BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

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General, Physical, and Inorganic Chemistry.

One-metre vacuum spectrograph. R. A. Sawyer (J. Opt. Soc. Amer., 1927, **15**, 305—308).—A convenient type of vacuum spectrograph designed to use the standard N.P.L. one-metre grating and to operate from 3000 to 1700 Å. is described.

R. W. Lunt.

Fine-structure constant as a numerical constant. S. Ray (Naturwiss., 1927, **15**, 408; Chem. Zentr., 1927, ii, 15).—According to Jeans ("Report on radiation and the quantum theory") $hc/2\pi=(4\pi e)^2$; hence the fine-structure constant $\alpha=2\pi e^2/hc=\pi^2/16$.

A. A. Eldridge.

Extension of the irregular doublet law. M. N. Saha and P. K. Kichlu (Nature, 1928, **121**, 244—245).—"On comparison of the spectra of a group of successive elements which are reduced by electric discharge to the same electronic constitution, frequencies of corresponding lines arising out of a transition in which the total quantum number remains unchanged will form an arithmetical progression." Hence, if the spectra of two elements, preferably successive, in any group be known, the spectra of the remaining elements can be predicted.

A. A. Eldridge.

Width of the lines of the Balmer series. (Mlle.) M. Hanot (Ann. Physique, 1927, [x], **8**, 555—625).—The width of a line is defined as the wave-length interval over which the average intensity of illumination is equal to one half of the intensity maximum, although this does not necessarily completely characterise the distribution of energy over the line as supposed by some. The width of the primary lines in the Balmer series has been studied for a spark spectrum in hydrogen, the conditions being closely defined by measurements of capacity, potential, and frequency of the circuit. The width of the lines was measured by a microphotometric method, using a Rowland grating.

For a given initial temperature and pressure, the width l of the lines is determined by the intensity of the current traversing the spark, according to the law $l=f(I_0)$, where I_0 is given by $I_0=V\sqrt{C/L}$ and so represents the maximum intensity of current in an undamped circuit. The width increases very rapidly with rising I_0 for small intensities and then tends to a maximum; its variation with pressure p is given approximately by $l=l_1\times p^m$, where l_1 is a constant and m is very close to unity for small intensities but decreases with increasing I_0 down to 2/3.

The chief causes of the enlargement of lines are (*a*) the absorption by the source of some of its own radiation and (*b*) the intermolecular field due to ions and quadruplets. The magnitude of the former was studied experimentally by passing radiation from one spark through a second; for $I=300$ amp. the width of the lines due to a very small region of the source is thus found to be 85—90% of the total width. The main cause of enlargement, however, is the intermolecular field due to the ions, which has a mean value of 10^5 volts/cm. and is proportional to the 2/3 power of the ionic density. The effect of the quadruplets is secondary, being greater for large currents than for small, whilst the absorption effect is greater in the small-current region, as expected by theory. The sum of these two effects is approximately constant at 10—15% of the width of the line. Like l, the current density in the spark follows a law of the form $i=\varphi(I_0)$, so that the theory explains the independence of the width of the lines and the damping of the circuit.

S. J. Gregg.

Continuous spectrum of hydrogen. J. Kaplan (Proc. Nat. Acad. Sci., 1927, **13**, 760—763).—A mechanism is suggested to account for the continuous spectrum emitted by the blue glow which occurs when hydrogen at pressures less than 1 mm. is excited by electrons of less than 15 volts.

R. W. Lunt.

Reversal of helium lines. T. Takamine and T. Suga (Phil. Mag., 1928, [vii], **5**, 141—149).—An examination of the reversal of helium lines has been made first with a long capillary tube viewed end-on and, secondly, with a long tube of wider bore placed between the capillary tube and the spectrograph. The lines of the principal and of the diffuse series show reversal, but there are great differences in the manner of their reversals. The lines of the principal series connected with the metastable states 2*s* and 2*S* are strongly absorbed in passing through the wider tube. This effect of the less luminous vapour is marked for the lines 5016 and 3889 Å. The lines of the diffuse series, such as 6678 and 5876 Å., are seen reversed with the capillary tube alone excited, the wider tube having little effect. The polarity of the capillary has a marked effect on the clearness of the reversals, indicating the effect of a heterogeneous distribution of the excited atoms along its length.

A. E. Mitchell.

Excitation of the auroral green line in discharge tubes. D. A. Keys (Trans. Roy. Soc. Canada, 1927, [iii], **21**, III, 257—261).—In an apparatus which is described, spectrograms have been taken of the light emitted from the electrical discharge through mixtures of (1) helium and oxygen and (2) argon and oxygen. With a large pressure of helium, *e.g.*, 15 mm. of helium to 1·5 mm. of oxygen, the auroral green line, 5577 Å., was obtained with a suitable current density. Under other conditions bands, which appeared to be the second group of Swan bands, were obtained instead, probably due to hydrocarbons present as impurities. With argon at a pressure of about 40 mm. and oxygen from 8 to 10 mm., the auroral green line was brought out with great intensity (cf. A., 1927, 179), but it was difficult to suppress the bands. The results support McLennan's view (Proc. Roy. Soc., 1927, **A**, **114**, 1) that the auroral green line is due to oxygen excited with enhanced intensity by the presence of helium or argon at comparatively high pressures. The diameter of the tube had a marked effect, a wide tube favouring the appearance of the line. M. S. Burr.

Spark spectrum of oxygen (O II). H. N. Russell (Physical Rev., 1928, [ii], 31, 27—33).—Ninety-nine lines, including all the strong lines not previously classified, are accounted for, and the electron configurations corresponding with the new terms have been identified. Bowen's conclusions concerning the origin of the nebular lines near 3727 Å. are confirmed. A. A. Eldridge.

Distribution of ionised oxygen in the gaseous nebulæ. J. H. Reynolds (Nature, 1928, **121**, 206—207).—There is no recorded evidence of the existence of neutral oxygen in the gaseous nebulæ; the distribution of O III and O II in Orion's nebula is discussed. A. A. Eldridge.

Nebulium spectrum in new stars. S. R. Pike (Nature, 1928, **121**, 136—137).—Elvey's reasoning (this vol., 98) is criticised. Alternatively, it may be supposed that the oxygen and hydrogen shells originate in different layers of the star.
A. A. Eldridge.

Metallic spectra excited by active nitrogen. J. Okubo and H. Hamada (Phil. Mag., 1928, [vii], 5, 372—380).—An examination of the after-glow spectrum of active nitrogen has confirmed the results of Strutt and of Johnson and Jenkins (A., 1926, 991). No evidence for the second group of positive bands reported by Ruark and others (A., 1927, 395) was obtained. The emission spectra of the vapours of mercury, cadmium, zinc, magnesium, sodium, potassium, thallium, and calcium under the bombardment of active nitrogen have been examined. Owing to the immediate formation of solid nitrides, only negative results were obtained with calcium. In the other cases the arc lines but none of the spark lines were excited. The highest energy level developed was the *4d* level of mercury corresponding with an excitation potential of 9·51 volts. Although the ionisation potentials of the other metals are less than 9·51 volts (so that ionisation of their vapours should be possible), no energy levels higher than those corresponding with 9·51 volts were developed. No traces of band spectra due to the formation or decomposition of metallic nitride were obtained. The results are in support of the hypothesis of Sponer (A., 1926, 8) that active nitrogen is neutral atomic nitrogen produced as the result of triple collisions the dissociation energy of which should be between 11·4 and 13 volts, so that the spectral lines of other gases excited in the after-glow should have energies less than 11·4 volts. A. E. Mitchell.

