*, m. p. 214°). α-Benzamido-*p*-methoxycinnamanilide has m. p. 254° (Wittenberg, Diss., Basel, 1903, gives m. p. 205°). The lactimide of *p*-anisylidenehippuric acid and ethylenediamine react to form *di*-(α-*benzamido*-p-*methoxycinnamic acid*)-*ethylenediamide*, m. p. 236°, which when heated in a vacuum yields a dark yellow *substance*, m. p. 285—286°, apparently formed by elimination of 1 mol. of water only.

H. Burton.

Sulphonation of glyoxalines. III. G. R. Barnes and F. L. Pyman (J.C.S., 1927, 2711—2714).—Oxidation of 2-thiolglyoxaline with hydrogen peroxide (Balaban and King, A., 1927, 977) yields *glyoxaline*-2-*sulphonic acid* (+1H_2O), anhyd. m. p. 303° (corr.) [*barium* salt (+2H_2O)]. This acid differs from the sulphonation product of glyoxaline, which must therefore be glyoxaline-4(5)-sulphonic acid, as previously suggested (J.C.S., 1920, **117**, 1429). Sulphonation of 4(5)-methylglyoxaline yields 4(5)-*methylglyoxaline*-5(4)-*sulphonic acid* (+1H_2O), anhyd. m. p. 278° (corr.) [*sodium* (+3H_2O), *barium* (+3H_2O), and *ammonium* salts], since the product is not identical with 4(5)-methylglyoxaline-2-sulphonic acid (Balaban and King, *loc. cit.*). This acid is readily decomposed by cold bromine water. It fails to react with phosphorus pentachloride at 160°. Like glyoxaline-4(5)-sulphonic acid, it is hydrolysed almost quantitatively when heated for 3 hrs. at 170° with concentrated hydrochloric acid, whereas glyoxaline-2-sulphonic acid shows only a 12% hydrolysis under these conditions.

M. Clark.

Some derivatives of di-(2-pyridyl)amine, and tri-(2-pyridyl)amine. J. P. Wibaut and G. L. C. La Bastide (Proc. K. Akad. Wetensch. Amsterdam, 1927, 30, 664—669).—Di-(2-pyridyl)amine (cf. Tschitschibabin, A., 1915, i, 591; Steinhäuser and Diepolder, A., 1916, i, 740) is also obtained by heating 2-chloropyridine with the sodium derivative of 2-aminopyridine at 170—180°. It is nitrated by warm nitric and sulphuric acids to a *dinitrodipyridylamine*, m. p. 195—196°, and is brominated in acetic acid solution, yielding a *dibromodipyridylamine*, m. p. 191° (*dihydrobromide*, m. p. 253—254°). Treatment of several substituted aminopyridines with 2-halogenopyridines under various conditions does not furnish substituted dipyridylamines. 5-*Bromo*-2-*iodopyridine*, m. p. 117°; 2-*bromo*-5-*iodopyridine*, m. p. 122·5°, and 2 : 5-*diiodopyridine*, m. p. 70·5°, are described. *Tri*-(2-*pyridyl*)*amine*, m. p. 132·5° (*picrate*, m. p. 149°; *mercurichloride*, $C_{15}H_{12}N_4,HCl,HgCl_2$, m. p. 180°), is obtained by heating a mixture of 2-aminopyridine, 2-iodopyridine, mesitylene, potassium hydroxide, potassium, and a trace of copper powder at 150—160°. Tripyridylamine is a feeble base, the order of basicity for the series, determined by conductivity measurements and p_H values, being tri $<$ mono $<$ di.

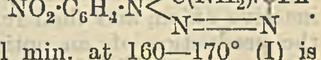
H. Burton.

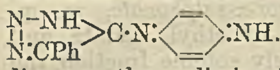
1 : 5-Naphthyridine and certain of its derivatives. L. Klisiecki and E. Sucharda (Rocz. Chem., 1927, 7, 204—217).—7 : 9 : 10-*Trihydroxybenzo*-1 : 5-*naphthyridine*, m. p. 378° (*acetyl* derivative, m. p. 338°), is prepared by the condensation of aminopicolinic acid with phloroglucinol. Oxidation with fuming nitric acid yields 8-*hydroxy*-1 : 5-*naphthyridine*-6 : 7-*dicarboxylic acid*, decomposing at 170—180° to yield 8-*hydroxynaphthyridine*-7-*carboxylic acid*, which at 340° is converted into 8-*hydroxy*-1 : 5-*naphthyridine*; this sublimes without decomposition at 340° and yields on reduction 1 : 5-*naphthyridine*, m. p. 74°. Dilute nitric acid yields also 6 : 8-*dinitro*-7 : 9 : 10 - *trihydroxybenzo* - 1 : 5 - *naphthyridine*, decomposing explosively at 277°.

R. Truszkowski.

Preparation of carbocyanine dyes. F. M. Hamer (J.C.S., 1927, 2796—2804).—The names thiocarbocyanine (cf. Mills, J.C.S., 1922, **121**, 455), oxacarbocyanine, and indocarbocyanine are suggested for the carbocyanine dyes derived from benzthiazole, benzoxazole, and indolenine, respectively. Carbocyanine dyes of every known type are prepared in optimum yield by condensation in boiling pyridine solution of ethyl orthoformate with the appropriate quaternary salt containing a reactive methyl group. The solvent must be dry and four times the calculated quantity of ester is required. No carbocyanine containing two pyridine nuclei has yet been isolated. 2-Methylpyridine ethiodide does not condense with ethyl orthoformate in presence of boiling pyridine. The indocarbocyanines and oxacarbocyanines act, like other cyanine dyes, as photographic sensitisers. The following are described: 2 : 6-*dimethylquinoline alliodide*, m. p. 198—199° (decomp.) [*allobromide*, m. p. 214—215° (decomp.)]; 6 : 6′-*dimethyl*-1 : 1′-*diallyl*-2 : 2′-*carbocyanine iodide*, m. p. 280—281° (decomp.) [*bromide*, m. p. 281—282° (decomp.)]; 1 : 1′-dimethyl-4 : 4′-carbocyanine iodide, m. p. 290—295° (decomp.); *lepidine alliodide*; 1 : 1′-*diallyl*-4 : 4′-*carbocyanine iodide*, decomp. 150°; 2 : 2′-dimethylthiocarbocyanine iodide, m. p. about 280° (decomp.) (lit. 254°); 1-*methylbenzthiazole allobromide*, m. p. 202° (decomp.); 2 : 2′-*diallylthiocarbocyanine bromide*, m. p. about 260° (decomp.); 2 : 2′ - dimethyloxacarbocyanine iodide, m. p. 275—277° (decomp.) (lit. 259°); 1-*methylbenzoxazole ethiodide*, m. p. 195—197° (decomp.); 2 : 2′-*diethyloxacarbocyanine iodide*, m. p. 277—279° (decomp.); 3 : 3 : 3′ : 3′-*tetramethyl*-1 : 1′-*diethylindocarbocyanine iodide*, pleochroic, m. p. 260—263° (decomp.). Absorption spectra and sensitising action are described.

M. Clark.

Intramolecular change in 5-amino-1 : 2 : 3-triazoles. O. Dimroth and W. Michaelis (Annalen, 1927, 459, 39—46).—A reply to Dutt (J.C.S., 1923, **123**, 265) and Carnelley and Dutt (A., 1925, ii, 165). *p*-Nitrophenyl azide condenses with phenylacetonitrile in presence of sodium ethoxide to give 4-*phenyl*-1-p-*nitrophenyl*-5-*amino*-1 : 2 : 3-*triazole* (I), m. p. 182°, which is strongly basic (*hydrochloride*). It was diazotised and coupled with β-naphthol and then gave an *azo*-compound, m. p. 220—225° (decomp.), which must have the formula  $NO_2\cdot C_6H_4\cdot N<\begin{matrix}C(NH_2):CPh\\ N\text{===}N\end{matrix}$.
When heated for several min. at 160—170° (I) is converted into the isomeric 5-p-*nitroanilino*-4-*phenyl*-1 : 2 : 3-*triazole* (II), m. p. 164°. Stannous chloride converts (I) into 4-*phenyl*-1-p-*aminophenyl*-5-p-*amino*-1 : 2 : 3-*triazole*, m. p. 166°, and (II) into 5-*amino-anilino*-4-*phenyl*-1 : 2 : 3-*triazole*, m. p. 177° (*hydrochloride*), which by fusion is converted into its isomeride, m. p. 166°. The structure assigned to the amine, m. p. 177°, is confirmed by its ready oxidation with ferric chloride to the *quinoneimine*

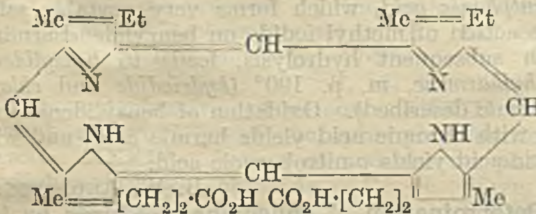


These facts are held to disprove the endimino-type of formulæ applied by Carnelley and Dutt (*loc. cit.*) to these compounds.

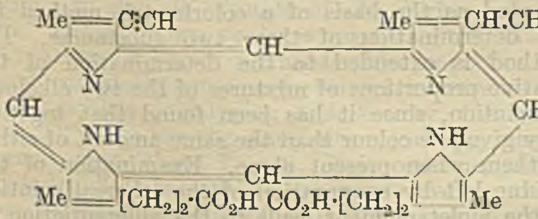
J. W. Baker.

Syntheses of mesoporphyrin, mesohæmin, and the constitution of hæmin. (Synthesis of porphyrins. XIII.) H. Fischer and G. Stangler (Annalen, 1927, 459, 53—98).—The synthesis of the four possible isomerides of ætioporphyrin has been effected by methods which prove their structure. One isomeride, 1 : 3 : 5 : 7-tetramethyl-2 : 4 : 6 : 8-tetraethylporphin, m. p. 400—405°, has previously been synthesised (Fischer and Klarer, A., 1926, 962). The second, 1 : 4 : 5 : 8 - tetramethyl - 2 : 3 : 6 : 7-tetraethylporphin, identical with *iso*ætioporphyrin (Fischer and Halbig, A., 1926, 963; Fischer, Halbig, and Walach, A., 1927, 469), is synthesised as follows: ethyl propionylacetate is converted into its *iso*nitroso-derivative which, when reduced with zinc dust in the presence of ethyl acetoacetate, affords *ethyl* 2-*methyl*-4-*ethylpyrrole*-3 : 5-*dicarboxylate*, m. p. 115°. This by hydrolysis of the β-ester group with concentrated sulphuric acid at 40° yields the 3-*carboxylic acid*, m. p. 245°, which, by loss of carbon dioxide, yields *ethyl* 2-*methyl*-4-*ethylpyrrole*-5-*carboxylate*, converted by means of hydrogen cyanide and hydrogen chloride into the 3-aldehyde; this is reduced by hydrazine hydrate to hæmopyrrole. The latter reacts with magnesium ethyl bromide and ethyl chloroformate to give *ethyl* 2 : 3-*dimethyl*-4-*ethylpyrrole*-5-*carboxylate*, m. p. 97°, from which the free *acid*, m. p. 142° (decomp.), is obtained on hydrolysis. Bromination converts the latter into the *hydrobromide*, m. p. 115° (decomp.), of *ethyl* 2-*bromomethyl*-3-*methyl*-4-*ethylpyrrole*-5-*carboxylate*, m. p. 134°, from which *bis*-(3-*methyl*-4-*ethyl*-5-*carbethoxypyrryl*)*methane* (I), m. p. 148°, is obtained by heating with methyl alcohol. This is hydrolysed to the corresponding *acid*, m. p. 211°, which by aëration in formic acid yields *iso*ætioporphyrin, m. p. 365°. Bromination of (I) yields the *hydrobromide* of *bis*-(2-*bromo*-3-*methyl*-4-*ethyl*-5-*pyrryl*)*methene* (II), m. p. 180° (*picrate*, m. p. 169°), which when heated with bis-(2 : 4-dimethyl-3-ethyl-5-pyrryl)methene and hydrogen bromide in acetic acid at 150° yields the same *iso*ætioporphyrin. The third isomeride, 1 : 3 : 5 : 8-tetramethyl-2 : 4 : 6 : 7-tetraethylporphin, is synthesised as follows: cryptopyrrolealdehyde condenses with hæmopyrrole in warm alcoholic hydrogen chloride to give the *hydrochloride* of (4 : 5-*dimethyl*-3-*ethylpyrryl*)-(2 : 4-*dimethyl*-

3-*ethylpyrrolenyl)methene*, m. p. 80° [*picrate*, m. p. 185° (decomp.)], which when heated with bis-(2-bromo-3-methyl-4-ethyl-5-pyrryl)methene and hydrogen bromide in acetic acid at 140°/12—14 atm. yields the *ætioporphyrin*, m. p. 360° (*copper* and *iron* salts; *hexabromo*-compound). The same isomeride is obtained by heating (2-*bromomethyl*-3-*methyl*-4-*ethylpyrryl*)-(2-*bromomethyl*-4-*methyl*-3-*ethylpyrrolenyl*)-*methene hydrobromide* (III), decomp. above 230° (obtained by dibromination of the corresponding methene), and bis-(2-bromo-3-methyl-4-ethyl-5-pyrryl)methene hydrobromide or bis-(2-bromo-4-methyl-3-ethylpyrryl)methene hydrobromide with succinic acid at 190°. The fourth isomeride, 1 : 4 : 6 : 7-tetramethyl-2 : 3 : 5 : 8-tetraethylporphin, m. p. 355° (Fischer, Halbig, and Walach, *loc. cit.*), is similarly obtained from (II) and (2-*bromomethyl*-3-*methyl*-4-*ethylpyrryl*)-(2-*bromomethyl*-3-*methyl*-4-*ethylpyrrolenyl*)-*methene hydrobromide* (IV) (by dibromination of the corresponding methene). When (III) is heated with the hydrobromide of bis-(2-bromo-3-methyl-4-β-carboxyethyl-5-pyrryl)methene (V) and succinic acid at 175—180°, mesoporphyrin, identical in all respects with a pure specimen, is obtained, and has, therefore, the constitution,



When the hydrochloride is heated in acetic acid solution with ferrous acetate, mesohæmin is obtained and therefore the position of the side-chains in hæmin must be the same, the constitution



being assigned to it (cf. Fischer and Lindner, A., 1927, 261). By a similar condensation of (V) with (IV) is obtained *iso*mesoporphyrin, isolated as its *methyl* ester, m. p. 275—279°. Bromination of hæmopyrrole in acetic acid yields the *perbromide* of (2-bromo-4-methyl-3-ethylpyrryl)-(2 : 3-dimethyl-4-ethylpyrrolenyl)methene, m. p. 141°, from which the free *methene*, m. p. 125°, is obtained by the action of sodium hydroxide on a chloroform solution. The same methene is obtained by bromination, with loss of carbon dioxide, of 2 : 3-dimethyl-4-ethylpyrrole-5-carboxylic acid. Further bromination affords (2-*bromo*-4-*methyl*-3-*ethylpyrryl*)-(2-*bromomethyl*-3-*methyl*-4-*ethylpyrrolenyl*)*methene hydrobromide*, decomp. 240°. The methene when heated with formic acid gives the ætioporphyrin, m. p. 400°. Bromination of ethyl 2-methyl-4-ethylpyrrole-3 : 5-dicarboxylate in acetic acid or carbon tetrachloride yields the corresponding -2-*bromomethyl* derivative, m. p. 156°, which, when heated with water, gives formaldehyde and *bis*-(4-*ethyl*-3 : 5-*dicarbethoxypyrryl*)-2 : 2′-*methane*, m. p. 130°. By the action of nitrous acid and zinc dust on ethyl propionylacetate is obtained *ethyl* 2 : 4-*diethylpyrrole*-3 : 5-*dicarboxylate*, m. p. 97°, from which, by hydrolysis of the β-carbethoxyl group, the corresponding 3-*carboxylic acid*, m. p. 220°, is obtained. This, on dry distillation, yields *ethyl* 2 : 4-*diethylpyrrole*-5-*carboxylate*, m. p. 49°, which is converted by hydrogen cyanide and hydrogen chloride into the corresponding 3-*aldehyde*, m. p. 84°; this is reduced by hydrazine hydrate, sodium, and alcohol at 160° to 3-methyl-2 : 4-diethylpyrrole. When a mixture of ethyl 2-methyl-4-ethyl-3-aldehydopyrrole-5-carboxylate, malonic acid, and aniline is heated in alcohol solution, *ethyl* 2-*methyl*-4-*ethyl*-3-β-*carboxyvinylpyrrole*-5-*carboxylate*, m. p. 240°, is obtained, reduced by sodium amalgam and ice water to the corresponding 3-*propionic acid* (3-β-*carboxyethyl* derivative), m. p. 148°. When heated at its m. p. the acrylic acid loses carbon dioxide and yields *ethyl* 3-*vinyl*-2-*methyl*-4-*ethylpyrrole*-5-*carboxylate*, m. p. 79°, which on catalytic reduction with platinum-black affords *ethyl* 2-*methyl*-3 : 4-*diethylpyrrole*-5-*carboxylate*, m. p. 75° (also obtained by a Grignard reaction from 2-methyl-3 : 4-diethylpyrrole). By the action of nitromethane on ethyl 2-methyl-4-ethyl-3-aldehydopyrrole-5-carboxylate with dimethylamine hydrochloride as a condensing agent is obtained 3-*nitrovinyl*-2-*methyl*-4-*ethylpyrrole*-5-*carboxylate*, m. p. 199° (corr.). Hæmopyrrole condenses with ethyl cyanoformate in the presence of hydrogen chloride to give the *imine hydrochloride*, m. p. 146°, from which *ethyl* 2 : 3-*dimethyl*-4-*ethylpyrrole*-5-*glyoxylate*, m. p. 83°, is obtained. The free *acid*, m. p. 191° (decomp.), when heated at 190° in a vacuum yields *hæmopyrrolealdehyde*, m. p. 85°; the latter is also obtained by the action of hydrogen cyanide and hydrogen chloride on hæmopyrrole. These products serve as intermediates for the synthesis of coproporphyrins. J. W. Baker.