Reversal of neon lines. H. Nagaoka and T. Mishima (Proc. Imp. Acad. Tokyo, 1927, **3**, 586—589).—By means of a combination of a Lummer–Gehrcke plate with a concave grating, the interval of reversal has been determined for a number of neon lines of the type $1s-2p$, beginning with 5852 Å. ($1s_2-2p_1$) and extending to 6507 Å. ($1s_4-2p_8$).
R. A. Morton.

Spectrum of ionised sodium. F. H. Newman (Phil. Mag., 1928, [vii], 5, 150—159).—Accurate measurements of the Na II spectrum excited by an electrodeless discharge have been made and 137 lines between 2386·41 and 4830·9 Å. measured. The lines at 2138·4 and 3318·0 Å., previously observed by Schillinger (A., 1909, ii, 369) and Foote, Meggers, and Mohler (A., 1922, ii, 598), respectively, were not obtained. The series includes a number of lines not reported by these observers and does not include other lines attributed by them to the Na II spectrum. A preliminary analysis of the results shows no sequences or lines obeying the Ritz formula, but there are many pairs of lines with constant frequency separations.
A. E. Mitchell.

Series spectra of chlorine, Cl II, Cl III, Cl IV, Cl V, and of Si II, P III, and S IV. I. S. Bowen (Physical Rev., 1928, [ii], 31, 34—38).—Twenty-six lines in Cl II, 88 in Cl III, 26 in Cl IV, and 17 in Cl V are classified. Five additional lines in Si II, 15 in P III, and 13 in S IV are identified. A. A. Eldridge.

Spectrum of the corona. I. M. Freeman (Nature, 1928, **121**, 169—170).—About two thirds of the coronal lines given by Campbell and Moore can be connected with the argon lines and terms given by Meissner. A. A. Eldridge.

Inverse Stark effect in principal potassium series. W. Grotrian and G. Ramsauer (Physikal. Z., 1927, 28, 846—856).—The inverse Stark effect in the second term of the potassium lines 4047·201 and 4044·140 Å. and in the third term of the lines 3447·701 and 3446·722 Å. has been determined as a function of the electric force up to 10^5 and 8×10^4 volts cm.$^{-1}$, respectively. The total displacement towards the red varies as the square of the electric force. The shorter wave-length component of each doublet is resolved into two further components. The results are in good agreement with the theories of Becker and Thomas. R. W. Lunt.

Intensities of forbidden multiplets. J. Taylor (Phil. Mag., 1928, [vii], 5, 166—172).—Measurements have been made of the intensities of the $1^2S-3^2D_{5/2}$ and $1^2S-3^2D_{3/2}$ lines of potassium. The results show that for dilute concentrations the ratio of the intensities is given by the Sum rule and in conjunction with the results of Ornstein and Burger (Naturwiss., 1927, **15**, 32) it is concluded that the ratio is normal for forbidden multiplets. The relative change of the ratio of the maximum intensity of these lines to the non-forbidden $1^2S-3^2P_{3/2}$ and $1^2S-3^2P_{1/2}$ lines shows that the relative intensity of the forbidden to the permissible lines increases with both current and vapour density. It is suggested that the forbidden lines are brought up by the action of ionic electric fields and that their intensities increase with the field strength, a view which is in accordance with the results of Takamine and Werner. A. E. Mitchell.

New lines in the arc spectrum of manganese and rectification of these between 2500 and 2300 Å. S. Piña de Rubies (Anal. Fís. Quím., 1927, **25**, 494—502).—Since a previous investigation of the arc spectrum of manganese (A., 1927, 802) yielded a spectrum different from that of Fuchs (A., 1915, ii, 497) in the region 2500—2300 Å., this portion of the spectrum has been re-examined. It is shown that the difference is due to the presence of 22 new lines of manganese and to the absence of 20 lines due to iron and nickel considered by Fuchs as lines of manganese. Various other lines in Fuchs' spectrum which are apparently due to impurity are recorded and attention is drawn to errata in Kayser's "Tabelle der Hauptlinien der Linienspektra aller Elemente (1926)." J. S. Carter.

Arc spectrum of antimony. S. L. Malurkar (Proc. Camb. Phil. Soc., 1928, **24**, 85—88).—Provisional term values are given for the arc spectrum of antimony. Certain levels have been fitted into the Hund–Heisenberg scheme. R. A. Morton.

Under-water spark spectra of various metals. (Miss) E. J. Allin (Trans. Roy. Soc. Canada, 1927, [iii], **21**, III, 231—235).—A continuation of previous work (Clark and Cohen, A., 1926, 766). The under-water spark spectrum of tungsten shows about 90 reversals between 4000 and 2300 Å. Tellurium and thorium also show some reversed lines in the region 2100—2600 Å. and 2400—3000 Å., respectively. No reversed lines have been observed in the under-water spark spectrum of uranium. The spectrum is perfectly continuous and intense, with neither absorption nor emission lines in it, and extending well below 2000 Å. The under-water spark between uranium terminals should, therefore, be useful as a source of continuous radiation in the ultra-violet. The intensity remains practically constant to about 2050 Å., after which it falls off rapidly. M. S. Burr.

Iodine resonance spectra excited by the yellow mercury lines. C. N. Warfield (Physical Rev., 1928, [ii], **31**, 39—51).—The spectrum of iodine vapour excited by the yellow mercury line 5771·2 Å. consists of a series of doublets the main lines of which conform closely to Mecke's formula. That excited by the yellow line 5792·3 Å. consists of three series of doublets, one of which embraces two anti-Stokes members, and another one such member. A. A. Eldridge.

Emission spectra of various elements in the lower quartz region. (Miss) M. C. M. McDonald (Trans. Roy. Soc. Canada, 1927, [iii], **21**, III, 223—230).—A continuation of previous work (A., 1927, 390). In the lower quartz region, spark spectra only of the following elements have been determined: thulium, lutecium, praseodymium, europium, and hafnium, and both arc and spark spectra of samarium, gadolinium, erbium, ytterbium, dysprosium, and niobium. A few new lines are recorded for thulium, dysprosium, ytterbium, lutecium, praseodymium, and europium; niobium has more; hafnium resembles zirconium in having many lines in this region. M. S. Burr.