Condensation of *o*-aminothiophenol with αβ-unsaturated acids. W. H. Mills and J. B. Whitworth (J.C.S., 1927, 2738—2753).—When *o*-aminothiophenol and αβ-unsaturated acids are heated together in an atmosphere of carbon dioxide, β-addition of the thiol group to the ethylenic linking occurs and water is eliminated, giving 4-ketotetrahydro-1 : 5-heptabenzthiazine derivatives. 4-*Ketotetrahydro*-1 : 5-*heptabenzthiazine*-2-*acetic acid*, m. p. 235—236° (*ethyl* ester, m. p. 139—140°), obtained from the thiophenol and glutaconic acid, is resolved by brucine and cinchonine into d-4-*ketotetrahydro*-1 : 5-*heptabenzthiazine*-2-*acetic acid*, m. p. 230°, $[\alpha]_{5780}^{20}$ +436·9° in alcohol (l-*brucine* salt, m. p. 164—165°; *ethyl* ester, m. p. 145—146°, $[\alpha]_{5780}^{20}$ +425·5°), and the corresponding l-*acid*, m. p. 229—230°, $[\alpha]_{5780}^{20}$ —435·5° (d-*cinchonine* salt, m. p. 193—195°). Condensation of *o*-aminothiophenol with ethyl α-bromoglutarate yields the isomeric *ethyl* 3-*keto*-2 : 3-*dihydro*-1 : 4-*benzthiazine*-2-*propionate*, m. p. 91°. Cinnamic acid and *o*-aminothiophenol react on heating at 160—170° to give 4-*keto*-2-*phenyltetrahydro*-1 : 5-*heptabenzthiazine*, m. p. 177° (*acetyl* derivative, m. p. 155—156°; *sulph*-

oxide, m. p. 210°; *sulphone*, m. p. 234—235°). Careful heating with small excess of potassium hydroxide solution hydrolyses this benzthiazine to o-*cinnamamidothiophenol*, m. p. 147—148° (*mercurichloride*, m. p. 211—212°), which is reconverted into the benzthiazine on heating at 165—170°. *oo'-Dicinnamamidodiphenyl disulphide*, m. p. 163—164° [*dibromo*-derivative, m. p. 213° (decomp.)], readily formed by oxidation of *o*-cinnamamidothiophenol, is also obtained by reaction of cinnamoyl chloride with *oo'*-diaminodiphenyl disulphide. α-Bromo-β-phenylpropionic acid and ethyl cinnamate each condense with *o*-aminothiophenol, yielding 3-*keto*-2-*benzyl*-2 : 3-*dihydro*-1 : 4-*benzthiazine*, m. p. 159—160°, whilst cinnamoyl chloride and sodium *o*-aminothiophenoxide in absolute alcohol yield 2-styrylbenzthiazole (*picrate*, m. p. 195—196°). This base is also formed when 4-keto-2-phenyltetrahydro-1 : 5-heptabenzthiazine is heated at 240—260° and when cinnamic acid and *o*-aminothiophenol are heated at 210—220°. β-Phenylpropionic acid and *o*-aminothiophenol yield 2-β-*phenylethylbenzthiazole*, m. p. 60—61° (*picrate*, m. p. 132—133°). Crotonic acid reacts with the thiophenol, giving 4-*keto*-2-*methyltetrahydro*-1 : 5-*heptabenzthiazine*, m. p. 205—206° (*acetyl* derivative, m. p. 93°). Acrylic acid and the thiophenol yield 4-ketotetrahydro-1 : 5-heptabenzthiazine, m. p. 215—216° (215—216°), identical with the ε-lactam of *o*-aminophenylthiolpropionic acid, m. p. 87—88° (84°). The hydrochloride, m. p. 173—174° (189°), of this amino-acid is obtained by reduction of *o*-nitrophenylthiolpropionic acid, m. p. 148—149° (145°), which is formed by condensation of acrylic acid and *o*-nitrothiophenol in presence of piperidine. The m. p. given by Mayer and Horst (A., 1923, i, 844) for these compounds are shown in brackets. Maleic, fumaric, and monobromosuccinic acids condense with *o*-aminothiophenol, giving 3-*keto*-2 : 3-*dihydro*-1 : 4-*benzthiazine*-2-*acetic acid*, m. p. 195—196°.

[With G. E. WATTS.]—*o*-Aminothioanisole yields with acetic anhydride a *diacetyl* derivative, m. p. 69—70°. Reduction of *ethyl* o-*nitrophenylthiolformate*, a yellow oil decomposing when heated in a vacuum, gives *ethyl*-o-*aminophenylthiolformate* (*hydrochloride*, m. p. 120—122°). This amino-ester, mixed with a little of its hydrochloride and heated at 115°, gives benzthiazolone, which is readily acetylated. M. CLARK.

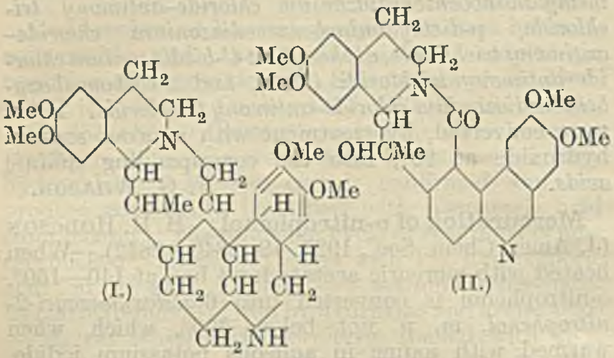
Quaternary salts in the benzselenazole series. L. M. CLARK (J.C.S., 1927, 2805—2809; cf. *ibid.*, 1923, **123**, 2353).—The zinc salt of *o*-aminoselenophenol, which reacts with benzoyl chloride to give phenylbenzselenazole (Bauer, A., 1913, i, 263), reacts similarly with formic acid, giving *benzselenazole* (I), b. p. 154°/45 mm. (*methiodide*, m. p. 188—189°; *methopicrate*, m. p. 173°). The *methiodide*, m. p. 211—212° (decomp.), and *chloroplatinate* of 2-phenylbenzselenazole (II) are described. The methiodides of (I) and (II) react with two equivalents of sodium hydroxide, giving first the carbinol base and afterwards the sodium salt of the ψ-base $COR\cdot NMe\cdot C_6H_4\cdot SeNa$. Oxidation with iodine or potassium ferricyanide then yields *di*-o-*formylmethylaminodiphenyl diselenide*, m. p. 104°, and *di*-o-*benzoylmethylaminodiphenyl diselenide* (III), m. p. 170°, respectively. Atmospheric oxidation of the methiodide of (I) in ammoniacal solution gives *di*-o-*methylaminodiphenyl diselenide*, m. p. 89°, yielding on benzoylation the compound (III). *Di*-o-*formamidodiphenyl diselenide*, m. p. 174°, obtained as a by-product in the preparation of benzselenazole, is reduced in alcoholic solution by stannous chloride, yielding some benzselenazole by intermediate production of *o*-formamidoselenophenol. When di-*o*-formamidodiphenyl diselenide is heated with phenyl hydrazine, the formyl groups are readily removed with formation of α-formylphenylhydrazine. A satisfactory method for the determination of selenium in organic compounds of this type is described. M. CLARK.

Properties of benzylideneharmine. V. HASENFRATZ and R. SUTRA (Compt. rend., 1927, **185**, 1048—1050).—Benzylideneharmine reacts with bromine to give two isomeric *hydrobromides*, from which α- and β-*bromobenzylideneharmines*, m. p. 230° and decomp. about 125°, respectively, are obtained. These yield insoluble *chloroplatinates*. A solution of benzylideneharmine in sulphuric acid, when poured into water, gives a precipitate of *benzylideneharmine*-N-*sulphonic acid*, which forms very unstable salts. The action of methyl iodide on benzylideneharmine, with subsequent hydrolysis, leads to *benzylidenemethylharmine*, m. p. 190° (*hydriodide* and *chloroplatinate* described). Oxidation of benzylideneharmine with chromic acid yields harmic acid, and with nitric acid yields *p*-nitrobenzoic acid. B. W. ANDERSON.

Determination of ephedrine mixtures by the biuret reaction. C. T. FENG (Chinese J. Physiol., 1927, **1**, 397—406).—The ether-soluble violet pigment obtained by performing the biuret reaction on solutions of ephedrine and ψ-ephedrine has been adapted as the basis of a colorimetric method for the determination of these two substances. The method is extended to the determination of the relative proportions of mixtures of the two alkaloids in solution, since it has been found that together they give less colour than the same amount of either of them when present alone. Examination of the residue left by evaporation of the ethereal solution of the violet pigment leads to the differentiation of ephedrine in solution from ψ-ephedrine; the former leaves a gelatinous residue, the latter rhombic, violet crystals. E. A. LUNT.

Alkaloids of ipecacuanha. H. STAUB (Helv. Chim. Acta, 1927, **10**, 826—837; cf. Späth and Leithe, A., 1927, 471; Brindley and Pyman, *ibid.*, 682).—Emetine hydrobromide, $C_{29}H_{40}O_4N_2,2HBr$ (cf. Carr and Pyman, J.C.S., 1914, **105**, 1591), becomes yellow at 210° and melts to an orange liquid at 248°. Oxidation of emetine with bromine (cf. Carr and Pyman, *loc. cit.*) yields rubremetine bromide, $C_{29}H_{33}O_4N_2Br$ (*methiodide* $+5H_2O$, m. p. 199° after sintering at 174°), which crystallises with 2, 3, or $6H_2O$, according to the solvent used for crystallisation, and is anhydrous from acetone. Careful oxidation of rubremetine bromide with alkaline potassium permanganate yields *dihydroxyrubremetine*, $C_{29}H_{28}O_6N_2$, m. p.

above 305°, a "*substance* D," $C_{29}H_{34}O_{13}N_2$, decomp. 244° after darkening at 220°, and *m*-hemipinimide.


(I.) (II.)

Formula (I) is suggested for emetine and formula (II) for dihydroxyrubremetine. H. Burton.

Oxyquinine and peroxyquinine. Frèrejacque (Compt. rend., 1927, 185, 1052—1055).—In the course of preparation of oxyquinine a *peroxyquinine*, $C_{20}H_{24}N_2O_2{\cdot}O_2,CHCl_3$ (?), m. p. 153°, $[\alpha]_D$ −60°, was isolated, having all the properties of a peroxide, but losing them on recrystallisation from acetone. The *N*-oxyquinine prepared by the author differed from Speyer and Becke's product (cf. A., 1922, 674) in having m. p. 188° and $[\alpha]_D$ −17·5°.

B. W. Anderson.

Organic derivatives of silicon. XXXIII. An amorphous variety of octaphenyl*cyclo*silicotetrane. XXXIV. Action of sodium on phenoxydiphenylsilicyl chloride. F. S. Kipping (J.C.S., 1927, 2719—2728, 2728—2734).—XXXIII. Acetone solutions of the product (*E*) originally obtained, together with the four (*A*, *B*, *C*, *D*) silicohydrocarbons $[SiPh_2]_n$, by heating diphenylsilicon dichloride with sodium (J.C.S., 1921, **119**, 830), continue to deposit crystals of (*B*) during several years. (*E*) is shown to be a mixture of a silicohydrocarbon (E_1) with a considerable proportion of oxygen-containing compounds, arising from impurity in the dichloride (Kipping and Murray, following abstract). (E_1) has the composition $[SiPh_2]_n$, where *n* ranges from about 7 to 9; it is resinous, melts very indefinitely below 150°, is miscible with acetone, ether, benzene, and chloroform, and behaves like (*B*) towards iodine and nitric acid. When (*B*) is heated for a few secs. above 400°, it melts to a transparent mass, readily soluble in cold acetone; the solution after an interval deposits crystals of (*B*) and the mother-liquors then give with alcohol a flocculent precipitate of an amorphous silicohydrocarbon $[SiPh_2]_n$, closely resembling (E_1). It is concluded that (E_1) is an allotropic form of octaphenyl*cyclo*silicotetrane (*B*), in which the molecules of the (*B*) form have become so entangled by interlocking of the phenyl groups that relatively stable aggregates incapable of forming crystals have been formed. In a single experiment, which could not be repeated, when (*E*) was heated slowly to about 400°, a considerable proportion of (*B*) separated in crystals. When (*E*) is distilled under 5 mm. pressure, a small quantity of oil is obtained. The latter yields triphenylsilicol on oxidation or on treatment with acetone and alkali, hydrogen being evolved in the latter case. This compound is not obtained from unheated (*E*) under similar conditions. The silico-hydrocarbon $[SiPh_2]_n$ is apparently very slowly decomposed at high temperatures, decomposition being accompanied by a transference of phenyl groups from one silicum atom to another, giving triphenylsilicyl $SiPh_3$ or some other compound containing this group.

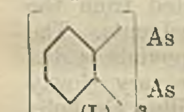
XXXIV. *Phenoxydiphenylsilicyl chloride* (I), b. p. 252—254°/40 mm., and *diphenoxydiphenylsilicane* (II), m. p. 70—71°, are obtained by interaction of phenol and diphenylsilicon dichloride. The compound (I) is immediately soluble in a 5% solution of potassium hydroxide, giving the potassium derivatives of phenol and diphenylsilicanediol. The compound (II) is relatively stable towards 5% sodium hydroxide solution, but is very readily hydrolysed in presence of acetone or alcohol with separation of trianhydrotrisdiphenylsilicanediol. The compound (I) reacts with sodium in hot toluene solution, giving a complex mixture from which octaphenylsilicotetrane, *diphenoxyoctaphenylsilicotetrane* (III), m. p. 215—216°, and diphenoxydiphenylsilicane were extracted by the use of anhydrous solvents. Phenol, diphenylsilicanediol, *hydroxyphenoxyoctaphenylsilicotetrane* (or the corresponding oxide) and *diphenoxytetraphenylsilicoethane* (?) were extracted from the remaining material, using undried solvents. The mechanism of formation of these compounds is discussed. The compound (III) is only very slowly hydrolysed by hydrochloric acid in boiling alcoholic solution, but is completely decomposed by an aqueous solution of piperidine and sodium hydroxide, giving hydrogen and the sodium derivatives of phenol and diphenylsilicanediol. M. Clark.

Organic derivatives of silicon. XXXV. Preparation of diphenylsilicon dichloride: "Grignard" ether and its action on silicon tetrachloride. F. S. Kipping and A. G. Murray (J.C.S., 1927, 2734—2737).—The impurities (up to 20%) present in diphenylsilicon dichloride prepared by the action of magnesium phenyl bromide on silicon tetrachloride (J.C.S., 1912, **101**, 2113) are ascribed to three possible sources: (1) phenylphenoxysilicon dichloride or diphenylphenoxysilicyl chloride, arising from partial oxidation of the Grignard reagent (A., 1921, i, 140); (2) *diethoxydiphenylsilicane*, b. p. 197—198°/50 mm., 302—304°/767 mm., or ethoxydiphenylsilicyl chloride, formed by reaction of diphenylsilicon dichloride with alcohol present in the "Grignard" ether; (3) ethoxydiphenylsilicyl chloride arising from the interaction product of ether and silicon tetrachloride. Even at the ordinary temperature these substances show slight reaction, probably thus: $SiCl_4+Et_2O \longrightarrow OEt{\cdot}SiCl_3+EtCl$. The b. p. of the ethoxychloride may be expected to approximate still more closely to that of the dichloride than that of diethoxydiphenylsilicane. Separation by distillation would therefore be impossible. An improved method for the preparation of diphenylsilicon dichloride, limiting the operation of these three sources of impurity, is described. The product still contains, however, a small amount of some ethoxy-compound. M. Clark.