Double excitation of upper levels in the mercury atoms by collisions of the second kind. H. Bentler and B. Josephy (Phil. Mag., 1928, [vii], **5**, 222).—An explanation of the observations of Wood (*ibid.*, 1927, [vii], **4**, 466) of the abnormal excitations of the mercury lines at 2856 and 4916 Å. is offered from the author's results (Naturwiss., 1927, **15**, 540). There it was shown that the upper levels of an atom are excited in high selectivity by collisions of the second kind if the energy of the colliding atom can be accepted very completely by the atom struck. It is suggested that at the collision of two metastable mercury atoms this effect of resonance can have the result that one absorbs the whole energy, 2×4·68 volts, whilst the other returns to the normal state. It is significant that mercury has a resonance level at 9·25 volts, leaving only 0·11 volt to be transformed into translational energy. The level giving rise to the above-mentioned lines would then be that under the resonance point $3S$. A. E. Mitchell.

Fine structure of mercury lines. W. H. McCurdy (Phil. Mag., 1928, [vii], **5**, 386—392).—See this vol., 100.

Laws of *X*-ray absorption. J. A. Gray (Trans. Roy. Soc. Canada, 1927, [iii], **21**, III, 179—184).—Certain empirical formulæ connecting the wavelength of *X*-rays with the atomic absorbing coefficient and atomic number of the absorbing body have been tested by application to the available experimental data for the *K*, *L*, and *M* absorptions, respectively, and have been found to be in much closer agreement with the experimental observations than those hitherto proposed. Values for the ratio of the fluorescent mass absorption coefficients $(\tau/\rho)_K/(\tau/\rho)_L$, $\lambda=\lambda_K$ have been calculated.

M. S. Burr.

Intensity relationships in *L X*-ray series. A. Jönsson (Z. Physik, 1928, **46**, 383—391).—The intensities of the stronger lines in the *L*-spectra of molybdenum, rhodium, palladium, and silver have been obtained by the use of the Geiger chamber, and the results corrected for anticathode absorption. The doublets $L\alpha_1$, α_2, β_1, as well as l, η, obey the intensity rules valid in the optical region, but the β_2, γ_1 doublet fits these rules only for metals in which the N IV and N V levels have the full complement of electrons. For the doublets, $\alpha_1 : \alpha_2 : \beta_1$ the calculated intensities are 9 : 1 : 5; for $l : \eta$, 2 : 1; for $\beta_2 : \gamma_1$, 2 : 1; for silver and palladium the observed intensity ratios are in good agreement, but for rhodium and molybdenum the results do not agree, *e.g.*, $\beta_2 : \gamma_1$ for molybdenum is 2 : 1·7. R. A. Morton.

***K*-Series spectrum of tungsten.** K. C. Mazumder (Z. Physik, 1928, **46**, 449—450).—The $K\alpha_3$ line (0·218 Å.) in the *X*-ray spectrum of tungsten has been observed in the first order. R. A. Morton.

Discontinuities of absorption in the intermediate region (*K*-bands of carbon, nitrogen, and oxygen). J. Thibaud (Compt. rend., 1928,

186, 308—309).—By means of the author's spectrograph (A., 1927, 803) using a current of 100 milliamp. on an anticathode of high at. wt., a continuous radiation has been observed for carbon, nitrogen, and oxygen similar to that produced by ordinary *X*-rays, but with abrupt discontinuities. The discontinuities which show a fine structure and are bounded on the high-frequency side by a white ray decrease in intensity in the order carbon, nitrogen, oxygen, and their wave-lengths are 43·5, 31·1, and 23·5 Å., respectively. Since the absorption bands are produced with much smaller quantities of absorbing material than in the case of ordinary *X*-rays, a very sensitive method of analysis is indicated. J. GRANT.

Scattering of *X*-rays by gases. J. A. GRAY and H. M. CAVE (Trans. Roy. Soc. Canada, 1927, [iii], **21**, III, 157—161).—A continuous-flow method for measuring the distribution of *X*-rays scattered by gases is described, and the results of preliminary experiments on carbon dioxide, nitrogen, and oxygen are given. The intensity I_θ of the radiation scattered per unit solid angle in the direction θ, by the extra-nuclear electrons of an atom, ion, or a molecule, equals $I(e^4/2m^2c^4)F^2(1+\cos^2\theta)$, where I is the intensity of the primary radiation per sq. cm., e the charge and m the mass of an electron, and c the velocity of light. F, the scattering function for a single molecule, depends on the wave-length, and θ on the distribution and natural frequencies of the electrons, and, in the case of a molecule, on the orientation. The wave-lengths used were 1·50 and 0·9 Å. For small angles of scattering, F is proportional to the number n of electrons in the molecule, and, for zero angle, is probably equal to n, whilst I_θ varies as n^2. $I_0/I_{\pi/2}$ is of the order $2n$ and $F_0/F_{\pi/2}$ of the order $n^{1/2}$. These values are considerably smaller than those obtained for atoms by measurement of the intensities of *X*-rays reflected from crystal planes, probably because, in the latter, the unmodified radiation alone contributes to the final result. Curves are also given showing the distribution of the scattered radiation from thin plates of paraffin wax and graphite. M. S. BURR.

Experimental study of the absorption formula of the *X*-rays. I. M. ISHINO and S. KAWATA (Mem. Coll. Sci. Kyoto, 1927, **10**, 311—316).—The variation of the absorption coefficient of *X*-rays with the atomic number of the absorbers has been studied for the absorption of the $K\alpha$ line of molybdenum. The absorbers were chiefly used in the form of salts dissolved in water. The results are in substantial agreement with those of Wingårdh (A., 1922, ii, 249). W. E. DOWNEY.

Measurement of *X*-radiation in *R*-units. H. KÜSTNER (Physikal. Z., 1927, **28**, 797—803).—The technique appropriate to the measurement of *X*-radiation in terms of a new unit of dosage called the Röntgen- or *R*-unit is described. R. W. LUNT.

Excitation of spectra by high-frequency oscillations. M. PONTE (Nature, 1928, **121**, 243—244).—Clarke's results (A., 1927, 1119) are attributed to the kind of discharge employed, and not to the wave-length. An oscillator of wave-length 1·90 m., and power only 20 watts, produces a brilliant electrodeless mercury discharge. This mode of excitation is extremely sensitive to the presence of organic impurities. Experiments with the electrodeless or one-electrode discharge, using wave-lengths of 1·90 or 5—10 m., have not demonstrated any modification of the emitted wave-lengths, alterations in the relative intensities of the lines being due to changes in pressure or strength of excitation. A. A. ELDRIDGE.

Duration of Stark effect in hydrogen and nitrogen. H. KERSCHBAUM (Ann. Physik, 1927, [iv], **84**, 930—938).—The duration of the Stark effect in H_β and H_γ has been determined from observations on canal rays and is found to be constant; the duration of the negative nitrogen band 4278 Å. is $2 \cdot 54 \times 10^{-8}$ sec., *i.e.*, approximately twice that of the spark-excited band. R. W. LUNT.