Arseno-organic compounds. E. Grischkievitch-Trochimovski, L. Matejak, and W. Zabłocki (Rocz. Chem., 1927, 7, 230—240).—The following substances were prepared : *Phenyldicyanoarsine*, m. p. 78·5—79·5°, by the action of silver cyanide on phenyldichloroarsine, *α-naphthyldicyanoarsine*, m. p. 159·5—160·5°, *di-α-naphthylcyanoarsine*, m. p. 191·5—192·5°, *methyldicyanoarsine*, m. p. 115·5—116·5°, from cacodyl cyanide and cyanogen bromide, and *phenarsazine cyanide*, m. p. 227—228°. All the above dicyano-derivatives are readily converted by water into the corresponding acids and hydrogen cyanide.
R. Truszkowski.

Manufacture of organic compounds of arsenic. R. W. E. Stickings, and May and Baker, Ltd.—See B., 1927, 925.

Organic compounds of arsenic. III. Tri-o-phenylenediarsine. N. P. McCleland and J. B. Whitworth (J.C.S., 1927, 2753—2757).—Diazotised *o*-aminodiphenylarsinic acid couples with phenylarsenious oxide, giving *phenylene*-1 : 2-*diphenylarsinic acid*, unmelted at 310°. Distillation of the product obtained by reduction of this compound with phosphorus trichloride gives *tri*-o-*phenylenediarsine* (regarded as being I), m. p. 295—296° (*mercurichloride*, m. p. 285—286°; *oxide*, unmelted at 360°; *tetrabromide* (II), m. p. 255—256°). The tetrabromide (II) is decomposed when heated under reduced pressure, giving, in addition to bromine and triphenylenediarsine, *o*-dibromobenzene and arsanthrene bromide. Distillation of arsanthrene oxide gives triphenylenediarsine and arsenious oxide. Crystallographic data for the compound (I) are given.
M. Clark.



(I.)

Azo dyes containing antimony. II. F. Dunning and E. E. Reid (J. Amer. Chem. Soc., 1927, 49, 2869—2877; cf. A., 1927, 65).—*p*-Aminophenylstibinic acid is obtained in about 50% yield by diazotising *p*-aminoacetanilide in presence of antimony trioxide and sufficient hydrochloric acid to dissolve the latter, with subsequent decomposition of the resulting precipitated diazonium chloride–antimony trichloride additive product (cf. May, J.C.S., 1912, 101, 1037) with alkali. Dyes were prepared by coupling diazotised *p*-aminophenylstibinic acid with *dimethylaniline*, brown, *diethylaniline*, purple, *α-naphthol-4-sulphonic acid*, dark red, 2 : 5-*aminonaphthol*-7-*sulphonic acid*, light reddish-brown, 2-*naphthylamine*-3 : 6-*disulphonic acid*, dark brown, 1 : 8-*aminonaphthol*-3 : 6-*disulphonic acid* (*sodium* salt, purple), 2-*naphthol*-3 : 6-*disulphonic acid* (*sodium* salt, orange-brown) and 1 : 8-*dihydroxynaphthalene*-3 : 6-*disulphonic acid* (*sodium* salt, purple). The first two of the above dyes, as well as the six previously prepared (*loc. cit.*), are practically non-toxic to *Trypanosoma equiperdum* in white rats, but the remainder exhibit definite curative properties. Dyeings on wool and cotton with the above products and certain others not isolated indicate that they give fast shades on cotton directly, and that the stibinic acid group is more strongly auxochromic than the sulphonic group. The following additive compounds, obtained by diazotising the appropriate amines in presence of an equivalent of antimony trioxide and excess of hydrochloric acid, were prepared : p-*dimethylaminobenzenediazonium chloride–antimony trichloride*, p-*diethylaminobenzenediazonium chloride–antimony trichloride*, *diphenyl*-4 : 4′-*bisdiazonium chloride–antimony trichloride* (1 : 2), and o-*carbomethoxybenzenediazonium chloride–antimony trichloride.* These were converted, by treatment with aqueous sodium hydroxide at 90°, into the corresponding *stibinic acids.*
F. G. Willson.

Mercuration of o-nitrophenol. H. H. Hodgson (J. Amer. Chem. Soc., 1927, 49, 2840—2842).—When heated with mercuric acetate for 4 hrs. at 140—150°, *o*-nitrophenol is converted into 6-*acetoxymercuri*-2-*nitrophenol*, m. p. not below 300°, which, when warmed with iodine in aqueous potassium iodide, affords 6-*iodo*-2-*nitrophenol*, m. p. 110°. The latter yields quantitatively 4 : 6-di-iodo-2-nitrophenol when treated with iodine and mercuric oxide in glacial acetic acid. Treatment of the 3-acetoxymercuri-2-nitrophenol obtained by the method of Raiziss and Proskouriakoff (A., 1922, i, 604) with iodine and potassium iodide as above yields 4-iodo-2-nitrophenol, 4 : 6-di-iodo-2-nitrophenol, and a small proportion of 6-iodo-2-nitrophenol. *Sodium* 6-*hydroxymercuri*-2-*nitrophenoxide*, scarlet, is converted by the appropriate aqueous halogen acids into 6-*fluoro*-, m. p. 187°, 6-*chloro*-, m. p. 185°, and 6-*bromo-mercuri*-2-*nitrophenol*, m. p. 177°. 4-*Fluoro*-, m. p. 195°, 4-*chloro*-, m. p. 205°, and 4-*bromo-mercuri*-2-*nitrophenol*, m. p. 236°, were prepared analogously. 6-*Iodo*-, m. p. 215°, and 4-*iodo-mercuri*-2-*nitrophenol*, m. p. above 300°, were obtained by addition of sulphuric acid to solutions of the appropriate sodium salts in presence of potassium iodide.
F. G. Willson.

Reaction of complex chromium salts with magnesium phenyl bromide. F. Hein and F. Pintus (Ber., 1927, 60, [*B*], 2388—2390; cf. A., 1927, 549).—In confirmation of previous observations (*loc. cit.*) the compounds $[CrCl_3(EtOH)_3]$, $[CrCl_3[CS(NH_2)_2]_3]$, and $[CrBr_3(C_5H_5N)_3]$, all of which contain the three halogen atoms in direct, non-ionic union with the central atom, react with magnesium phenyl bromide giving compounds regarded as salts of chromium tri-, tetra-, and penta-phenyl hydroxide.
H. Wren.

Side-chain reactions of hæmatin. Conversion of α-hæmatin into hæmatoporphyrin methyl ether, and Mörner's method for preparation of hæmatin. O. Schumm (Z. physiol. Chem., 1927, 170, 161—166; cf. Schumm and Mertens, A., 1927, 685).—Priority against Fischer and Lindner (A., 1927, 886) is defended.
C. Hollins.

Porphyratin of yeast. IV. Iron porphyratin from oats and yeast. O. Schumm [with E. Mertens] (Z. physiol. Chem., 1927, 170, 1—5; cf. A., 1926, 1277).—The iron-free porphyratin prepared from flaked oats is identical with hæmatin of animal origin; it shows the same solubilities, the same solution colour and absorption spectra; the hydrochloride, methyl and ethyl esters, and the iron and copper complex compounds all agree in properties with the corresponding hæmatin derivatives. The higher

plants are therefore able to synthesise a hæmatin having all the known properties of blood hæmatin.
C. Hollins.

Conversion of hæmatoporphyrin into hæmateric acid, and the "reversible" side-chain reaction of hæmatin. O. Schumm [with E. Mertens] (Z. physiol. Chem., 1927, **170**, 6—12; cf. A., 1927, 685, 886).—The conversion of Nencki's hæmatoporphyrin into hæmateric acid by means of 25% hydrochloric acid (*loc. cit.*) is confirmed and the product completely identified with hæmateric acid from hæmin. The following cycle of reactions is now established: hæmatin (boiled with 1% hydrochloric acid in methyl alcohol) → tetramethylhæmatohæmatin (removal of iron by hydrazine and acetic acid) → tetramethylhæmatoporphyrin (boiled with 25% hydrochloric acid) → hæmateric acid (converted into iron complex salt) → hæmatin. The cycle of reactions is applicable also to iron porphyratins of vegetable origin, but not to phyllohæmin-β. The second and fourth phases may be omitted, tetramethylhæmatohæmatin being converted directly into hæmatin by 25% hydrochloric acid. Methyl-alcoholic hydrogen bromide or fluoride may be used for the first phase, and 5% potassium hydroxide for hydrolysis in the second phase before removal of iron. For the conversion into hæmateric acid hot glacial acetic acid with 1—10% of sulphuric acid is very suitable. Crude hæmatoporphyrin prepared by Nencki's and Sieber's processes always contains appreciable amounts of hæmateric acid, and should be fractionated with 0·1% hydrochloric acid by Willstätter's method. Hæmatin and other iron porphyratins are converted by ether containing acetic acid into yellow colouring matters, and it is therefore necessary to use carefully purified ether.
C. Hollins.

Behaviour of polypeptides and their derivatives towards dilute alkalis and acids. I. E. Abderhalden and H. Sickel. **II.** E. Abderhalden and H. Brockmann. **III. Glycine polypeptides.** E. Abderhalden and S. Suzuki (Z. physiol. Chem., 1927, **170**, 134—145, 146—157, 158—160).—I. Polypeptides containing a glycine residue are much more readily hydrolysed than others by dilute alkali (*e.g.*, p_H 7·8), the ease of attack becoming greater with increasing p_H and with increasing mol. wt. *l*-Tryptophylglycylglycine is hydrolysed by erepsin at p_H 7·8 as rapidly as by *N*-alkali. Hydrolysis by dilute acids is considerably slower, but here again the presence of a glycyl residue facilitates attack.

II. Chloroacetyl-*dl*-leucine is largely hydrolysed by *N*-alkali at 37°, and the yields in reactions between amino-acids or polypeptides and acid chlorides are appreciably increased by acidifying as soon as the reaction is over. Diglycylglycine is attacked by aqueous ammonia at 37°, and aminations should therefore be performed at lower temperatures. In equal times *N*-alkali liberates more amino-groups from *dl*-α-bromo*iso*hexoyldiglycylglycine than from diglycylglycine. Hydroxides of potassium, sodium, and lithium are equally effective in equivalent concentrations. Water hydrolyses diglycylglycine at 150° in a sealed tube. By the action of *N*-alkali on *l*-leucylglycyl-*d*-alanine either of the terminal groups may be removed; in the case of glycyl-*l*-leucylglycyl-*d*-alanine hydrolysis proceeds from one end only, the products being glycine, *l*-leucine, and glycyl-*d*-alanine.

III. Glycylglycine, diglycylglycine, and triglycylglycine are quantitatively hydrolysed both by *N*- and by 0·5*N*-alkali, more quickly at 37° than at 17°, the rates of hydrolysis increasing with increasing mol. wt. The action of *N*-hydrochloric acid is small.
C. Hollins.

Gelatin. IX. Scission of gelatin into constituent proteins. S. B. Schryver and K. V. Thimann (Biochem. J., 1927, **21**, 1284—1301).—Electrolysis of the hydrochloride of purified gelatin yields a gel with very little nitrogen in the supernatant fluid whilst in the electrolysis of the sodium salt two fractions are obtained, an insoluble fraction (insoluble ana-gelatin) and a soluble fraction (soluble ana-gelatin). The former is soluble in water to the extent of about 15 parts in 100,000 at 15°. The mol. wt. of soluble ana-gelatin is 50,000—60,000. The diamino-nitrogen value of the hydrolysed insoluble fraction is higher than that of the insoluble one. It is not possible to resynthesise a gel by combining the soluble and insoluble ana-gelatins owing to an intramolecular change produced in the process of electrolysis. The irreversible change produced in purified gelatin by heating with water is not accompanied by peptide scission. The name "meta-gelatin" is suggested for the products thus formed. Insoluble gelatin cannot be dispersed in water without undergoing a slight irreversible change and conversion into a soluble form.
S. S. Zilva.

Gelatin. X. Effect of previous treatment with acid and alkali on the diamino-nitrogen fraction of the hydrolysis products of gelatin. B. Thornley (Biochem. J., 1927, **21**, 1302—1304).—The value of this fraction increases with increase of strength of the acid with which the gelatin has been previously treated and decreases again when the acid is stronger than 2·3*N*. With heated gelatin this is not observed. Previous treatment with alkali also increases the diamino-nitrogen fraction. Preparatory treatment with pepsin or trypsin also affects the Hausmann numbers.
S. S. Zilva.

Combination of proteins with phthalein dyes. L. F. Hewitt (Biochem. J., 1927, **21**, 1305—1313).—Phthalein and fluorescein dyes which change colour on the acid side of the isolectric point of proteins are not discharged or altered as usual on acidification, in the presence of such proteins. This is not due to physical adsorption, but to the chemical combination of the protein with the dye possessing a quinonoid structure and the consequent formation of a coloured oxonium salt. The addition of acid to a mixture of a phthalein or fluorescein dye and a protein solution produces a precipitate at the isoelectric point of the protein which dissolves at about p_H 2·5. The "protein error" of indicators, acid-fast staining of tissue sections, and acid-fast staining of fabrics are discussed.
S. S. Zilva.

Preparation of an arginine peptide from clupeine. A. Kossel and E. Staudt (Z. physiol.

Chem., 1927, **170**, 91—105).—Prolonged hydrolysis of clupeine with 70% (vol.) sulphuric acid at 37° yields an arginylarginine, readily isolated by means of flavianic acid. The oil has $[\alpha_D]_N$ +29·80° (cf. arginine carbonate, $[\alpha_D]_N$ +40·49°), shows feebly but definitely the Abderhalden picric acid reaction characteristic of diketopiperazines and the biuret reaction, and is hydrolysed quantitatively to arginine by 25% sulphuric acid at 140° in 24 hrs. It thus differs from Fischer's product from arginine methyl ester (Fischer and Suzuki, A., 1906, i, 73; cf. Edlbacher and Bonem, A., 1925, i, 863), which is extremely resistant to hydrolysis, gives no biuret reaction, and a strong picric acid reaction. The action of 70% (vol.) sulphuric acid shows some analogy with the action of trypsin (Kossel and Mathews, A., 1898, i, 612), the protone stage being passed and the products being peptides and free amino-acids. C. Hollins.

Elementary organic analysis for carbon and hydrogen without the use of catalysts. I. Marek (Arh. Hemiju, 1927, **1**, 188—194).—An apparatus for the determination of carbon and hydrogen in organic substances is described, in which combustion takes place in a current of pure oxygen. R. Truszkowski.

Determination of sulphur in organic substances. I. Marek (Arh. Hemiju, 1927, **1**, 194—199).—Sulphur is determined by the combustion of organic substances in a current of moist oxygen and absorption of the acid gases produced in 2% hydrogen peroxide. Sulphuric acid is then determined gravimetrically or volumetrically. R. Truszkowski.

Stepanov's method for determining halogens in the benzene nucleus. G. Favrel and Bucher (Ann. Chim. anal., 1927, [ii], **9**, 321—324).—A modification of the procedure of Stepanov (A., 1907, ii, 50) for the determination of halogeno-benzene derivatives is described. C. W. Gibby.

Gas-volumetric determination of SO_2H in organic sulphinic acids. S. Krishna and B. Das (J. Indian Chem. Soc., 1927, **4**, 367—374).—Sulphinic acids react with potassium iodide and iodate as follows, $6R\cdot SO_2H+5KI+KIO_3=6R\cdot SO_2K+3I_2+3H_2O$. In 19 cases studied there was no elimination of the sulphinic acid grouping, as is the case with sulphonic acids. The details of the method are: to an ice-cold solution of the acid (0·2 g.) in water (40 c.c.) a cold solution of potassium iodide (2 g.) and potassium iodate (0·2 g.) is added gradually. The mixture is warmed to 18—20°, treated with hydrogen peroxide and potassium hydroxide solution, and the evolved oxygen collected and measured. The method gives trustworthy results. H. Burton.

Analysis of nitrogenous compounds. H. Müller (Biochem. Z., 1927, **188**, 56—64).—Applications of the author's procedure for the analysis of organic compounds which involves the determination of the nitrogen content and the "oxygen requirement" (A., 1927, 996) to the determination of carbon and hydrogen in nitrogenous substances are described, together with the appropriate procedure for the derivation of empirical molecular formulæ. E. A. Lunt.

Microchemical detection of volatile aldehydes and ketones. C. Griebel and F. Weiss (Mikrochem., 1927, **5**, 146—160).—The paper deals with the identification of aldehydes and ketones such as those present in fruits and essences, by the microchemical examination of derived semicarbazones, *o*-, *m*-, or *p*-nitrophenylhydrazones, or *m*- or *p*-nitrobenzhydrazones. A. R. Powell.

Hypobromite titration of amino-acid derivatives. C. Granacher and G. Wolf (Helv. Chim. Acta, 1927, **10**, 815—819).—When an aqueous solution of about 0·2 g. of (*a*) hydantoin-3-acetic acid, (*b*) α-5-methylhydantoin-3-propionic acid, (*c*) 4-ethoxy-2-methyloxazole, and (*d*) 2-phenyl-4-benzylglyoxalidoneacetic acid is treated with an excess of sodium hypobromite solution at 0° and the number of mols. of reacting hypobromite determined, it is found that in cases (*a*), (*b*), and (*d*) there is an increase in the amount of hypobromite used up to approx. 3 mols. with increase of time of reaction. The value for (*c*) remains steady at about 2 mols. of hypobromite reacted with after 1·75 min. H. Burton.

Biochemistry.

Limitations of Warburg's theory of the rôle of iron in respiration. J. W. Buchanan (Science, 1927, **66**, 238—239).—Wide divergence between Warburg's theory and the actual facts of respiration is discussed. A. A. Eldridge.

Modification of the Barcroft blood-gas apparatus. L. Drastich (Biochem. Z., 1927, **188**, 35—39).—A description of a modified type of Barcroft's blood-gas apparatus for the analysis of 1 c.c. of blood which is so designed that it is also suitable for use as a microrespirometer. E. A. Lunt.

Blood pigment. W. Küster and G. F. Koppenhöfer (Z. physiol. Chem., 1927, **170**, 106—109).—By the alcoholysis of blood pigment at 180° there is obtained, in addition to water-soluble protein degradation products, an insoluble residue containing 4% of iron, in which probably a proline-bearing group of the globin is combined with the iron complex of hæmoglobin. C. Hollins.

Tryptoporphyrin. S. Fränkel and H. Prinz (Biochem. Z., 1927, **188**, 90—100).—A substance named *tryptoporphyrin* has been prepared by digestion of crystalline oxyhæmoglobin for 3 months with trypsin. It exhibits no absorption bands when examined spectroscopically. The following derivatives have been prepared: the *ethyl* ester and its *hydrochloride*, the *anhydride*, and *hepta-acetyltryptoporphyrin*. The formula $C_{19}H_{14}O_9N_4$ is advanced, but the presence of a small amount of iron in the compound leads to the supposition that there may be two substances present. E. A. Lunt.

Differentiation of the proteins of blood-serum. A. VILA and R. ANCELLE (Compt. rend., 1927, 185, 1164—1167).—In the separation of proteins, useful control is afforded by determining their sulphur content, which indicates their nature. "Myxoprotein," a complex containing 1·45% of sulphur, was separated by successive flocculations with oxalic acid (thus removing the calcium which stabilises the complex) into serum-albumin (1·84—2·00% S) and serum-globulin (0·90—1·00% S). B. W. ANDERSON.

Antitrypsin of normal serum. L. UTKIN-LJUBOVZOV (Biochem. Z., 1927, 188, 134—146).—Dog and rabbit sera were heated at 65° for 40 min. in buffered solutions of varying p_H and tested for antitryptic action on tryptic digests of caseinogen. The destruction of antitrypsin on heating at 65° for 40 min. was a maximum at p_H 5·2—4·7 for rabbit serum, 4·5 for dog serum, and 4·4—4·1 for serum-albumin solutions. This destruction optimum lies near the isoelectric point and coagulation optimum for serum-protein but is not displaced by the presence of salts with a bivalent anion, *e.g.*, sodium sulphate. Precipitation of the protein in the serum does not remove its antitryptic properties. E. A. LUNT.

Phosphorus of serum. M. MÂCHEBŒUF (Ann. Inst. Pasteur, 1927, 41, 1036—1044).—The hypothesis is advanced that a very stable phosphoric ester is present in serum and that some of the phosphoric acid is combined with glyceric acid forming a stable compound fairly resistant to acid hydrolysis. Greenwald's claim to have isolated diphosphoglyceric acid from pig's blood is confirmed. W. ROBSON.

Changes in blood after parenteral administration of foreign proteins. T. ASAKURA (Japan. J. Med. Sci., 1927, 1, 183—220).—After intraperitoneal administration of sterilised cow's milk or caseinogen solution to rabbits, the following changes in certain blood constituents are observed. There is an increase in the amount of non-protein nitrogen, amino-nitrogen, fibrinogen, sugar, lipase, catalase, and protease, a decrease in serum-protein and antitrypsin. Diastase, complement, and normal hæmolysin remain without definite change. H. D. KAY.

Is kephalin necessary for the activation of prothrombin? C. A. MILLS (Chinese J. Physiol., 1927, 1, 435—438).—Experimental evidence is cited in agreement with Bordet (Ann. Inst. Pasteur, 1920, 34, 561) that calcium and kephalin, together with prothrombin, are the necessary precursors to the formation of thrombin. E. A. LUNT.

Origin of indican in fœtal blood. K. SHIBAYAMA (Japanese J. Med. Sci., 1927, 1, 111—117).—The blood of the fœtus contains more indican than that of the mother. The concentration of indican and of amino-acids in the blood of the fœtus, retroplacental hæmatoma, and cubital vein decreases in the order named, and it would appear that indican is produced in the organism both in intestinal putrefraction and in metabolic processes. *B. coli* appear in the fæces of the newly born 12—24 hrs. after birth.

P. W. CLUTTERBUCK.

Action of low temperatures on the crystalline lens. G. BERGAMI (Atti R. Accad. Lincei, 1927, [vi], 6, 117—121).—At low temperatures, the crystalline lens of the sheep or ox behaves similarly to dialysed blood-serum, undergoing a partial and reversible coagulation and becoming opaque in the central portion. Similar opacity, probably due to dehydration of the lenticular colloids, is produced by hypertonic Ringer's solution, subsequent immersion of the lens in hypotonic Ringer's solution causing the disappearance of the opacity. When acting together, a low temperature and hypertonic Ringer's solution cause opacity, reversible at the ordinary temperature, even in the crystalline lens of the dog, although in this case neither of these agents alone produces the change. T. H. POPE.

Existence of reserve proteins in the mammalian liver. T. CAHN and A. BONOT (Compt. rend., 1927, 185, 1212—1214).—In guinea-pigs, rabbits, and dogs, the nitrogen content of the proteins in the liver attains, after starvation, a more constant and distinctly higher value than normal, and at the same time the nucleic acid content is raised. These facts prove the presence in the liver of reserve proteins having a different constitution from protoplasmic proteins. B. W. ANDERSON.

Lipoids. P. A. LEVENE and K. LANDSTEINER (J. Biol. Chem., 1927, 75, 607—612).—The "white matter" of the lipins of horse kidney was separated into pyridine-soluble and pyridine-insoluble fractions. The soluble portion was freed from pyridine, extracted with a mixture of chloroform and methyl alcohol, and the residue purified by dissolution in water and precipitation with Fehling's solution; the resulting substance was free from sulphur and phosphorus. The pyridine-insoluble part, after extraction with chloroform and methyl alcohol, was separated by glacial acetic acid into an insoluble fraction containing 2·55% of sulphur but no phosphorus and a soluble fraction containing 1·89% of phosphorus but no sulphur; the latter substance gave a purple colour with orcinol. C. R. HARINGTON.

Iodine content of thyroid in various animals. T. NOSAKA (Folia endocrinol. japon., 1926, 2, 878—933).—The iodine content per g. of thyroid is highest in the chicken, but low in the monkey, horse, ox, dog, cat, rabbit, guinea-pig, and snake.

CHEMICAL ABSTRACTS.

Chemistry of the ovary. XIII. Water-soluble extractives of ovarian residue. F. W. HEYL and M. C. HART (J. Biol. Chem., 1927, 75, 407—415).—Ovarian residue (4·53 kg.) was extracted with ether and then with alcohol; the latter was concentrated, giving a precipitate of *iso*leucine and sodium chloride; the filtrate, on treatment with ether, gave a further precipitate which was extracted with water, as was also the ethereal solution; the combined aqueous extracts contained total creatinine 2·63 g., carbamide 2·99 g., ammonia 1·53 g.; the solution was treated with phosphotungstic acid and the precipitated substances, after recovery from the phosphotungstates, were fractionally precipitated with silver nitrate; there was thus detected adenine, histidine, choline, and δ-aminovaleric acid; from the filtrate from the phosphotungstic acid precipitate there was obtained *d*-lactic acid. The ovarian residue was further extracted with hot water, and the extract was cleared with tannic acid and precipitated with phosphotungstic acid; the precipitate contained creatinine, guanine, adenine, histidine, arginine, lysine, and carnosine. The filtrate was hydrolysed with sulphuric acid and again treated with phosphotungstic acid; the precipitate contained guanine, adenine, and choline, and the filtrate glycine, alanine, serine, aspartic acid, and proline. C. R. Harington.

Determination of total creatinine in small amounts of tissue. W. C. Rose, O. M. Helmer, and A. Chanutin (J. Biol. Chem., 1927, **75**, 543—548).—The tissue is autoclaved with 2N-sulphuric acid for 45 min., the solution treated with sodium tungstate, made up to standard volume, and filtered; the creatinine in the filtrate is determined by the method of Folin and Wu (A., 1919, ii, 308); the error of the method is ±4%. C. R. Harington.

Use of the starch–iodine end-point in Tunnicliffe's method for the determination of glutathione in tissues. W. A. Perlzweig and G. Delrue (Biochem. J., 1927, **21**, 1416—1418).—The addition of potassium iodide to trichloroacetic acid extracts of tissues permits the employment of the delicate starch–iodine end-point in the titration of glutathione by Tunnicliffe's method (A., 1925, i, 752). S. S. Zilva.

Activities of a constructed colloidal cell. D. T. MacDougal and V. Moravek (Protoplasma, 1927, **2**, 161—188).—Cholesterol–lecithin solutions, together with cholesterol particles with a protective layer of lecithin, have been obtained by using ether as an intermediary, and the mixture has been incorporated in hydratable gels. The properties of such cells in endosmosis, permeability, and p_H are described. Chemical Abstracts.

Cetacea. XXIV. Composition of the urine. T. Ichimi, S. Morimura, Y. Masumizu, and T. Yazawa. **XXV. Oxalic acid content of the urine.** Y. Okahara. **XXVI. Relationship between different kinds of whales.** K. Hayasi. **XXVII. Milk of different kinds of whales.** K. Takemura. **XXVIII. Total urinary base.** Y. Furuhashi. **XXIX. Alkali and alkaline-earth content of different horny tissues. Keratinisation.** H. Hayashi. **XXX. Function of the liver.** Y. Furuhashi and T. Yazawa. **XXXI. Synovial fluid.** K. Takemura. **XXXII. Urinary organic acids.** T. Yazawa and T. Sasaki **XXXIII. Glycogen content of the liver.** Y. Masumizu (Japan. J. Med. Sci., 1927, **1**, 119—124, 125—126, 127—129, 131—134, 135—136, 137—149, 151—152, 153—157, 159—162, 163—164).—XXIV. The total, amino-acid-, and purine-nitrogen, the urea, ammonia, creatine, creatinine, allantoin, uric and hippuric acids, chloride, sulphate, and phosphate contents of the urine of several whales are tabulated, and the composition is shown to be similar to that of a diluted urine of a carnivorous animal.

XXV. The oxalic acid content of three samples of urine varied between 23 and 44 mg./litre.

XXVI. The results obtained by application of the precipitin reaction to the serum of a number of different kinds of whales are tabulated.

XXVII. Milk from three kinds of whales gave the following values: *d*, 1·013—1·041; f. p., −0·751° to 0·789°; solid constituents, 42·28—44·83%; total nitrogen, 1·42—1·887 g.-%; residual nitrogen, 0·152—0·18 g.%; protein (precipitated by tannic acid), 3·73—4·51%; fat, 23·76—37·38%, and sugar, 0·12—0·13%.

XXVIII. The urinary chloride, phosphate, sulphate, and total base for a number of whales are tabulated. The total base is remarkably constant for the different animals.

XXIX. Skin of whales contains much more water than whalebone, the latter being related more closely to horn. The keratin of whale skin has a similar sulphur content to that of land mammals (0·75%), whereas whalebone contains 3·6%. The horn cells of the mucous membranes contain slightly more water and less fat than those of the outer skin, whilst in all tissues protein makes up about the same percentage of the dried material. The fat content of the skin and whalebone is between 3 and 4% and of the mucous membrane of the first stomach, 2%. When the various tissues are compared in the fresh condition, whalebone has the highest ash content, but in the dry state and after removal of fat the latter has the least ash content. The assumption that hardness of horn depends on the deposition of inorganic salts is therefore not valid. In both land and sea animals the formation of hard horn corresponds with the presence of alkaline earths and sulphur-rich keratins. Although there is little difference in the various tissues in total ash content in the dried and fat-free condition, there is considerable difference in respect to the amounts of the constituents of the ash. Whereas in skin the alkalis (especially potassium) predominate, in whalebone the alkaline earths (especially calcium) are present in amounts equal to the alkalis. The alkaline-earth content of whalebone is due to the deposition, in the hardening process, of sparingly soluble calcium compounds of protein containing little water.

XXX. Whale's liver when heated with potassium dihydrogen phosphate gave a protein-free filtrate containing 0·99 g. of soluble nitrogen and 2·3 g. of sugar (after hydrolysis) per 100 g. of liver. A portion of the filtrate was freed from glycogen and then contained 1·3% of sugar. The amount of glycogen therefore by difference corresponds with 1·0% of sugar and a direct determination confirmed this.

XXXI. Synovia contained 0·008—0·013% of sugar, 0·2% of sodium, 0·004% of potassium, 0·06% of calcium, a trace of magnesium, and 0·37% of chlorine. The total nitrogen is 0·27—0·3%, and the residual nitrogen, after precipitation of protein with trichloroacetic acid, 0·089—0·104%. The protein-nitrogen by difference is 0·19%, the percentage of nitrogen in synovial protein being 13%. The weight of protein precipitated by dilute acetic acid corresponds with 1·5—1·7% of the synovial fluid.

XXXII. The total nitrogen and creatinine (in g. per litre) and the organic acids (in c.c. 0·1N-acid per litre) of the urine are tabulated.

XXXIII. The glycogen content of the liver of different whales varied from 3·7% to 0·36%, according as the sampling took place from 6 to 16 hrs. after death. P. W. Clutterbuck.

Cetacea. XXXV. Content of ovarian follicles. K. Hayashi. **XXXVI. Bile.** M. Takata. **XXXVII. Reaction between alcoholic extracts of heart and luetic sera.** M. Matsuura. **XXXVIII. Calcium, magnesium, and phosphorus in various organs [of fin-back whale].** H. Kusakari and H. Tsutsui. **XXXIX. Ambraporphyrin, a red pigment from ambergris.** Y. Okahara (Japan J. Med. Sci., 1927, 1, 221—234, 235—239, 241—244, 245—246, 247—266). XXXV. Fluid from medium-sized follicles (volume from 0·5 to 1 c.c.) has d^{20} 1·0395—1·0408 and p_H 6·21—6·41. It contains 91·4—92·1% of water and about 6·2% of protein, part of which is precipitated by acetic acid and part is coagulated spontaneously on keeping the original fluid. The latter part is probably not identical with blood-fibrin. The proteins in the fluid may be separated by precipitation with increasing concentrations of sodium sulphate. Of the non-protein nitrogen about two thirds is amino-nitrogen. The fluid contains 0·9% of ether-soluble material and traces of reducing substances. The inorganic constituents have been determined; the sodium content is considerably higher than that of the serum of the same animal (rorqual).

XXXVI. Like that of the majority of mammals, whale (rorqual) bile contains taurocholic and glycocholic acids. The relative quantity of the former to the latter is 6 : 4. Whale bile contains fats, soaps, sterols, and phosphatides in amounts similar to those present in human bile. Since the rorqual has no gall bladder, the secretion of bile into the intestine is probably continuous.

XXXVII. An alcoholic extract of the heart muscle of the rorqual or of *Berardius bairdii*, but not of the sperm whale, contains a substance which is capable of acting as antigen in Meinicke's reaction for diagnosis of syphilis (Münch. med. Woch., 1919, 66, 932).

XXXVIII. Figures are given for the average total content of calcium, magnesium, and phosphorus per 100 g. of dried pancreas, spleen, liver, kidney, testicles, ovary, brain, and mammary gland.

XXXIX. The red pigment found by Suzuki (A., 1925, i, 1348) in ambergris has been purified and submitted to spectroscopic analysis. Ambraporphyrin in ethereal solution gives an absorption spectrum recalling that of coproporphyrin, although the two substances are not identical. It is, like other porphyrins, unstable, particularly in presence of light. On keeping, even in the dark, before there is any evidence of chemical change in the porphyrin, the four-banded spectrum characteristic of the pure material is changed by the appearance of a new band in the extreme red. H. D. Kay.

p_H of normal saliva. M. Henderson and J. A. P. Millet (J. Biol. Chem., 1927, 75, 559—566).—The p_H of normal saliva varies regularly during the day, being lowest on awakening, and showing a sharp rise and fall after each meal; the average range of variation is p_H 6·7—7·3. Exertion lowers the p_H of the saliva. C. R. Harington.