Measurement of the life-period of excited atomic states. K. W. MEISSNER and W. GRAFFUNDER (Ann. Physik, 1927, [iv], **84**, 1009—1046).—Experimental methods are reviewed and a new arrangement is described. The maximum half-life period for the s_5 state of neon is about 7×10^{-4} sec., and for argon 3×10^{-3} sec. The investigation of the relation between life-period and pressure discloses a maximum for neon at 1·5—2 mm. The half-value period for the absorption capacity varies with different lines with the same end term. The interpretation of this result is discussed. Intense irradiation decreases the persistence of metastable states. R. A. MORTON.

Ionisation potential and atomic number. G. PICCARDI (Atti R. Accad. Lincei, 1927, [vi], **6**, 305—311).—It is shown that a family of parabolic curves is obtained if the difference between the primary ionisation potential of an element and that of the element possessing but one electron in the outermost orbit of the first element be plotted as a function of the atomic number. R. W. LUNT.

Relations between the first- and second-order ionisation potentials of homologous elements. G. PICCARDI (Atti R. Accad. Lincei, 1927, [vi], **6**, 428—431).—Using the relationships found previously (cf. preceding abstract), the following ionisation potentials have been calculated: germanium 7·52, arsenic 9·04, antimony 8·46, bismuth 8·48, selenium 9·02, tellurium 8·43, polonium 8·46, chlorine 12·26, bromine 10·47, iodine 9·76, element 85 9·65, xenon 12·33, radon 11·96. It is shown that the first- and second-order ionisation potentials (V_{I} and V_{II}) of a group of homologous elements are related by the expression $V_{\mathrm{II}} : V_{\mathrm{I}} = r$, where r is constant in any but the alkali metal group, with a value of 1·9—2·2. Use is made of this relationship to calculate the first-order ionisation potentials of radium and of the missing element 87 from the known value of 10·23 of the second-order ionisation potential of radium. The values are 5·35 and 4·24 volts, respectively. O. J. WALKER.

Actino-electric effects in argentite. W. A. SCHNEIDER (Physical Rev., 1928, [ii], **31**, 82—89).—The seat of conversion of light into electronic energy is at both contacts as well as at certain points on the crystal; if the crystal structure is destroyed, no effect is observed. The current $i = Ae^{-at}$, where t is the total time of exposure and values of a depend on the time of recovery. A. A. ELDRIDGE.

Photo-electric effect. P. W. Bridgman (Physical Rev., 1928, [ii], **31**, 90—100).—The equality of the stopping potentials follows from very general considerations, not involving any assumptions as to mechanistic details, or even the third law of thermodynamics. The differences between (*a*) the photoelectric and thermionic work functions, (*b*) the specific heat and surface charge, (*c*) the entropy and surface charge at 0° Abs. are universal constants for all metals, and probably each zero.

A. A. Eldridge.

Spatial distribution of photo-electrons produced by *X*-rays. E. J. Williams (Nature, 1928, **121**, 134—135).—Results of an investigation of the longitudinal distribution of photo-electrons indicate an average forward component of momentum of the photo-electrons which is appreciably greater than the momentum, $h\nu/c$, of an incident quantum. The results of other observers, except those of Auger, exhibit an "excess asymmetry." Experimental results on dispersion seem to prohibit all theories except Auger and Perrin's "$\cos^2 \theta$" law.

A. A. Eldridge.

Work of evaporation of thermions. A. Smekal (Z. Physik, 1928, **46**, 451—452).—Michel (A., 1927, 919) claims that the work of evaporation $\Delta\varphi$ of thermions from alkaline-earth oxides is better expressed by the relation $\Delta\varphi \, . \, b^2 =$ constant than by $\Delta\varphi \, . \, b =$ constant, b being the shortest distance between two atoms at the surface of the emitting oxide. On the basis of measurements by Espe (A., 1927, 604), it is contended that the claim rests on inadequate evidence. R. A. Morton.

[Work of evaporation of thermions.] G. Michel (Z. Physik, 1928, **46**, 453—454).—A reply to Smekal (preceding abstract). The data of Espe do not invalidate the argument. Sommerfeld (Naturwiss., 1927, **15**, 825) uses a formula for the work of evaporation of thermions, which corresponds with the use of b^2 rather than b. R. A. Morton.

Behaviour of slow electrons in mercury vapour. H. Beuthe (Ann. Physik, 1927, [iv], **84**, 949—975).—Ramsauer's method for determining the effective cross-sectional area of a gas has been adapted to mercury vapour by using thermions instead of photo-electrons. The effective cross-sectional area has been plotted against electron velocities expressed in volts$^{1/2}$; the curve exhibits two maxima, one at 3 volts being well marked, and another at 4·9 volts being less definite. At low pressures (0·002—0·006 mm.) the maximum at 3 volts is higher and more clearly defined than at higher pressures. The effective cross-sectional area is very small for small electron velocities, so that mercury vapour resembles the noble gases in respect of its behaviour towards very slow electrons. The mercury atom seems capable of accumulating and retaining for a fairly long period those electrons which strike it at velocities too small to effect excitation. R. A. Morton.

Energy distribution among secondary electrons from nickel, aluminium, and copper. D. A. Wells (Phil. Mag., 1928, [vii], 5, 367—371).—An examination of the distribution of secondary electrons from nickel, aluminium, and copper has shown that in all cases there are a few secondary electrons with energies of the same order as those of the primary beams. The number having high energy values is relatively small. Within a certain range the number of electrons having a given energy or greater up to the maximum energy of any being emitted is a probability function of the secondary current and secondary voltage. A. E. Mitchell.

Tracks and radiation of electrons emitted by hydrogen. T. Engst (Ann. Physik, 1927, [iv], 84, 880—890).—Mathematical. R. W. Lunt.

New evidence of the existence of charges smaller than the electron. (*a*) The micromagnet. (*b*) Law of resistance. (*c*) Computation of errors of the method. F. Ehrenhaft and E. Wasser (Phil. Mag., 1928, [vii], 5, 225—241).—A new method for the measurement of heterogeneous strong magnetic fields of small dimensions is described. By this means the mass susceptibilities of colloidal particles of silver and selenium have been shown to be in perfect agreement with the accepted values for the materials in bulk. The results of measurements of 140 particles of various densities show that single particles produced in different ways have their normal densities and structures. The smallest charge associated with a particular particle has been shown to be less than the electron. For gold particles the value 1×10^{-10} *E.S.U.* was often found. Depending on whether the law of resistance is linear or exponential, these values may vary by 10—15%, but in any case they do not approach the charge on the electron. A. E. Mitchell.

Production of the atomic and molecular rays of sodium and of iodine. W. Jono (Sexagint [Osaka celebration], Kyoto, 1927, 273—278).—Sodium to be used for the production of atomic rays may be obtained by the thermal decomposition of sodium azide. Apparatus for the production of the atomic rays of sodium and of iodine is described.

H. F. Gillbe.

Production and measurement of molecular beams. T. H. Johnson (Physical Rev., 1928, [ii], **31**, 103—114).—The beam is detected and its intensity measured by the increase in pressure produced in an ionisation gauge when the gauge is moved to allow the beam to enter it through a narrow slit. The method is applicable to beams of non-condensible and chemically inactive gases, as well as to condensible or chemically active molecules. A change of pressure of 3×10^{-8} mm. (3 mm. galvanometer deflexion) corresponds with a beam intensity of about 5×10^{13} mol./cm.^{2}/sec. The probability of adsorption of a mercury molecule on glass is found to be 10^{-4} per collision. A. A. Eldridge.

Cathode rays in the electrodeless ring discharge. G. Herzberg (Phil. Mag., 1928, [vii], 5, 446—448).—An investigation of the electrodeless ring discharge in hydrogen in a quartz tube has shown a phosphorescence of the tube walls, continuing after the discharge has ceased, similar to that reported by J. J. Thomson (A., 1926, 988) on glass walls. Contrary to Thomson's experience, it is shown that the radiation causing the phosphorescence is affected by adjacent magnetic fields, thus indicating that it is composed of cathode rays coming from the middle of the tube where the discharge took place under ordinary conditions. The velocity of these rays is heterogeneous. A mechanism for their production is suggested. A. E. Mitchell.

Continuous emission spectra produced by electrodeless discharge. G. Balasse (Compt. rend., 1928, **186**, 310—311).—The theory previously proposed (A., 1927, 490) and the fact that elements in five different columns of Mendeléev's table show continuous emission spectra produced by electrodeless discharge indicate that this phenomenon is characteristic of all elements. The spectra, which appear to increase in intensity with the atomic number of the element used, may be correlated with the continuous spectra observed in the *X*-ray region. J. Grant.

Influence of very small quantities of substances on the running-voltage in noble gas [discharges]. F. M. Penning (Z. Physik, 1928, **46**, 335—348).—Quantitative experiments have been made on the discharge voltages of mixtures of mercury, argon, etc., in very small amount, in otherwise practically pure neon. The results indicate that the foreign atoms become ionised by the metastable neon atoms. This process is conditional upon the relation $V_i' < V_{\text{met.}}$, V_i' being the ionisation potential of the foreign gas and $V_{\text{met.}}$ the energy of the metastable states of neon, *i.e.*, 16·5 and 16·6 volts. The validity of this explanation has been tested for mercury, argon containing 0·01—0·05% of krypton, hydrogen, and nitrogen. Similarly, experiments with argon as the principal gas ($V_{\text{met.}}$ 11·5 and 11·7 volts) and mercury, iodine, krypton, xenon, carbon monoxide, carbon dioxide, and nitric oxide as added substances indicated that the only departure from the above explanation was with nitric oxide. The term-scheme of nitric oxide does not render this result very surprising. Preliminary experiments with helium as the main gas also fall into line with the theory. R. A. Morton.

Measurement of mobilities of ions in gases. M. Laporte (Ann. Physique, 1927, [x], **8**, 710—745).—The experimental results so far obtained in this field support the view that ionic mobilities are distributed according to a continuous curve (cf. this vol., 102). Zelény (Phil. Trans., 1901, **A**, **195**, 193) supposed that his extrapolated figure for the ionic mobility from the gas-stream method indicated the presence of only one mobility, but actually it may be only an average figure. The results of Erikson (Physical Rev., 1922, [ii], **20**, 117) also demand the existence of ions of different velocities and cannot be explained by ions of different ages. Nolan (Proc. Roy. Irish Acad., 1920, **35**, 38) on plotting the current passing through the ionised gas against voltage obtained breaks, and concluded thence that the ions were divided into groups each with a specific mobility; most of the breaks, however, are probably due to irregularities in his gas stream, and the remainder can be explained by changes of curvature in the mobility distribution curve. Franck and Pohl's method (Verh. Physikal. Ges., 1907, **9**, 69) gives very different results from those of other workers, since the metallic gauze employed does not completely divide the auxiliary field which separates the positive and negative ions from the field of observation. Tyndall and Grindley (A., 1926, 219) have studied the effect of humidity on the mobility of ions in air, and their results, which agree with those of the authors, give continuous curves with no maxima, showing that ionic mobilities do not fall into a number of sharply separated groups. S. J. Gregg.

Ionisation by collision. J. Taylor (Phil. Mag., 1928, [vii], **5**, 445—446).—A reply to a discussion by Huxley (A., 1927, 709) of the author's previous contribution to the controversy. A. E. Mitchell.

Unsöld's theory of the chromosphere. W. Anderson (Z. Physik, 1928, **46**, 445—448).—The theory of the chromosphere developed by Unsöld (A., 1927, 1006) is open to serious objections. The partial pressure of singly-ionised calcium atoms in the upper layers of the chromosphere is calculated to be not greater than 10^{-13} atm., whilst the partial pressure of electrons is of the order 10^{-11} atm., whereas Unsöld's theory assumes that the partial pressure of calcium is of the order 10^{-8} atm. Milne's theory is also criticised. R. A. Morton.

Diamagnetic susceptibility of hydrogen and of helium. S. C. Wang (Proc. Nat. Acad. Sci., 1927, **13**, 798—800).—Mathematical. R. W. Lunt.

Report of the German Commission on atomic weights. VIII. M. Bodenstein, O. Hahn, O. Hönigschmid, and R. J. Meyer (Ber., 1927, **61**, [*B*], 1—31).—The report is divided into three sections treating respectively determinations of at. wts. by physico-chemical and chemico-gravimetric processes and the progress in the question of isotopes among ordinary, non-radioactive elements. The values A=39·94 instead of 39·88, Ti=47·90 instead of 48·1, and Y=$88{\cdot}9_3$ instead of 88·90 are adopted. For certain elements the at. wts. of which depend more or less directly on that of silver (107·880), regarded as affected with a possible uncertainty of 1 in 10,000, the second decimal is given as sub-index since new investigations of the at. wt. of silver tend greatly to confirm the value adopted previously. H. Wren.

Exact determination of radon. J. von Weszelszky (Physikal. Z., 1927, **28**, 757—761).—Modifications introduced into the author's earlier technique (A., 1911, ii, 453; Physikal. Z., 1912, **13**, 240) are described. The procedure for the exact determination of radon by the intensity of its radiations is given. Probable errors and methods of calibration are discussed. R. W. Lunt.

Number of α-particles emitted by thorium-*C*+*C′*. S. W. Watson and M. C. Henderson (Proc. Camb. Phil. Soc., 1928, **24**, 133—138).—By an ionisation method, the α-particle emission of thorium-*C*+*C′* has been determined as $4{\cdot}26 \pm 0{\cdot}08 \times 10^{10}$ particles per sec. per curie-equivalent of γ-ray activity when in equilibrium with radiothorium, and when measured by the γ-rays of thorium-*C″* through 18 mm. of lead. Data on the Bragg curve over the first 3 cm. of the range are in agreement with the work of I. Curie and Behounek, but not with that of Henderson (A., 1921, ii, 617). R. A. Morton.