Modifications in blood accompanying gastric secretion. III. Carbon dioxide. T. G. Ni and A. C. Liu (Chinese J. Physiol., 1927, 1, 355—362).—Experiments with fistula, Pavlov-pouch, and Heidenhain-pouch dogs have shown that the prolonged loss of gastric secretion induced by repeated injections of histamine results in an increase in the carbon dioxide content of the arterial blood, the change occurring in the corpuscles as well as in the plasma. The increase in alkali reserve observed after great loss of gastric secretion is not equivalent to the loss of hydrochloric acid involved. E. A. Lunt.

Disgenetic milk. C. Gorini (Compt. rend., 1927, 185, 970—972).—Milk which has been sterilised at high temperatures and also occasional samples of milk unsterilised and from healthy cows do not function as culture media for certain bacteria, and those introduced therein fail to live. Such "disgenetic" milk is at once made normal in this respect if small amounts of vitamins or other suitable stimulants are added to it. The occurrence of disgenetic milk may explain the discrepancies often encountered in cheese-making etc. B. W. Anderson.

Normal urinary pigment. I. Relationship to diet and metabolism. II. Relationship to basal metabolism. D. L. Drabkin (J. Biol. Chem., 1927, 75, 443—479, 481—487).—I. Normal urinary pigment was determined colorimetrically by comparison with a standard solution of alizarin mixed with a little aniline-orange. In normal dogs on a basal diet as free as possible from pigment, the average diurnal variation in output of pigment was 4%, and the output was not appreciably affected by addition of pigments such as hæmoglobin and chlorophyll to the diet. The pigment excretion was considerably increased by starvation, by administration of acid, phloridzin, adrenaline, and thyroxine; in the normal animal it was little affected by administration of alkali, whilst it was reduced by thyroidectomy; increased output of pigment was accompanied by diuresis. Except during the period of rapid growth, the output of pigment, in various species, is proportional to the body surface area. In normal human adults, the excretion of pigment is lower in women than in men; it is increased in pregnancy and in exophthalmic goitre, and is normal in diabetes and nephritis except when there is retention of urine. In general, therefore, the urinary pigment appears to be an endogenous product, the output of which is proportional to the endogenous metabolic rate.

II. The above conclusion is supported by investigations of cases of exophthalmic goitre and of fever. C. R. Harington.

Sugar of normal urine. I. Greenwald, J. Gross, and G. McGuire (J. Biol. Chem., 1927, 75, 491—508).—"Grape nuts," after exhaustive fermentation with yeast, yielded a non-dextrose residue which, however, gave glucosazone; the substance was apparently analogous to the mixture of lævulosan and *iso*saccharosan obtained by heating sucrose (cf. Pictet, A., 1924, i, 1045); ingestion of such substances caused small, but scarcely significant, increases in the urinary sugar; the latter was not increased by administration of dextrose, either alone or in conjunction with a mixed meal; the urinary sugar appears to consist, in part, of non-dextrose yeast-fermentable substances; it is suggested that it may be of bacterial origin. C. R. HARINGTON.

Rapid determination of sugar in urine. T. J. F. MITSCHKE (Virginia Med. Monthly, 1927, 54, 251—252).—Benedict's quantitative solution (5 c.c.) is titrated with undiluted urine. CHEMICAL ABSTRACTS.

Cytolysis in cancer. II. N. WATERMAN and L. DE KROMME (Biochem. Z., 1927, 188, 65—74).—The lytic factor present in normal serum has been isolated from the organs of the reticulo-endothelial system of the dog, and the variation in its activity with varying p_H has been determined. Its activity is changed by exposure to *X*-radiation. E. A. LUNT.

Glutathione content of chicken sarcoma. H. YAOI and W. NAKAHARA (Biochem. J., 1927, 21, 1277—1278).—Polemical. The authors agree with Kennaway and Hieger (A., 1927, 789) that glutathione is present in abundance in malignant tumours. They maintain, however, that this is not true in the case of Rous sarcoma. S. S. ZILVA.

Choline and urea of cerebrospinal fluid in meningocele. H. SIEVERS (Z. Biol., 1927, 86, 535—541).—The cerebrospinal fluid from a case of myelomeningocele has been examined for choline and for urea. No choline could be detected, although 0·00196% of urea was found. E. A. LUNT.

Storage of cerebrosides in splenomegaly (Gaucher's type). H. LIEB (Z. physiol. Chem., 1927, 170, 60—67; cf. A., 1925, i, 189).—The identification of kerasin as the cerebroside present in alcoholic extract of spleen from cases of Gaucher's disease is confirmed. No phrenosin (cerebrone) could be detected. Confirmatory experiments of Klercker (Acta Pædiatrica, 1927, 6, 302—351) are quoted. C. HOLLINS.

Acetone substances in the urine on carbohydrate and fat diets. N. B. DREYER (Proc. Nova Scotian Inst. Sci., 1926—1927, 17, 26).—On a mixed diet the daily excretion of acetone substances is variable, whilst on carbohydrate diets the amount diminishes until only traces are present. Replacement of the carbohydrate diet by a fat diet results in an increase in excretion of acetone substances which is only tenfold after 24 hrs., the glycogen stores presumably acting as catalyst for the complete oxidation of fatty acids; on the fourth day, however, the increase is several hundredfold. A. WORMALL.

Relative nutritional values of fats. II. J. OZAKI (Biochem. Z., 1927, 189, 233—241, and Proc. Imp. Acad. Tokyo, 1927, 3, 439—444).—Further feeding experiments (cf. A., 1926, 1272; B., 1926, 930) on rats with fats containing saturated straight-chain acids show that laurin and myristin have the highest nutritional value. None of the saturated fats has the toxicity of *iso*valerin. The nutritional value of olein, linolein, and linolenin decreases with increasing unsaturation, whilst fats containing αβ-unsaturated fatty acids are of less value than the corresponding saturated fat. In general, fats containing straight-chain acids are better utilised than those having branched-chain acids. The lower aliphatic aldehydes are toxic or of poor, the higher aldehydes (margaric and palmitic) of considerable nutritional value. Methyl and ethyl esters of fatty acids are utilised generally better than, and soaps as well as, the corresponding glycerides. Experiments with fatty acid, fatty acid + glycerol, and glyceride (in corresponding amounts) show that, although little difference is obtained in nutritional value in the case of stearic and palmitic acids, yet there is a considerable increase in value in the order named in the case of myristic and lauric acids. Finally, it is shown that the nutritional values correspond quite clearly with the absorption coefficients of these fats and that the absorption of the fat depends, not only on its m. p., but also much more on its chemical nature. P. W. CLUTTERBUCK.

Intermediary carbohydrate metabolism. XXII. Formation of lactic acid from malic, fumaric, and maleic acids by the liver. T. IBUKI (Biochem. Z., 1927, 188, 164—171).—From perfusion experiments on the liver of the normal dog it is concluded that the liver does not convert the sodium salts of malic, fumaric, or maleic acid into lactic acid. E. A. LUNT.

Intermediary carbohydrate metabolism. XXIII. Lactic acid formation by the liver on perfusion with lævulose. Y. HARADA (Biochem. Z., 1927, 188, 172—177).—Perfusion of the livers of the normal and of the depancreatised dog with solutions containing varying concentrations of either dextrose or lævulose shows that both the normal and the diabetic liver form more lactic acid from lævulose than from dextrose. The increase in lactic acid output on perfusion with lævulose in contrast with dextrose was greater in the diabetic than in the normal liver. E. A. LUNT.

Is there a relation between tonic muscular contraction and lactic acid formation? S. G. ZONDEK and F. MATAKAS (Biochem. Z., 1927, 188, 40—55).—The increase in lactic acid content and the excitatory effect brought about by immersion of the gastrocnemius of the frog in solutions of potassium salts, quinine, chloroform, ammonium chloride, and acetylcholine have been measured as a function of the time of immersion. Acetylcholine produced no appreciable lactic acid but produced true increased tonus. The other excitants effected increased lactic acid formation, but an irreversible contraction followed by diminution in sensitivity to further stimulation. The time for immersion necessary to produce the maximum excitatory effect does not correspond with that required to produce the maximum amount of lactic acid. It is concluded that lactic acid formation bears no special relation to tonic muscular contraction. E. A. LUNT.

Ammonia content of blood. IX. Variation of ammonia content with muscular work. J. K. PARNAS, W. MOZOLOWSKI, and W. LEWINSKI (Biochem. Z., 1927, 188, 15—23).—The ammonia content of blood taken from the cubital vein before and after exercise of the hand and fore-arm has been determined and is shown to increase from 100% to 800%. This variation in the percentage increase is attributed to individual variations in rate of blood-stream and distribution of capillaries as well as to variation in the duration and the vigour of the exercise. Running results in no increase in ammonia in the blood taken from the arm. E. A. Lunt.

Metabolism of tissues growing *in vitro*. II. Effect of dextrose on ammonia and urea production of kidney tissue. E. Watchorn and B. E. Holmes (Biochem. J., 1927, 21, 1391—1397).—The addition of dextrose to the medium makes no difference to the occurrence of ammonia and urea production by non-growing but surviving embryonic rat-kidney tissue. On the other hand, when this tissue is growing *in vitro* the addition of dextrose inhibits the production of ammonia and urea which would otherwise take place (cf. A., 1927, 479) and frequently actually causes a reduction in the amount of these substances initially present. S. S. Zilva.

Utilisation of nucleic acids of animal and vegetable origin. T. B. Robertson, C. S. Hicks, and H. R. Marston (Austral. J. Exp. Biol., 1927, 4, 125—150).—The effects of the oral administration of animal and of vegetable nucleic acids to subjects on an otherwise purine-free diet have been compared. The duration of experiment was divided into 4-day periods; during the first 4 days, a purine-free diet was administered to which were added during the second and fourth periods 15 g. daily of animal or of vegetable nucleic acid. The urine was analysed daily, and the daily phosphate content of the fæces was determined. Data are given for four complete experiments in which three different subjects were employed. The average absorption of phosphoric acid from vegetable nucleic acid is 25% in excess of the absorption of phosphoric acid from animal nucleic acid, but the average production of uric acid from vegetable nucleic acid was 100% greater than the production from animal nucleic acid. The loss of renal activity following such a large daily ingestion of nucleic acid rendered the 4-day purine-free period between the administration of the two nucleic acid periods slightly deficient. E. A. Lunt.

Basal metabolism of man on a diet rich in nucleic acid. C. S. Hicks (Austral. J. Exp. Biol., 1927, 4, 151—154).—The basal metabolism of one subject has been determined over a period of 20 days divided into five 4-day periods, with a diet similar to that described in the preceding abstract. No alteration in basal metabolism was detected. E. A. Lunt.

Nutritive properties of the Mung bean. V. G. Heller (J. Biol. Chem., 1927, 75, 435—442).—Mung beans (grown in Oklahoma) contained protein 23·31%, fat 1·02%, nitrogen-free extract 59·85%, water 9·31%, fibre 3·64%, and ash 2·87%; figures are given for the nitrogen distribution of the protein. Young rats attained maturity on diets in which the whole of the protein was supplied in the form of the beans, although growth was slightly subnormal and reproduction was not satisfactory; the beans contain considerable amounts of vitamin-*A* and -*B*, and their nutritive value is improved by moderate cooking. C. R. Harington.

Kidney changes in animals with increased blood-pressures while on high-protein diets. F. R. Nuzum (Arch. Int. Med., 1927, 40, 364—376).—Definite kidney changes were found in animals fed on high-protein diets over a period of 2 years. No similar changes were found in animals kept under similar conditions but fed with lucerne and greens. The urines of the first group of animals were acid, contained albumin and casts, whilst the non-protein-nitrogen and urea-nitrogen contents were increased. Blood-plasma carbon dioxide was decreased and the systolic pressures were increased. The urines from the second group were excessively alkaline, whilst clinical evidences of kidney injury were also evident. W. Robson.

Effect of cystine on the endogenous metabolism of moulting hens. C. W. Ackerson and M. J. Blish (Poultry Sci., 1926, 5, 162—165).—Cystine exerts a protein-sparing effect entirely out of proportion to its nitrogen content. Chemical Abstracts.

Availability of disulphide acids as supplementing agents in diets deficient in cystine. B. D. Westerman and W. C. Rose (J. Biol. Chem., 1927, 75, 533—541).—Neither dithiodiglycollic nor dithiodipropionic acids could replace cystine in the diets of growing rats; the latter of these two acids was entirely without physiological effect, but the former reduced the food consumption of the rats, and, even in presence of cystine, had an inhibitory effect on their growth. C. R. Harington.

Effect of creatine on growth; its distribution in tissues of normal rats. A. Chanutin (J. Biol. Chem., 1927, 75, 549—557).—In normal albino rats the creatine content of the muscles is 0·449%, testes 0·281%, heart 0·174%, brain 0·129%, kidney 0·046%, and liver 0·033%. Addition of creatine to the diet had no effect on growth nor did it cause an increase in the creatine content of any organ except the liver, which is apparently concerned, therefore, in the metabolism of creatine. C. R. Harington.

Zinc and normal nutrition. R. B. Hubbell and L. B. Mendel (J. Biol. Chem., 1927, 75, 567—586).—Figures are given for the content of various food substances in zinc, which metal was present in all cases. Addition of 0·02 mg. of zinc, as sulphate, to a basal diet containing only 0·005 mg. of zinc had a slight stimulating effect on the growth of young mice, which was more evident in females than in males; addition of 0·04 mg. had less favourable results; no significant storage of zinc was observed. It is suggested that the nutritional value of zinc may be due, not to this metal itself, but to its relationship with other metals present in small amounts in the diet. C. R. Harington.

Diurnal variation of gaseous constituents of river waters. II. R. W. Butcher, F. T. K. Pentelow, and J. W. A. Woodley (Biochem. J., 1927, 21, 1423—1435).—The investigation carried out in the spring (cf. A., 1927, 899) has been extended to the summer months. The oxygen curves for May, June, and August are in general similar to those obtained in March and April, although the times of the maximum and minimum values vary to a certain extent. There is a progressive shortening of the period of minimum of oxygen in the curves, probably due to the variation of the duration of the periods of darkness at the different dates. The time of the increase from the minimum value does not appear to be influenced by the time of sunrise so much as by the meteorological conditions. The current weather conditions have a considerable effect on the times of the maximum and minimum values. The minimum oxygen values in May, June, and August are considerably lower than those of March and April, and it is possible that the larger green plants present during the summer but absent during the spring have caused a decrease in oxygen during the night owing to increased respiration. The outstanding feature in the ammoniacal nitrogen curves was the small differences obtained throughout the 24 hrs. on August 4th—5th. The p_H curves were similar in structure to those of March and April and in general follow the oxygen curves. All the temperature curves show the expected diurnal similarity but over different ranges. A detailed account is given of the vegetation on the rivers Lark and Itchen.

S. S. Zilva.

Effects of polarisation on the steel wire–nitric acid model of nerve activity. G. H. Bishop (J. Gen. Physiol., 1927, **11**, 159—174).—A steel wire rendered passive by immersion in 65% nitric acid has been further investigated, particularly with regard to the effect on it of anodic or cathodic polarisation. As in nerve, the duration of the refractory state is decreased at the anode and increased at the cathode and the duration of activity is increased at the anode and decreased at the cathode. A non-corrosive chrome–nickel steel wire is not rendered active by anodic polarisation in 65% nitric acid, but a type of irritability is observed in 20% nitric acid. Soft iron wire immersed in 65% nitric acid becomes passive only under anodic polarisation and it then exhibits properties resembling those of the passive steel wire.

W. O. Kermack.

Hypoglycæmic action of dihydroxyacetone in man. E. P. Cathcart and J. Markowitz (Biochem. J., 1927, **21**, 1419—1422).—The administration of 50 g. of dihydroxyacetone to a fasting human subject lowers the blood-sugar to about 0·04—0·08% within 40—80 min. S. S. Zilva.

Reaction of the blood-sugar to poisons. F. Bertram (Arch. exp. Path. Pharm., 1927, **126**, 267—283).—Substances influencing the blood-sugar are divided into two classes, namely, those which affect the resting carbohydrate metabolism and those which act only when the latter is abnormal. E. A. Lunt.

Relative toxicity of halogen derivatives of chaulmoogra. B. E. Read (Chinese J. Physiol., 1927, **1**, 345—354).—The saturated dihalogeno-ethyl esters of chaulmoogra have a lethal dose similar to that of the unsaturated ethyl esters. The di-iodo-ester produces albuminuria, but the dibromoethyl ester, in contrast to chaulmoogra esters, does not produce emesis, local irritation, or hypersensitivity and suggests further investigation as a therapeutic in leprosy. These halogen-substituted esters produce a large increase in the urinary neutral sulphur content and no appreciable increase in the urinary ethoreal sulphate content. E. A. Lunt.

Effect of therapeutic substances on the p_H of blood. A. Feldt and R. Vara-Lopez (Biochem. Z., 1927, **188**, 112—116).—The modifications of p_H of the blood of syphilitic rabbits on intravenous injection of "salvarsan," "solganol," and "trypaflavine" have been compared with the corresponding effects of similar injections into the normal rabbit. The drugs exert a delayed action on the blood p_H, eventually lowering it in normal animals. The p_H of the blood of syphilitic rabbits is lower than that of the blood of normal animals and is raised by the administration of the above drugs. E. A. Lunt.

Hæmatoporphyrin in urine. F. G. Germuth (Amer. J. Pharm., 1927, **99**, 685—689).—The continued intake of trional leads to a greater amount of hæmatoporphyrin in the urine than the corresponding intake of sulphonal. Salkowski's technique was used for the detection and comparison of the amounts of hæmatoporphyrin present.

E. A. Lunt.

Variations in the ionic equilibrium as factors of pharmacological action. I. Potassium and convulsant drugs. L. Scremin (Atti R. Accad. Lincei, 1927, [vi], **5**, 1011—1016).—Experiments on the effects produced by intravenous injection of pyramidone or codeine hydrochloride into the rabbit show that modification of the equilibrium $Na^+K^+/Ca^{++}Mg^{++}$ by simultaneous injection of potassium chloride results in more pronounced reaction of the cells of the posterior cornu towards the drugs, the specific action of which is to increase the reflex excitability. The cause of this action of potassium ions on the cells of the posterior cornu is not known, but it may be that these ions render the cell walls more permeable and thus facilitate the entry of the drug. T. H. Pope.

Arginase. V. Occurrence of arginase in blood, and the effect of serum on its activity. S. Edlbacher, F. Krause, and K. W. Merz (Z. physiol. Chem., 1927, **170**, 68—78; cf. Edlbacher and Röthler, A., 1925, i, 1505).—Arginase is shown to occur in the erythrocytes of men, oxen, sheep, and pigs. In each case the serum greatly diminishes the activity of the enzyme. The inhibitory effect is largest in alkaline media and reaches a maximum after addition of an optimum (small) amount of serum. The inhibiting agent is not destroyed at 90°, but is completely precipitated by coagulation of the proteins. Arginase is absent from the blood of dogs and rabbits, but serum from these animals contains the inhibiting agent. On the other hand, arginase from the liver of dogs or rabbits is unaffected by serum from dogs, rabbits, oxen, or pigs. It is suggested that the inhibitory effect is due to formation of a system: inhibitor–co-adsorbent–enzyme, the co-adsorbent being absent from dog and rabbit sera.

C. Hollins.

Asymmetric action of phosphatase and the resolution of the *dl*-isomerides of racemic alcohols. C. Neuberg, J. Wagner, and K. P. Jacobsohn (Biochem. Z., 1927, **188**, 227—240).—Vegetable phosphatase hydrolyses the potassium salts of racemic monoborneolorthophosphate into the *dl*-isomerides of borneol with no appreciable decomposition of either isomeride. The liberation of *l*-borneol occurs in a few hours, the *d*-borneol after several days. By filtration after a few hours' hydrolysis it is possible to effect a partial separation of the optical isomerides.

E. A. Lunt.

Succino-dehydrase. F. G. Fischer (Ber., 1927, **60**, [*B*], 2257—2263; cf. Thunberg, A., 1918, i, 140; ii, 87; 1920, i, 784).—The dehydrase nature of succino-dehydrase is established by the observation that the decolorisation of methylene-blue occurs parallel with the dehydrogenation of succinic acid and leads to the same products as are obtained with oxygen as acceptor. Fumaric acid, amounting to 30% of the succinic acid, and malic acid are obtained by the action of well-washed muscle in the presence of a phosphate buffer on sodium succinate solution containing an equivalent amount of methylene-blue in the absence of oxygen. The products are firmly retained on the tissue by the *leuco*methylene-blue so that their isolation can be effected only by allowing the latter substance to become re-oxidised by exposure to air and repeatedly treating the tissue with boiling water. Dehydrogenation of succinic acid by oxygen affords 25% of fumaric acid and 75% of malic acid. Under the action of fumarase the two acids form an equilibrium mixture. Muscle-tissue in the absence of oxygen converts fumaric acid into *l*-malic acid to the extent of 70% and *l*-malic acid into fumaric acid to 23%. The results obtained are apparently contradictory to those of Bach and Michlin (A., 1927, 591), but their observation that about 300 times as much oxygen is absorbed by muscle as corresponds with the amount of reduced methylene-blue is accounted for by the constant concentration of the solution of the gas throughout the experiment, whereas the concentration of the methylene-blue falls continuously, whilst also *leuco*methylene-blue is deposited on the muscle and diminishes the active surface of the enzyme. Aconitic acid does not appear to be transformed into citric acid in the presence of muscle; the conversion of oleic or elaidic acid into hydroxystearic acid is not observed.

H. Wren.

Biochemical transformation of tyrosine into pyrrole derivatives. A. Angeli (Atti R. Accad. Lincei, 1927, [vi], 6, 87—90).—Consideration of the established facts relating to the pigmentation of pyrrole and its derivatives indicates that aromatic compounds containing in their molecules the grouping $(1)\cdot O\cdot C_6H_4\cdot C\cdot C\cdot N(4)$ should be capable of conversion into melanins. With reference to Bloch and Schaaf's hypothesis that melanins are formed from 3 : 4-dihydroxyphenylalanine by the action of a special enzyme termed "dopa-oxidase" (A., 1926, 87), it is pointed out that 3 : 4-dihydroxyphenylalanine has not yet been found in the animal organism and that extracts of melanotic tumours do not colour tyrosine although they readily blacken pyrrole. It seems probable that, in these cases, the formation of melanin is due to a less complicated oxidation of products diffused throughout the animal organism and containing a ready-formed pyrrole group in their molecules.

T. H. Pope.

Xanthine oxidase. IX. Specificity of the system. II. H. I. Coombs (Biochem. J., 1927, **21**, 1259—1265).—3-Methyl-, 8-methyl-, 9-methyl-, 1 : 3-dimethyl-, and 3 : 8-dimethyl-xanthine, 1-methyl-, 7-methyl-, and 1 : 7-dimethyl-guanine and glyoxaline are not activated by the enzyme; 6 : 8-dihydroxypurine and 2-thioxanthine are activated. These two purines take up one atom of oxygen per molecule in the process of oxidation. The enzyme adsorbs compounds possessing the two-ring purine structure. The introduction of an amino-group strongly favours adsorption and the introduction of methyl groups especially in the glyoxaline ring tends to prevent adsorption.

S. S. Zilva.

Fixation of acetaldehyde. C. Neuberg and M. Kobel (Biochem. Z., 1927, **188**, 211—216).—Data are cited for the use of thiosemicarbazide as a fixing agent for the acetaldehyde produced in the fermentation of dextrose by yeast. The reagent is not toxic and hence does not interfere with the process of fermentation. The separation of the free aldehyde from the carbazone is effected by hydrolysis with phthalic anhydride and subsequent steam distillation, both processes being carried out at low pressure (Biochem. Z., 1902, **35**, 2049). About 9% of the theoretical amount of acetaldehyde can be isolated by this method.

E. A. Lunt.

Fermentation and phosphorylation of sugar anhydrides. A. Gottschalk (Z. physiol. Chem., 1927, **170**, 23—30).—α-Glucosan is readily fermented by top or bottom yeast, the initial velocity being greater than in the case of dextrose; Gelis' negative results (Compt. rend., 1860, **51**, 331) were due to very impure material. In the presence of dipotassium hydrogen phosphate α-glucosan is converted by dried yeast into a hexosephosphate. For both fermentation and phosphorylation the presence of co-zymase is essential. *l*-Glucosan and tetra-α-glucosan are not attacked by fresh yeast or yeast extract, and the former is not converted into a phosphoric ester by the action of dried yeast and phosphate.

C. Hollins.

Existence of cell-free fermentation. A. J. Kluyver and A. P. Struyk (Z. physiol. Chem., 1927, **170**, 110—117).—Contrary to the statement of Kostytschev and his co-workers (A., 1927, 902), fermentation by cell-free preparations does take place. Yeast-juice after passing through a Seitz filter is proved to be free from bacteria but retains its power of fermenting sterilised dextrose solution.

C. Hollins.

Occurrence of calcium citrate crystals in cultures of butyric acid-forming bacteria. Water of crystallisation of calcium citrate. W. H. Peterson, P. W. Wilson, E. McCoy, and E. B. Fred (J. Amer. Chem. Soc., 1927, **49**, 2884—2888).—Crystals of calcium citrate appear in old milk cultures and on potato slants to which calcium carbonate has been added, after fermentation by butyric acid bacteria. Their formation is hastened by changes in hydrogen-ion concentration brought about by the action of the bacteria. Practically all the water of crystallisation of calcium citrate tetrahydrate is lost at 110°, and a dihydrate could not be obtained by heating the tetrahydrate at this temperature (cf. Soldaini and Berté, A., 1899, ii, 820).

F. G. Willson.

Autolytic power of *B. coli communis*. E. G. Young (Proc. Nova Scotian Inst. Sci., 1926—1927, 17, 79).—Sterile solutions obtained by alternately freezing and thawing emulsions of *B. coli communis* and then filtering through a Berkefeld filter have no action on dextrose in an atmosphere of nitrogen at 37° for several weeks, but effect a very slow hydrolysis of peptone as evinced by an increase in the free amino-nitrogen. A. Wormall.

Toxin and anatoxin of diphtheria. V. Koulikov and P. Smirnov (Ann. Inst. Pasteur, 1927, 41, 1166—1174).—Various amounts of hydrochloric acid have been added to solutions of diphtheria toxin and the mass and relative toxicity of the precipitates so formed have been determined. Maximum toxicity of the precipitate occurs at p_H 4·8, whilst the maximum precipitate is formed at p_H 3·8 to 4·0. The temperature of maximum stability for diphtheria toxin is 20°; precipitation at 37° results in a 66% loss of toxicity and at 0° 75% of toxicity is lost in 3—4 days. The chemical nature of substances neutralising diphtheria toxin and the mechanism of the reaction are discussed. E. A. Lunt.

Metabolism of *B. tetani*. I. H. Sievers and E. Müller (Z. Biol., 1927, 86, 527—534).—Cultures of *B. tetani* were made on a broth–peptone medium at an initial p_H of 7·2. After growth the medium became slightly acid and was found to contain *N*-methylhydantoin, acetic, propionic, and butyric acids, and *r*- and *d*-lactic acids. The origin of each of these products of metabolism is discussed.

E. A. Lunt.

Effect of adrenaline on ketosis in phloridzinised and normal rats. A. B. Anderson and M. D. Anderson (Biochem. J., 1927, 21, 1398—1403).—The administration of adrenaline to phloridzinised rats on a protein–fat diet causes a very large temporary increase in the excretion of acetone substances. This is not the case with non-phloridzinised rats on the protein-fat diet or on a standard diet containing carbohydrates. Adrenaline also causes an increase in the ketosis of rats on a fat diet. The addition of sodium hydrogen carbonate to the protein–fat diet does not prevent this effect of adrenaline. It is suggested this effect may be due to a temporary intense stimulus to the oxidation of fat.

S. S. Zilva.

The sulphur of insulin. V. du Vigneaud (J. Biol. Chem., 1927, 75, 393—405).—Preparations of insulin, purified by the method of Abel and Geiling (A., 1925, i, 1218) to contain 15—40 units per mg., showed a content of cystine which was roughly proportional to their physiological activity; the figures for cystine were slightly increased after acid hydrolysis of the insulin. The greater part of the sulphur of insulin, but not of its acid hydrolysis products, was eliminated as sulphide on heating with 0·1*N*-sodium carbonate; moreover, the reaction of Sullivan (A., 1926, 1266) for cystine was not given by insulin itself, but was given by the solution of its hydrolytic products; support is therefore given to the view that insulin contains cystine in peptide linking; the sulphur appears to be present as disulphide, which would involve the doubling of the empirical formula for insulin recently proposed by Abel (A., 1927, 701). C. R. Harington.

Ineffectiveness of insulin introduced into the intestine. A. Stasiak (Biochem. Z., 1927, 188, 24—34).—A slight hyperglycæmia follows the direct injection of a solution of insulin into the small intestine of the rabbit. Minced small intestine *in vitro* at 37° destroys the activity of insulin in 3 hrs.

E. A. Lunt.

Effect of insulin on fat content of body and organs. S. Omura and K. Nitta (Folia endocrinol. japon., 1927, 2, 103—121).—On injection of insulin into rabbits, the fat in the heart, kidney, and skeletal muscle increases, whilst that in the liver decreases; with mice, or with the use of dextrose and insulin, there is a general increase of fat.

Chemical Abstracts.

Intermediary carbohydrate metabolism. XXI. Effect of insulin on dextrose, lactic acid, and phosphoric acid formation by liver tissue. T. Brugsch and H. Horsters (Biochem. Z., 1927, 188, 147—163).—Addition of insulin to suspensions of liver cells from normal, phloridzinised, and depancreatised dogs, rabbits, and guinea-pigs in Ringer's solution with added phosphate results in an average decrease in dextrose content. This decrease is not due to oxidation, production of lactic acid, or the formation of phosphoric esters. E. A. Lunt.

Intermediary carbohydrate metabolism. XXIV. Lack of influence of insulin on the mutarotation of dextrose and lævulose. P. Radt (Biochem. Z., 1927, 188, 178—196).—The effect of insulin on the mutarotation of α- and β-dextrose and of lævulose in aqueous, potassium phosphate, and Ringer solutions has been determined at 18° for 0·1% concentration of insulin and 1% concentration of sugar. No change was observed either in the rate of mutarotation or in the final rotation.

E. A. Lunt.

Stereochemical transformation of dextrose by the action of insulin and of muscular tissue. G. Quagliariello and P. De Lucia (Atti R. Accad. Lincei, 1927, [vi], 6, 113—116).—The authors are unable to confirm Lundsgaard and Holbøll's statements that the body-fluids of normal animals contain an unstable form of dextrose ("neoglucose") with a very low rotatory power and that this compound is formed *in vitro* by the simultaneous action of insulin and fresh muscular tissue on dextrose (A., 1926, 1171).

T. H. Pope.

Action of insulin on glycolysis and on carbohydrate metabolism of muscle. J. Homma (Japanese J. Med. Sci., 1927, 1, 165—181).—The following phenomena have been investigated in the blood of normal and diabetic dogs and men: (*a*) the difference in sugar content between arterial and venous blood, (*b*) the rate of glycolysis. In the normal dog there is some 10% more sugar in arterial than in venous blood, a difference which is increased during short artificial hyperglycæmia. After pancreatectomy (*a*) practically disappears, whilst (*b*) is much reduced; insulin injected subcutaneously restores (*a*) to its pre-operative value and increases (*b*). Glycolysis of normal blood is not influenced by insulin *in vitro*.

In mild diabetes in man, (*a*) is quite marked, but is scarcely detectable in severe cases; (*b*) is less in severe than in mild diabetes. After insulin injection in severe diabetes, both (*a*) and (*b*) return to the normal. There is no direct relationship between the rate of glycolysis and the presence or absence of lipæmia. H. D. Kay.

Abel's pituitary tartrate. L. Hogben (Nature, 1927; **120**, 803—804).—Polemical.
A. A. Eldridge.

Preparation of highly active pancreatic secretin solution. A. B. Luckhardt, O. W. Barlow, and M. Weaver (Proc. Amer. Physiol. Soc., Amer. J. Physiol., 1926, **76**, 182).—The first 100—150 cm. of dogs' intestine, after being washed with tap water, is partly filled with 100—150 c.c. of 0·2—0·4% hydrochloric acid and maintained at the ordinary temperature for 10 min., the extract then being filtered through cotton. Chemical Abstracts.

Mineral nutrition of the living cell and vitamins. Mineral nutrition and natural resistance of vegetable and animals to infectious diseases. M. P. Mazé (Ann. Inst. Pasteur, 1927, **41**, 948—981).—A review of the work done in this field by various workers including the author, together with his conclusions. W. Robson.

Effects of cod-liver oil on the calcium and phosphorus metabolism of the lactating animal. D. Harvey (Biochem. J., 1927, **21**, 1268—1276).—The feeding of cod-liver oil to goats improves the balance of calcium by reducing the amount excreted in the fæces (the output of the latter is decreased) and in late lactation increases the percentage and total amounts of calcium in the milk. The fat content of the milk shows no definite change. The effects on phosphorus excretion, on the other hand, are variable. The iodine content of the milk is increased by the administration of either cod-liver oil or potassium iodide. The replacement of cod-liver oil by olive oil plus an equivalent amount of iodine as potassium iodide does not produce the above effects.
S. S. Zilva.