Ionisation curve of an average α-particle. N. Feather and R. R. Nimmo (Proc. Camb. Phil. Soc., 1928, **24**, 139—149).—Photographs have been taken under controlled illumination of the tracks of α-particles in a cloud expansion chamber, and the plates used have been calibrated. Photometry of the track images makes possible the calculation of the variation of the light-scattering power of an α-particle track over the last 2 cm. in dry air at 15° and 760 mm.; this quantity varies with the ionisation along the track. In air, helium, and hydrogen, the maximum ionising efficiency of the α-particle occurs at velocities respectively appropriate to the distances 3·0, 2·55, and 2·25 mm. from the end of its path in dry air at 15° and 760 mm. R. A. Morton.

Passage of α-rays and β-rays through matter. E. J. Williams (Mem. Manchester Phil. Soc., 1926—1927, **71**, 23—39).—The primary ionisation due to β-rays of approximate velocity 5×10^9 cm./sec. has been determined by Wilson's cloud method (Proc. Roy. Soc., 1923, **A**, **104**, 192) in hydrogen, nitrogen, and oxygen. The theoretical values calculated on the basis of J. J. Thomson's theory account for only about half of the observed ionisation. If, however, the motion of the atomic electrons is taken into account, there is good agreement between observed and calculated values, especially for hydrogen, for which the data on which the calculation is based are most certain. The atomic stopping powers for α- and β-rays and the relation between them are discussed. Bohr's theory (Phil. Mag., 1913, [vi], **25**, 10; 1915, [vi], **30**, 581) does not give values for the stopping powers of oxygen, nitrogen, hydrogen, and argon in agreement with the experimental results of Williams and Nuttall (A., 1926, 1191). Fowler's values (Proc. Camb. Phil. Soc., 1923, **21**, 521) calculated from Henderson's theory (Phil. Mag., 1922, [vi], **44**, 680) also differ considerably from the experimental results, but the discrepancy is markedly reduced by allowing for the motion of the atomic electrons. The residual discrepancy is probably real, and there are indications that it may be greater for α- than for β-rays. M. S. Burr.

Relative ranges of β-rays. J. A. Gray and B. W. Sargent (Trans. Roy. Soc. Canada, 1927, [iii], **21**, III, 173—178).—The relative ranges of the β-rays of radium-E and uranium-X_2 in carbon, aluminium, copper, tin, and lead have been determined by an ionisation method which is described. The range is the product of the total length of path traversed and the density of the substance. The average range of the β-rays of uranium-X_2 in lead is 2·2 times that of the β-rays of radium-E. The range increases with the atomic number of the substance penetrated, and the stopping power of an atom for the β-rays of uranium-X_2 is approximately proportional to the atomic number. M. S. Burr.

Absorption and scattering of γ-rays of radium. J. A. Gray and H. M. Cave (Trans. Roy. Soc. Canada, 1927, [iii], **21**, III, 163—171).—The formulæ generally employed for the variation of the mass scattering coefficient σ/ρ and the fluorescence mass absorption coefficient τ/ρ with λ give a value for the wave-length of hard γ-rays of 0·018 Å. This is too large to account for the observed properties of recoil electrons (cf. A., 1925, ii, 84), and, according to Compton's formulæ for the intensity of radiation scattered per unit mass and unit solid angle (Physical Rev., 1923, [ii], **21**, 483), it should be either less than 0·008 Å. or consist of a mixture of rays of wave-length 0·024 and 0·008 Å. in equal proportions. Absorption experiments have been made which indicate that there is only a small difference in wave-length between γ-rays filtered through 2 and 5 cm. of lead, respectively, and hence that hard γ-rays can have only a small proportion of rays of wave-length 0·024 Å. The formulæ generally accepted for the variation of σ/ρ and τ/ρ with λ give a value of 0·015 Å. for the most penetrating radiation obtained by filtration, and hence cannot be relied on. Experiments on the distribution of scattered radiation have been made, and there is no evidence of the presence in hard γ-rays of rays of wave-length of the order of 0·024 Å. The wave-length is probably nearer to 0·007 than to 0·008 Å. τ/ρ varies approximately as λ^2, and values of τ/ρ and σ/ρ for different values of λ are tabulated. M. S. Burr.

Spectrography of γ-rays by crystalline diffraction. Frilley (Compt. rend., 1928, **186**, 137—139).—A rotating-crystal method is described for spectrographical experiments with γ-rays, in which the crystal consists of a plate of mineral salt. Spectra attributed to radium-B and radium-C (35—284 X) were obtained from a tube of radon, the shortest wave-length measured (35 X) corresponding with 353 kilovolts and an angle of reflexion of 21·5′. J. Grant.

Action of heat on pleochroic haloes. J. H. J. Poole (Phil. Mag., 1928, [vii], **5**, 132—141).—Examination of some biotites has shown that the pleochroic haloes disappear when the minerals are heated at 500—700°. The haloes disappear owing to a progressive darkening of the body of the mineral and not to a change in the portion forming the haloes. The darkening of the mica is accompanied by dehydration. It is suggested that the formation of the haloes by α-rays is due to the decomposition of the weakly held water of the biotite leading to local areas of dehydration. Application of the results of Duane and Scheurer for the α-ray decomposition of water do not render the theory untenable. A. E. Mitchell.

Formation of pleochroic haloes in biotite. J. H. J. Poole (Phil. Mag., 1928, [vii], **5**, 444).—As an alternative to the theory advanced previously (preceding abstract) it is suggested that the water liberated from biotite under the action of α-rays causes direct oxidation of ferrous to ferric iron with the consequent change in colour and formation of haloes. A. E. Mitchell.

Pleochroic haloes and the age of the earth. J. Joly (Nature, 1928, **121**, 207—208).—Lotze's theory (this vol., 150) would involve a large reduction of density, of which there is no optical indication. Poole's theory is preferred. A. A. Eldridge.

Inversion phenomenon of biotite exposed to the action of α-rays. H. Jedrzejovski (Compt. rend., 1928, **186**, 135—137).—The determination by means of a potassium photo-electric cell of the blackening produced in a leaflet of biotite during exposure to α-rays has yielded a curve which shows that the amount of light traversing the leaflet falls off rapidly to a minimum (the inversion point) and then slowly increases. It is concluded that a phenomenon of inversion, analogous to that of an over-exposed photographic plate, actually occurs, but that the determinations of the ages of minerals from the haloes produced may lead to incorrect results.

J. Grant.

Influence of high-velocity electrons on lead and copper. A. Koenig (Physikal. Z., 1927, 28, 838—841).—The conductivity of the space surrounding a copper anticathode alone, and when covered with lead foil, has been examined by a sensitive method immediately after the anticathode had been bombarded by electrons of from 4 to 60 kilovolts. The results show that if a new element is formed from lead under such conditions it cannot have a β-particle emission of half-life from 33 seconds to 1300 years or an α-particle emission of half-life from 5×10^6 years to 2 seconds. R. W. Lunt.