Influence of fat-soluble vitamins and factors on total and inorganic phosphoric acid in rats' blood. H. von Euler, T. Lövgren, and M. Rydbom (Z. physiol. Chem., 1927, **170**, 79—90).—It is suggested that the antirachitic vitamin is concerned in an enzyme reaction which, with phosphatides and fat-soluble phosphoric acid derivatives as starting material, determines the resorption of phosphates, the formation of bone substance, and the regulation of the equilibrium between calcium and phosphate ions in serum and in cartilage. Rats on a rachitic diet show a phosphate ion content of 8 mg. per 100 c.c. of serum, contrasted with 20 mg. on normal diet. By irradiation of cod-liver oil the activity of the growth-factor is enhanced, but no well-defined alteration of the phosphate content of the blood is produced. Strong overdosage with the antirachitic vitamin produces the same effect on the inorganic phosphate content of the serum as on the growth, *i.e.*, beyond a maximum effect at double the minimum dose, further addition of the vitamin has no marked result. Ox-blood (0·15 mg. per day for young 50 g. rats) is a completely satisfactory antirachitic addendum to the diet. C. Hollins.

Antirachitic activation of substances by cathode rays. A. Knudson (Science, 1927, **66**, 176—178; cf. Knudson and Coolidge, Proc. Soc. Exp. Biol. Med., 1927, **24**, 363).—Cholesterol acquires antirachitic potency on exposure to cathode rays for 30 sec., and the potency is not destroyed by exposure for 900 sec., but cholesterol purified by way of the dibromide cannot be rendered antirachitic either by cathode rays or by ultra-violet light. Yeast, starch, and cottonseed oil can be activated with cathode rays.
A. A. Eldridge.

Attempted activation of tyrosine by ultra-violet irradiation. S. K. Kon and T. Moore (Biochem. J., 1927, **21**, 1368—1369).—McCollum's diet 3143 containing 0·5% of irradiated tyrosine does not prevent rickets. This is contrary to the statement of Waltner (Magyar Orsovi Arch., 1927, **28**, 19). S. S. Zilva.

Effects on pigeons of an exclusive diet of rice meal, bran, and polish. R. R. Williams (Biochem. J., 1927, **21**, 1349—1351).—The above rice mill by-products, although capable of preventing avian polyneuritis when incorporated in a basal diet consisting of polished rice, are distinctly harmful to pigeons when fed as the exclusive diet. This harmful effect varies with different samples. S. S. Zilva.

Physiological rôle of vitamin-*B*. V. Relation of inanition to vitamin-*B* deficiency in pigeons. G. F. Marrian, L. C. Baker, J. C. Drummond, and H. Woollard (Biochem. J., 1927, **21**, 1336—1348).—There is a hypertrophy of the adrenal glands in pigeons that are deprived of food, with a proportionate increase of the adrenaline content in most cases whether vitamin-*B* be administered or not. A slight but definite hyperglycæmia is observed in pigeons during most of the course of inanition, and is followed by a hypoglycæmia which is coincident with the premortal fall in body temperature. This variation in the blood-sugar content is independent of the consumption of vitamin-*B*. Nervous symptoms resembling those of avian polyneuritis were observed in a number of starving birds just before death, when the body temperature and blood-sugar were much reduced. The administration of vitamin-*B* or of large volumes of water did not prevent the occurrence of these symptoms. Typical nervous symptoms of beri-beri manifest themselves in about 16 days at a time when the loss of body weight is almost negligible in pigeons forcibly fed on large quantities of a diet deficient in vitamin-*B*. In these birds, although the adrenal glands were hypertrophied, no corresponding increase in their adrenaline content was observed. Vitamin-*B* in this research designates the accessory food factors in yeast. S. S. Zilva.

Basal metabolism in vitamin-*B* starvation. S. Okada, E. Sakurai, T. Ibuki, and H. Kabeshima (Arch. Int. Med., 1924, **40**, 292—313).—Vitamin-*B* starvation in patients with beri-beri causes aggravation of the symptoms and a decrease in the basal metabolism. Administration of a vitamin-*B* preparation ameliorates the symptoms and increases the

basal metabolic rate. Prolonged vitamin-*B* insufficiency in healthy persons causes typical avitaminosis and decrease in basal metabolic rate. The identification of beri-beri with avitaminosis is discussed.
W. Robson.

Influence of the nature of nutritive carbohydrates on the production of acute polyneuritic conditions, recurrent or chronic, obtained in spite of the presence of yeast or yeast extracts. (Mme.) L. Randoin and R. Lecoq (Compt. rend., 1927, **185**, 1068—1070; cf. A., 1927, 796).—Experiments on three groups of pigeons, fed on balanced artificial diets having the same percentage composition but with different carbohydrates and varying amounts of the two vitamins-*B*, showed that where galactose is the only sugar used, even with large daily doses of brewer's yeast, death occurs in 15—20 days. With other quickly-absorbed sugars, *e.g.*, dextrose, a slight deficiency in these vitamins causes prolonged recurrent polyneuritis followed by death, whilst a deficiency only in the antineuritic vitamin causes chronic polyneuritis. The importance of the nature as well as the amount of essential food constituents is thus shown. B. W. Anderson.

The antineuritic vitamin. I. A possible second factor. J. L. Rosedale (Biochem. J., 1927, 1266—1267).—Rice polishings were extracted with 1% acetic acid and the extract was precipitated with lead acetate. The fraction from the precipitate cured acute polyneuritis in pigeons; that from the filtrate enabled the birds to maintain growth, health, and natural functions. S. S. Zilva.

Absorption spectra of oils and oil constituents with special reference to pro-vitamin-*D*. I. M. Heilbron, E. D. Kamm, and R. A. Morton (Biochem. J., 1927, **21**, 1279—1283).—By introducing ergosterol into transparent oil showing no selective absorption in the ultra-violet region the three bands at 293·5 μμ, 281·5 μμ, and 270 μμ characteristic of the sterol are obtained. With a 0·2% ergosterol solution the three bands are detected with certainty, whilst with lesser amounts the results are less trustworthy. Utilising this method, a number of oils and oil extracts have been examined for ergosterol and the results are tabulated. Yeast-fat showed the most pronounced absorption of all the oils examined. Groundnut oil varied from sample to sample, no selective absorption being observed in some samples. Where, however, ergosterol bands were plainly present there was also a more or less well-defined band in the neighbourhood of 320 μμ. Sections of skin of 0·1 mm. are not transparent below 297 μμ. S. S. Zilva.

Induced fluorescence of ergosterol. O. Rosenheim (Biochem. J., 1927, **21**, 1335).—Specimens of ergosterol of different origin show a brilliant blue fluorescence when exposed to ultra-violet rays and screened from visible light. Pure cholesterol does not show this phenomenon. There is, however, no connexion between it and the formation of vitamin-*D*, since non-fluorescent ergosterol can be activated. The fluorescence is most probably due to the formation of traces of oxidation products. S. S. Zilva.

Behaviour of vitamin-*A*. H. Steudel (Z. physiol. Chem., 1927, **170**, 13—22).—The growth-factor *A*, as found in brain, is very sensitive to heat except when dissolved with its lipoid complement in fat or other suitable medium. Plant lipins contain little or none of the growth-factor, and the same is true of plant and animal lecithins. A certain relation between growth-factors and sterols is unmistakable. "Promonta," which contains the antirachitic vitamin in considerable amount, rapidly cures experimental keratomalacia without any arrest of growth during treatment. C. Hollins.

Absorption of vitamin-*D* from the skin. E. M. Hume, N. S. Lucas, and H. H. Smith (Biochem. J., 1927, **21**, 362—367).—Vitamin-*D* in irradiated cholesterol can be absorbed from a small area of undamaged skin to supply the needs of the rat and the rabbit. Rickets was prevented in rabbits fed on a rickets-producing diet and almost normal calcification of the bones was produced, when an area of skin 2·5×3·5 cm. was irradiated for 10 min. three times a week. S. S. Zilva.

Hydrogenation of "biosterin." Z. Nakamiya and K. Kawakami (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, **7**, 121—142; cf. A., 1925, i, 1365).—On reduction of biosterin by Fokin and Willstätter's method, a solid substance separates, in which nonacosane, batyl alcohol, octadecyl palmitate, and melissyl alcohol have been detected. The greater portion of the product is, however, liquid at the ordinary temperature, and can be separated by distillation into two fractions; it is not possible to ascertain which of these corresponds with vitamin-*A*, as the activity is destroyed by the reduction.
R. Cuthill.

Indispensable nature of zinc and boron for higher green plants. A. L. Sommer and C. B. Lipman (Plant Physiol., 1926, **1**, 231—249).—Experiments with sunflowers, cotton, barley, buckwheat, castor beans, flax, and mustard grown in culture solutions indicate that for good growth the presence of zinc and boric acid (0·5 in 10^6) is necessary.
Chemical Abstracts.

Effect of temperature on the unequal intake of the ions of salts by plants. A. K. H. Petrie (Austral. J. Exp. Biol., 1927, **4**, 169—186).—The effect of temperature over the range 4—30° on the absorption by isolated plant-tissue of the ions of single electrolytes has been studied. With rise of temperature the amount of cation absorbed falls and the amount of anion absorbed increases, and these alterations take place proportionally. It is suggested that the absorption of ions by plant cells is a process of base exchange in dissociated colloidal acids or their salts and that a Donnan equilibrium is set up between the colloidal anions of the protoplasm and the external medium. E. A. Lunt.

Hydrogen-ion concentration of plant tissues. III. *Helianthus annuus*. IV. Buffer of sunflower hypocotyl. S. H. Martin. **V. *Vicia faba*.** M. W. Rea and V. Small (Protoplasma, 1927, **1**, 497—521, 522—536; **2**, 45—58). Chemical Abstracts.

Isoelectric point for plant tissue and its importance in absorption and toxicity. W. J. Robbins (Univ. Mo. Studies, 1926, **1**, 3—60).
Chemical Abstracts.

Electroendosmosis through wood membranes. A. J. Stamm (Fourth Colloid Symposium Monograph, 1926, 246—257).—A study of Sitka spruce, Alaska cedar, western red cedar, western hemlock, Douglas fir, and yellow poplar woods. The wood/water potential was 0·0136. Chemical Abstracts.

Photocapillary reaction of plant sap. F. Herčík (Biochem. J., 1927, **21**, 1253—1258; cf. Publ. Fac. Sci. Univ. Masaryk, 1926, No. 74; Biologia Generalis, 1927, **3**, 83; Biol. Listy, 1927, **13**, 108).—The surface tension of the sap of the seedlings of *Sinapis alba* increases on illumination with 1356 lux. When the sap is diluted with distilled water the reverse takes place. In 80% dilution the surface tension at first decreases, then strongly increases and again decreases. In 60% dilution the first increase is smaller and on the contrary the second decrease is more intense. The 20% sap shows practically no increase, the surface tension decreasing in this case almost regularly after illumination. The 10% sap shows a surface tension decrease depicted by a smooth parabolic curve. The changes in the diluted and undiluted sap do not take place in the dark, whilst the surface tension of illuminated saps returns to its initial value in these circumstances. This photocapillary phenomenon is independent of the intensity of the light and can be observed also in the sap of the etiolated seedlings of *Pisum*, *Vicia*, or *Pharbitis*. S. S. Zilva.

Alkali tolerance of plants considered as a phenomenon of adaptation. J. F. Breazeale (Arizona Agric. Exp. Sta. Tech. Bull., 1926, **11**, 239—256).—The alkali tolerance of plants depends on the amount of alkali required to destroy the enzymes of the roots concerned with growth. Minimal amounts of calcium increase the tolerance of wheat seedlings for sodium chloride and other compounds. Calcium absorbed at one period of growth may effectively "immunise" the plant against alkali at a later period. Chemical Abstracts.

Nitrogen metabolism of the *Coniferæ*. K. Mothes (Ber. deut. bot. Ges., 1927, **45**, 472—480).—The rate of degradation of protein in leaves of *Vicia faba* and in seeds of *Pinus pinea*, growing in the dark and in the light under various conditions, has been followed. The carbohydrate deficiency induced by darkness results in the decomposition of the protein reserves. It is concluded that the nitrogen metabolism of the *Coniferæ* is analogous to that of the *Gramineæ* and *Leguminosæ*, and that arginine does not take the place of asparagine in the *Coniferæ*. Suzuki's statement that the administration of ammonia as ammonium chloride solution to the pine seedlings results in a great increase in arginine formation could not be confirmed. E. A. Lunt.

Treub's hypothesis. II. L. Rosenthaler (Biochem. Z., 1927, **190**, 168—180).—No relationship has been found between the amount of illumination and the extent of formation of hydrocyanic acid in cherry-laurel leaves. This does not support the second principle of Treub's hypothesis, which states that hydrocyanic acid is formed from carbohydrates and nitrates, for since the formation of carbohydrate is dependent on the exposure to light, the formation of hydrocyanic acid should be related to the amount of illumination. An increase in hydrocyanic acid content occurs in the young leaves of the cherry-laurel during the development of the leaf buds and this increase is related to protein formation, whilst with *Sambucus nigra*, manuring with amino-acids produces marked increases in the hydrocyanic acid of the stalk and leaves. It is suggested that hydrocyanic acid is formed in plants as a side-reaction of the nitrogen or protein metabolism, when the whole of the simple nitrogenous compounds such as amino-acids cannot be converted into more complex compounds, especially proteins. A. Wormall.

Speed of autumnal migration of nitrogenous substances from the leaves to the stems of woody plants. R. Combes and R. Échevin (Compt. rend., 1927, **185**, 1060—1062).—There is little or no movement of nitrogenous substances towards the stems and roots of trees until the leaves are definitely turning yellow; during this colour change the process is extremely rapid, 70% of the nitrogen content of the leaves migrating in about 20 days. B. W. Anderson.

Isolation and identification of some organic nitrogenous compounds occurring in etiolated maize seedlings. S. L. Jodidi (J. Agric. Res., 1927, **34**, 649—656).—Asparagine has been shown to be present in considerable quantity in maize seedlings germinated and grown in darkness for 5—7 days. Decomposition of the proteins in the seed into amino-acids by the process of germination (A., 1926, 761) appears to be followed by gradual conversion of the latter into asparagine. The occurrence of vernine in the seedlings was also indicated. C. T. Gimingham.

Comparative plant chemistry. XVIII. *Carex flacca*, Schreb. H. Swiatkowski and J. Zellner. **XIX. Chemistry of barks. VI.** J. Zellner. **XX. Latex-bearing plants. III.** E. Huppert, H. Swiatkowski, and J. Zellner (Monatsh., 1927, **48**, 475—478, 479—490, 491—500).—XVIII. The constituents of the fruit of *Carex flacca*, Schreb., have been determined by the usual methods. The air-dried fruit yielded: light petroleum extract 10·28%, ether extract 2·59%, aqueous extract 7·29%, water-soluble ash 3·44%, soluble polysaccharides 1·24%, free acids (as KOH) 1·26%, pentosans 11·19%, methylpentosans 0·36%, starch 23·56%, nitrogen 2·28%, crude proteins 14·25%, total ash 5·37%, and traces of reducing sugars and tannins. The light petroleum extract yielded an oil which is almost completely hydrolysed, the resulting fatty acids, on oxidation by potassium permanganate, yielding a dihydroxystearic acid, m. p. 135°, and a tetrahydroxystearic acid, m. p. 173°; hence the original fatty acids consist mainly of oleic and linoleic acids. The ether extract yielded only a trace of an amorphous substance which gives the cholesterol reaction. The alcohol extract yielded only phlobaphens, tannins, and dextrose or invert-sugar, whilst the aqueous extract contained chlorides, sulphates, nitrates, phosphates, malates, and starch.

XIX. The following barks have been investigated by the usual methods: [with C. L. Scherzer].—Purple willow (*Salix purpurea*, L.). The light petroleum extract on hydrolysis yielded 30% of unhydrolysable material which contained a *hydrocarbon*, m. p. 63° (C 84·53 ; H 14·92%), Hesse's phytosterol, a *substance*, m. p. 240°, and probably ceryl alcohol, whilst the acids separated by hydrolysis consisted of oleic, palmitic, and stearic acids. The alcohol extract (5% of the dried bark) contained phlobaphens, invert-sugar, and a trace of salicin. The aqueous extract (8% of the dried bark) yielded only amorphous products. Robinia (*Robinia pseudacacia*, L.) bark yielded : light petroleum extract 2·95%, ether extract 1·50%, alcohol extract 11·35%, aqueous extract 6·77%, free acids (as KOH) 2·85%, tannins 1·75%, soluble polysaccharides 0·72%, total nitrogen 1·87%, crude protein 11·69%, total ash 7·07%, and traces of reducing sugars. The light petroleum extract on hydrolysis yielded ceryl alcohol, a wax alcohol, m. p. 69—70°, Hesse's phytosterol which was separated into sitosterol (90%) and stigmasterol, and oleic and palmitic acids together with an acid of lower m. p., probably myristic acid. The alcohol extract contained phlobaphens, invert-sugar, and bases of the choline type, whilst the aqueous extract contained a pectin-like carbohydrate, together with phosphates, sulphates, oxalates, and tartrates.