Evolution of elements. B. Cabrera (Compt. rend., 1928, **186**, 228—230).—The formation of atoms by means of the association of protons and electrons is discussed in the light of Aston's conception of "packing fractions," with special reference to the building-up and disruption of atoms by cosmic processes and to the explanation of the stability of an atom in terms of its radioactive properties.

J. Grant.

Wave-mechanics of an atom with a non-Coulomb central field. I. Theory and methods. II. Results and discussion. D. R. Hartree (Proc. Camb. Phil. Soc., 1928, 24, 89—110, 111—132).—I. Methods are given for the determination of the characteristic values and functions of the wave equation of Schrödinger for a non-Coulomb central field, for which the potential is given as a function of the distance from the nucleus.

II. For a given atom it is possible by a method of successive approximations to find a field such that the solutions of the wave equation for the core electrons in this field (corrected in certain ways) give a distribution of charge which reproduces this "self-consistent" field. The field has been calculated for He, Rb^+, Na^+, and Cl^-; satisfactory agreement is shown between observed and calculated *X*-ray and optical terms, and for helium between observed and calculated ionisation potentials. R. A. Morton.

Simple derivation of the hydrogen energy levels in wave mechanics. A. E. Ruark (J. Opt. Soc. Amer., 1928, **16**, 40—43).—Mathematical. The values of the energy levels corresponding with the circular orbits in Bohr's theory of the hydrogen atom have been derived by wave mechanics.

W. E. Downey.

Waves associated with moving electrons. (Sir) J. J. Thomson (Phil. Mag., 1928, [vii], 5, 191—198).—The existence of the waves accompanying a moving electron, postulated by de Broglie in his theory of wave mechanics, is shown to be a consequence of classical dynamics if that be combined with the view that an electric charge is not a point without structure but is an assemblage of lines of force starting from the charge and stretching into space. The core of the uniformly moving electron is considered. A. E. Mitchell.

Quantum theory of aperiodic effects. J. R. Oppenheimer (Physical Rev., 1928, [ii], **31**, 66—81). —Mathematical. (*a*) The normalisation of the characteristic functions corresponding with a continuous spectrum satisfies the requirements of the δ-normalisation of the Dirac–Jordan theory. (*b*) The validity of classical mechanics is considered in relation to Rutherford's formula for the scattering of α-particles. (*c*) A method for computing the transition probabilities between states of the same energy and represented by almost orthogonal eigen-functions is applied to the ionisation of hydrogen atoms in a constant electric field. A. A. Eldridge.

Interaction between radiation and electrons. A. H. Compton (Physical Rev., 1928, [ii], **31**, 59—65).

Thermodynamic equilibrium and reciprocal effects in the new gas theory. W. Bothe (Z. Physik, 1928, 46, 327—334).—Reciprocal effects of atoms, molecules, electrons, and light quanta are discussed theoretically in terms of the methods of Bose and Einstein, Fermi, Pauli, Dirac, and others.

R. A. Morton.

Theory of molecular spectra. F. Hund (Physikal. Z., 1927, 28, 779—784).—A short and non-mathematical review of recent theories of molecular spectra. R. W. Lunt.

Hydrogen molecule. R. T. Birge (Nature, 1928, **121**, 134).—Data and constants for the hydrogen molecule and molecule ion, in terms of the older mechanics, are reviewed. The ionisation potential of the neutral molecule is $15{\cdot}34\pm0{\cdot}01$ volts, and the normal heat of dissociation 4·42 volts. The moment of inertia of H_2 in the normal state is $1{\cdot}99\times10^{-40}$. Richardson's method of calculating I_0 gives values 8—9% in error for the non-polar molecules tested. The heat of dissociation of H_2^+ is 2·62 volts.

A. A. Eldridge.

Triatomic hydrogen as an emitter of the secondary spectrum. C. J. Brasefield (Physical Rev., 1928, [ii], **31**, 52—58).—To obtain a correlation between the intensities of various parts of the secondary spectrum and the concentrations of H_2^+ and H_3^+, simultaneous positive-ray and spectroscopic observations were made on a discharge in hydrogen under various conditions. The concentration of H_3^+ in the positive column of a glow discharge decreases rapidly with pressure and becomes negligible at 0·01 mm. The relative concentration of H_3^+ has no effect on the intensity of the lines of the secondary spectrum, with the possible exception of some weak lines such as those of the Allen and Sandeman bands.

A. A. Eldridge.

"Non-combination" part systems in band spectra. E. Hulthén (Z. Physik, 1928, **46**, 349—353).—Band spectra of diatomic molecules are always divisible into two partial systems, between which only very weak intercombinations occur. The "non-combination" systems are designated as symmetrical and anti-symmetrical, since they are connected with

the distribution of symmetrical and anti-symmetrical rotation states through the different electron terms.
R. A. Morton.

Infra-red absorption spectra of several gases. C. F. Meyer, D. W. Bronk, and A. A. Levin (J. Opt. Soc. Amer., 1927, **15**, 257—265).—The infra-red absorption of the following gases has been examined in the range 3—4 μ using a grating with 1134 lines per cm.: acetylene, ethylene, *n*-butane, *n*-hexane, *n*-octane, benzene, toluene, cumene, ethyl alcohol, ethyl ether, and sulphur dioxide. The wave-number differences between the observed absorption maxima are discussed with reference to the structure of the bands.
R. W. Lunt.

Nature of the glow on heating finely-divided oxides and metals. M. Rabinovitsch (Kolloid-Z., 1928, **44**, 84—85).—The glow which is observed on heating finely-divided metals is not due, as Böhm has supposed (A., 1927, 823), to the liberation of the latent heat of crystallisation caused by the production of crystalline metal from the amorphous state, but is due to the sudden liberation of energy through the reduction of the total surface of the particles. The explanation given by Böhm is not probable for metals such as rhodium, ruthenium, platinum, gold, and silver, and the phenomenon is shown equally by many finely-divided oxides.
E. S. Hedges.

Radiation from glowing oxides. F. Skaupy (Physikal. Z., 1927, **28**, 842—846).—The intensity of the radiation from the following oxides has been determined at temperatures from 1500° to 2000° in the range 0·5—10 μ: aluminium oxide, sapphire, aluminium oxide + 2% of chromium oxide, ruby, chromium oxide, titanium dioxide, anatase, silicic acid, fused silica, thorium dioxide, and magnesium oxide. The maxima of intensity lie at about 2 μ, whilst the computed value for the oxygen in these substances is about 3·9 μ.
R. W. Lunt.