Carob bean tree (*Ceratonia siliqua*, L.). The light petroleum extract on hydrolysis yielded a wax alcohol, m. p. 68—72°, a phytosterol, a *substance*, m. p. 260—262° (*acetyl* derivative, m. p. 164°), and palmitic, stearic, and liquid acids. The alcohol extract contained only phlobaphens, tannins, and invert-sugar.

[With W. ROMANOFSKY.]—Spindle tree (*Euonymus europæa*, L.). The bark was extracted with hot alcohol. The precipitate which separated from the solution on cooling contained dulcitol (1—1·5% of the air-dried bark), which was converted by cinnamoyl chloride and quinoline in chloroform solution into its *hexacinnamate*, m. p. 232—233°, and ceryl alcohol. The alcoholic solution was evaporated to dryness. The light petroleum extract of the residue yielded, after hydrolysis, a *hydrocarbon*, m. p. 63—65°, ceryl alcohol, a phytosterol, and palmitic and stearic acids. The alcohol extract contained invert-sugar, phlobaphens, and a tannin which on fusion with potassium hydroxide yielded an unidentified *substance*, m. p. 195—197°.

[With P. BOMBERG.]—Tree of heaven (*Alianthus glandulosus*, Desf.). The bark yielded : light petroleum extract 4·33%, ether extract 1·41%, alcohol extract 12·18%, total water-soluble matter 34·25%, soluble ash 0·86%, free acids (as KOH) 5·12%, soluble polysaccharides 0·96%, total nitrogen 0·95%, total ash 7·62%. The precipitate which separated from an alcoholic extract of the dried bark consisted essentially of ceryl palmitate and a *hydrocarbon*, m. p. 68°. The light petroleum extract of the alcohol-soluble portion yielded, after hydrolysis, ceryl alcohol (probably contaminated with a lower homologue), and palmitic and stearic acids. The alcohol extract yielded phlobaphens, tannins, invert-sugar, and a bitter principle. The aqueous extract contained polysaccharides and salts of oxalic and inorganic acids.

XX. The whole of the air-dried plant *Euphorbia Cyparissias*, L., with the exception of the root, has been examined, the latex being investigated separately. The air-dried plant yielded : light petroleum extract 5·18%, ether extract 1·49%, alcohol extract 9·12%, aqueous extract 30·64%, soluble ash 6·63%, reducing sugars 2·81%, tannins 3·55%, soluble polysaccharides 3·74%, free acids (as KOH) 1·42%, nitrogen 1·73%, total ash 11·26%. The light petroleum extract, after hydrolysis, yielded ceryl alcohol, amorphous resins, and a substance resembling euphorbone isolated from the latex (below), together with oleic acid and fatty acids of m. p. 67—75°. The ether extract, after hydrolysis, yielded ceryl alcohol, a substance, m. p. 170°, probably stigmasterol, and amorphous products. The alcohol extract yielded phlobaphens, tannins, lævulose, choline, and *euphorbine*, $C_6H_{13}O_2N$, m. p. 240°, which is saturated and has not the reactions of an amino-acid. The aqueous extract contained polysaccharides including pentosans, and salts of tartaric, malic, phosphoric, sulphuric, and traces of hydrochloric acids. The latex (containing 84% of water) from 15 kg. of air-dried plant yielded 60 g. of air-dried substance. The light petroleum extract contained caoutchouc and an alcohol-soluble portion which, after hydrolysis, yielded C-*euphorbone*, $C_{26}H_{46}O$, m. p. 106—107° [*bromine additive* compound, m. p. 155° (decomp.); *acetyl* derivative, m. p. 105°; *benzoyl* derivative, m. p. 117°], which is dextrorotatory, together with amorphous substances and traces of acids. No characteristic products were obtained from the alcoholic and aqueous extracts. The dried latex of *Euphorbia austriaca* kernels was examined. The light petroleum extract yielded caoutchouc and amorphous resins and an alcohol-soluble portion which, after hydrolysis, yielded (after removal of amorphous resins with cold methyl alcohol) A-*euphorbone*, m. p. 88—89° (*acetyl* derivative, m. p. 115—116°). The alcoholic and aqueous extracts yielded only potassium chloride and amorphous substances which could not be characterised. A comparison of the properties of the various euphorbones with those isolated by other workers indicates that *A*-euphorbone is different from *R*-euphorbone.

J. W. BAKER.

Toxic constituent of richweed or white snakeroot (*Eupatorium urticæfolium*). J. F. COUCH (J. Agric. Res., 1927, 35, 547—576).—A disease of cattle and sheep, known as "trembles," is caused by the consumption of the plant *E. urticæfolium*, and milk or milk products from poisoned animals may give rise to "milk sickness" in human beings. A chemical and pharmacological investigation of the plant has led to the isolation of the toxic constituent, *tremetol*, $C_{16}H_{22}O_3$. Tremetol has the properties of an unsaturated alcohol; it is soluble in fats and fat solvents and may be excreted in milk. It gives a characteristic cherry-red colour when a solution in light petroleum is floated on sulphuric acid. The plant also contains a resin acid, which is toxic to rabbits and guinea-pigs but does not cause trembles in sheep; a volatile oil; a crystalline sterol, m. p. 148—149°; inulin; lævulose; an organic base, and a non-toxic glucoside. The tremetol content rapidly diminishes on drying. Sheep poisoned by the plant or by tremetol develop an acidosis and excrete acetone. C. T. Gimingham.

Variation of the protein content of maize. V. H. B. Arbuckle and O. J. Thies, jun. (J. Elisha Mitchell Sci. Soc., 1926, **42**, 113—117; cf. A., 1926, 439).—Immature maize is low in protein. Grains from the middle of the ears are higher in protein than those from the butt or tip. Nitrates slightly increase and phosphates slightly decrease the percentage of protein. Chemical Abstracts.

Methyl alcohol in tobacco smoke. C. Neuberg and B. Ottenstein (Biochem. Z., 1927, **188**, 217—226).—Data are given for the amount of methyl alcohol in the smoke from various brands of cigars, cigarettes, and pipe tobacco. The greatest amount occurs in cigarette smoke. 90% of the methyl alcohol inhaled dissolves in the saliva, and 20 cigarettes (av. weight 20 g.) yield 42 mg. of methyl alcohol.
E. A. Lunt.

Effect of acetate buffer mixtures, acetic acid, and sodium acetate on the protoplasm as influencing the rate of penetration of cresyl-blue into the vacuole of *Nitella*. M. Irwin (J. Gen. Physiol., 1927, **11**, 111—121; cf. A., 1926, 647; 1927, 72).—The inhibiting effect of sodium acetate–acetic acid buffer mixtures on the rate of penetration of brilliant-cresyl-blue into the vacuole of living *Nitella* is due partly to the specific action of the sodium ion on the protoplasm and partly to the effect of the presence of acetic acid. The rate of penetration of the dye from a borate or phosphate buffer mixture of p_H 7·85 is reduced if the cells have previously been exposed to a solution of acetic acid. This is probably due to the penetration of the undissociated acetic acid into the protoplasm and its subsequent retention and dissociation there.
W. O. Kermack.

Counteraction of inhibiting effects of various substances on *Nitella*. M. Irwin (J. Gen. Physiol., 1927, **11**, 123—139; see preceding abstract).—The rate of penetration of the dye from a borate buffer mixture at p_H 7·85 is also inhibited by previous exposure to solutions of phosphate buffer mixture, phosphoric acid, hydrochloric acid, sodium chloride, and sodium borate, but this decrease does not occur if the borate mixture contains a sufficient concentration of sodium ions or if a phosphate buffer mixture is substituted for the borate buffer mixture. The inhibiting effect may also sometimes be removed if the dye solution contains certain bivalent cations or if the cells are exposed to such ions.
W. O. Kermack.

Alleged formation of fumaric acid from pyruvic acid by *Rhizopus nigricans*. F. Ehrlich and I. Bender (Z. physiol. Chem., 1927, **170**, 118—133; cf. Gottschalk, A., 1926, 545).—Careful repetition of Gottschalk's experiments under a variety of conditions shows that *R. nigricans* is unable to grow in a solution of pyruvic acid and mineral salts or to transform pyruvic into fumaric acid. C. Hollins.

Production of gluconic acid by *Penicillium luteum-purpurogenum* group I. O. E. May, H. T. Herrick, C. Thom, and M. B. Church (J. Biol. Chem., 1927, **75**, 417—422).—Fungi of the above group grown on media containing 10—30% of commercial dextrose produced, in 14 days, gluconic acid in amounts of 20—60% of the dextrose originally present; *barium gluconate* (+H_2O) has $[\alpha]_D^{20}$ +9·0°.
C. R. Harington.

Nitrogen nutrition of *Penicillium glaucum*. H. Coupin (Compt. rend., 1927, **185**, 963—965).—In an otherwise suitable medium at 25°, *P. glaucum* assimilated the nitrogen necessary for its growth from proteins, amino-acids, urea, uric acid, and amygdalin, but not from alkaloids, pyrrole, aromatic amines, or cyano-compounds. Among inorganic compounds, ammonium salts and nitrates, but not nitrites, yielded their nitrogen to the fungus.
B. W. Anderson.

Nutritive value of mushrooms (*Cantharellus cibarius*. J. Bareš (Chem. Listy, 1927, **21**, 477—484; cf. A., 1927, 703).—Mushrooms contain 9·58% of dry matter, of which 12·85% is ash and 3·50% is nitrogen, present partly as digestible protein, but to a large extent as chitin. Carbohydrates are present to the extent of 32·7%, chiefly as *d*-mannitol, sorbitol, dextrose, trehalose, cellulose, and pentoses, other carbohydrates also being present. The nutritive value of mushrooms is small. R. Truszkowski.

Influence of the soluble silicic acid content of soil on the absorption of phosphoric acid by plants. A Němec (Biochem. Z., 1927, **190**, 42—56).—A method is described for the colorimetric determination of silicic acid in aqueous extracts of soil, and the effects of varying the duration of extraction and the amount of water, of drying the soil, and of other factors have been determined. Soil which has been extracted repeatedly with water until the soluble silicic acid is considerably depleted gives, after being air-dried, moistened with water, and kept at the ordinary temperature for 14 days, values for soluble silicic acid which are very near the original value. The water-soluble silicic acid of the soil has a marked influence on the assimilation of phosphoric acid by plants, and with soils poor in silicic acid there is little or no absorption of phosphoric acid.
A. Wormall.

Influence of surface-active substances on wheat grains and spores of *Tilletia tritici*. A. C. Wolf (Biochem. Z., 1927, **188**, 117—133).—The effect of methyl and ethyl alcohols and certain mordants on wheat seeds and the spores of *T. tritici* has been studied. The greatest toxic action with ethyl alcohol was exerted in 40—60% solution; the presence of this surface-active substance increases the toxicity of mercuric chloride. E. A. Lunt.

Rotating dialyser. N. C. Wright and W. Rule (J. Biol. Chem., 1927, **75**, 185—187).—The dialysing membrane is inserted between the mouths of two glass funnels with ground edges and the whole is mounted in an apparatus which can be rotated mechanically.
C. R. Harington.

Colorimeter based on the Lovibond colour system and its application to the testing of cod-liver oil and other purposes. O. Rosenheim with E. Schuster (Biochem. J., 1927, **21**, 1329—1334).—The standard glasses are arranged in frames containing ten each of the red, yellow, and blue units, so that they can be rapidly moved horizontally behind a window below the cell which contains the coloured solution to be matched. Details for the colorimetric determination of vitamin-*A* with arsenic chloride or antimony chloride are given. The application of this instrument for other colorimetric work such as the determination of $p_{\rm H}$ or of cystine is recommended.

S. S. Zilva.

Sucrose and potassium nitrate as plasmolysing agents. W. A. Beck (Protoplasma, 1926, **1**, 15—72).—Measurements of the osmotic value at incipient plasmolysis by sucrose solutions are trustworthy, but those using potassium nitrate are not.

Chemical Abstracts.

Micro-determination of chlorides in biological liquids and organs. E. Tschopp (Mikrochem., 1927, **5**, 161—165).—For liquids, 1 c.c. is treated with 10 c.c. of 0·02*N*-silver nitrate solution, 1 c.c. of 15% trichloroacetic acid solution (to coagulate the protein), and 1 c.c. of nitric acid (*d* 1·4) and the mixture is diluted to 25 c.c. After 30 min. the liquid is filtered through a dry paper and the excess of silver in 20 c.c. of the filtrate is titrated with 0·02*N*-potassium iodide using 1 c.c. of fuming nitric acid and 3 c.c. of starch solution as indicator. For solids, 1 g. is heated with 10 c.c. of the silver nitrate solution, 5 c.c. of nitric acid, and 2 c.c. of "perhydrol" in a micro-Kjeldahl apparatus until dissolution is complete, and, after dilution to 25 c.c., 20 c.c. of the filtrate are titrated as before. A. R. Powell.

Colorimetric micro-determination of sodium. H. K. Barrenscheen and L. Messiner (Biochem. Z., 1927, **189**, 308—313).—Sodium is precipitated as zinc uranyl sodium acetate (cf. Kolthoff, A., 1927, 436) and determined colorimetrically after conversion into the ferrocyanide. The method is successfully applied to biological material (*e.g.*, serum) by employing the filtrate after treatment with alcoholic zinc acetate to remove protein and phosphate; other cations, *e.g.*, potassium, calcium, magnesium, and ammonium, in their usual concentrations, do not interfere with the determination. The maximal error of determination is ± 1·5%. P. W. Clutterbuck.

Micro-determination of magnesium in biological liquids and organs. E. Tschopp (Helv. Chim. Acta, 1927, **10**, 843—846).—The method depends on the fact that phosphomolybdic acid is readily reduced to molybdenum-blue. After removal of calcium, magnesium is precipitated as magnesium ammonium phosphate. The washed precipitate is dissolved in dilute sulphuric acid and molybdic acid added. Reduction to molybdenum-blue is effected by means of a solution containing "eikonogen," sodium hydrogen sulphite, and sodium sulphite. The resulting colour is compared with that given by a standard solution of phosphoric acid.

J. S. Carter.

Determination of minimal amounts of manganese, copper, and iron in biological investigations. A. Quartaroli (Annali Chim. Appl., 1927, **17**, 361—375).—Copper or manganese in small proportion (as little as 1 : 10,000,000) may be determined by taking advantage of the catalytic action of the metal on hydrogen peroxide. The influence of 1 part of iron in 2000 parts of solution is negligible, and the other elements, occurring in organisms, such as alkali and alkaline-earth metals, are without effect. From 4 to 8 drops of ammonia solution (*d* 0·95) are added to 20 c.c. of the almost neutral liquid, which is kept at 20°, and then about 0·5 g. of powdered glass and 2 c.c. of hydrogen peroxide solution of such concentration that its complete decomposition furnishes about 20 c.c. of oxygen. At intervals of 5 min. from the addition of the peroxide the liquid is shaken vigorously and the volume of the gas evolved read; only when evolution is very slow need these readings be prolonged to 25 or 30 min.

When copper alone is present, 8 drops of the ammonia solution are used. The reaction may be disturbed by the presence of iron, which tends slightly to diminish the action of copper; manganese, which has a slightly lower catalytic effect than copper, and phosphates, especially of magnesium, which may be precipitated on addition of ammonia. With manganese alone, either 4 or 8 drops of the ammonia solution may be used.

This reaction may be employed for the determination of both copper and manganese in presence of only small proportions of iron, and for the determination of iron, manganese, and copper in presence of phosphates, magnesium salts, etc. The procedure is described in each case. T. H. Pope.

Determination of oxalic acid as urea oxalate in the fluids of the organism. J. Khouri (Bull. Soc. Chim. biol., 1927, **9**, 961—969; cf. A., 1923, ii, 795).—A reply to Guillaumin (A., 1927, 475). The method of the author for the determination of oxalic acid is considered to give satisfactory results.

W. O. Kermack.

Determination of free and combined benzoic acid by means of the rocking extraction method. E. M. P. Widmark (Biochem. Z., 1926, **179**, 263—271).—For the determination of free benzoic acid in urine, 40 c.c. of the latter are acidified with 5 c.c. or more of 5*N*-sulphuric acid and rocked in a specially devised glass vessel in contact with 325 c.c. of toluene; the benzoic acid, which passes into the toluene layer, is removed from the latter by 30 c.c. of 0·065*N*-sodium hydroxide in another part of the vessel, which is so constructed that the acid urine and alkali never come into contact with one another. The benzoic acid absorbed by the alkali is determined by titration, suitable allowance being made for the carbon dioxide absorbed from the urine and for the small amount of acid formed from the toluene. The total benzoic acid is determined in a similar manner, the urine (40 c.c.) being first subjected to alkaline hydrolysis (10 c.c. of 6*N*-sodium hydroxide) for 7 hrs. on a boiling water-bath; 10 c.c. of 7*N*-sulphuric acid are then added, and the determination is carried out as before. The method is suitable for determining the daily excretion of benzoic and hippuric acids in small animals such as rats. J. Pryde.