Displacement of spectra during the formation of compounds (observations with compounds of praseodymium). F. Ephraim and R. Bloch (Ber., 1928, **61**, [*B*], 65—72; cf. A., 1927, 121).—The work is based on the hypothesis that the electrostatic attraction of the cation for the electrons of the remaining sheaths becomes more pronounced when the anion involves the valency electrons of the cation with greater intensity; consequently these sheaths are drawn towards the nucleus and contraction ensues. The paths of the vibrating electrons therefore become shorter, thus causing emission of light of shorter wave-length and displacement of the spectrum towards the violet. This displacement is very marked in the series anhydrous iodide, bromide, chloride, and fluoride of praseodymium. Since the anhydrous compounds can unite with water, ammonia, etc. by means of residual affinities, the atom does not exert its full chemical affinity in them. This is, however, unfolded in solution in which the atom is freed from the circle of restricting atoms. The contraction thereby caused explains the observed displacement of the spectrum towards the violet in solution, and the lessened importance of the anion by reason of electrolytic dissociation renders account of the disappearance of the differences in position of the lines observed in solid salts. As expected, the definite hydrates occupy a well-marked, intermediate position. The specific action of the halogen is of less importance, since its contracting action is less marked owing to penetration of the water between it and the metallic atom. On the other hand, the water itself exercises compressive action on the metallic atom, which is more noticeable as the number of its molecules increases and the contracting action of the halogen is less. The production of ammonates results similarly in compression of the praseodymium atom, which is less marked than in the case of hydrates. It follows, therefore, that the valency demand of the praseodymium atom can be deduced from the position of the lines of its spectrum, being greater as they are displaced towards the violet. Explanation is thus afforded of the ability of the iodide to form a higher hydrate than the chloride. The insolubility of the fluoride is accounted for by the observation that its spectral lines are further towards the region of shorter wave-length than those of praseodymium solutions; solvate formation could therefore be brought about only by addition of energy which does not occur spontaneously. It is therefore remarkable that praseodymium fluoride is precipitated in the hydrated state and loses water only with relative difficulty. The spectra of the anhydrous and hydrated forms do not, however, differ appreciably from one another. The water has therefore little to do with the metallic atom and is regarded as "packing water" retained by capillarity as in a gel.

Anhydrous *praseodymium bromide* is prepared by heating a mixture of hydrated bromide and ammonium bromide (but not the hydrated bromide alone) in a current of hydrogen bromide. A similar process fails to yield anhydrous praseodymium iodide (corresponding *nonahydrate* and *hexahydrate*) completely free from basic salt. Evaporation of a solution of praseodymium iodide and 2 mols. of mercuric iodide followed by desiccation of the residue at 120° yields the double *salt*, (?) $PrOI,2HgI_2,9H_2O$, which, when moderately heated in hydrogen, is converted into the basic *salt*, $PrOI,2H_2O$.
H. Wren.

Spectrum of praseodymium salts of oxygenated acids. F. Ephraim and R. Bloch (Ber., 1928, **61**, [*B*], 72—80; cf. preceding abstract).—Great differences, similar to those observed in the spectra of praseodymium halides, are not encountered with praseodymium salts of oxygenated acids, since in the latter the element is directly united in every case with many oxygen atoms. The contraction of the atom thereby produced is so great that the spectrum of the sulphate is greatly displaced towards the violet when compared with that of the chloride or iodide, slightly towards the red in comparison with that of the fluoride. The spectrum of the hydroxide is of slightly longer wave-length than those of the oxygenated salts. The presence of water of crystallisation has little influence. In the nitrate, in which the metallic atom is influenced by nine oxygen atoms, the contraction is greater than in the fluoride. In the double nitrate, $(NH_4)_2[Pr(NO_3)_5],4H_2O$, contraction attains its maximum observed value and the spectrum of the dissolved salt is displaced towards the red in comparison with that of the solid. The alkali double sulphates are interesting, since the praseodymium atom is a component of a complex anion. It is united with many oxygen atoms and the spectra indicate considerable contraction and little influence of the portion of the molecule other than the SO_4-residues; replacement of sulphur by selenium somewhat diminishes the contraction. Many of the spectra exhibit a duplication of the lines, particularly in the third group, which is most marked in cases in which the opportunity of complex formation exists and the praseodymium atoms function differently from one another, *e.g.*, in the nitrate, $Pr[Pr(NO_3)_6]$. A complete duplication of the spectrum is not observed, possibly because the effect causes merely a broadening of the bands, showing actual duplication only of the narrowest.

The following compounds are incidentally described: cæsium praseodymium sulphate, $CsPr(SO_4)_2,4H_2O$ (a salt richer in cæsium does not appear to exist); *potassium praseodymium sulphate, dihydrate*, and *monohydrate* (in place of hemihydrate described previously); *praseodymium chromate* and its *hexahydrate*; *potassium praseodymium chromate*, $KPr(CrO_4)_2,H_2O$; *praseodymium oxalate nonahydrate*; praseodymium nitrate hexahydrate and *dihydrate*. H. WREN.

Reflexion spectrum of praseodymium in covalent compounds. F. EPHRAIM (Ber., 1928, **61**, [*B*], 80—83; cf. preceding abstracts).—In homopolar praseodymium oxide the metallic atom is surrounded by more electrons than in the chloride; its volume must consequently be greater since the electrostatic attraction of the nucleus is distributed over a great number of electronegative points and this expansion may be expected to find its expression in a displacement of the spectrum towards the red, which is actually observed. It is doubtful, however, if the individual lines of the chloride spectrum are exactly represented in that of the oxide, and the entirely different electronic configuration renders this scarcely probable. Praseodymium oxide of form B_1 is prepared by reducing the oxide, Pr_6O_{11}, with hydrogen at 900°; at 550°, a second *modification*, possibly B_2 or C, is produced, differing in density and spectrum from the variety B_1. Indications of the existence of further modifications of the oxide are found in the observation that specimens which have been preserved for some time in the apparatus in which they were prepared become brown and absorb oxygen when exposed to air, whereas this behaviour is not shown by freshly-prepared specimens. The spectrum of the compound PrOS differs completely from that of the oxide, having particularly well-defined lines beyond 600 mμ. H. WREN.

Resolution of an absorption band common to praseodymium and neodymium. L. FERNANDES (Atti R. Accad. Lincei, 1927, [vi], **6**, 413—417).—Solutions of salts of the above elements give a common absorption band in the region 4690 Å. It is shown that in the sharper spectra obtained with the crystalline sulphates (especially at a temperature near that of liquid air) this band is broken up into a series of finer bands which are different for the two elements. O. J. WALKER.

Organic media as spectral filters in the ultraviolet. T. M. DAHM (J. Opt. Soc. Amer., 1927, **15**, 266—284).—The extinction point for a constant source of ultra-violet radiation in aqueous solutions of concentration varying by the factor 0·5 has been determined for the following substances: mercuric chloride, methyl, ethyl, and allyl alcohols; oxalic, acetic, citric, tartaric, citraconic, mesaconic, fumaric, maleic, crotonic, aconitic, benzoic, salicylic, phthalic, *p*-hydroxybenzoic, gallic, tannic, phenylacetic, and picric acids; aniline arsenate, arsanilic acid, *p*-dichlorobenzene, acetanilide, benzamide, triphenyl phosphate, heliotropin, diphenyl, phenanthrene, quinine sulphate, thiocarbamide, phenol, quinol, phloroglucinol, strychnine sulphate; quinine, berberine, and cryptopine hydrochlorides; thiophen, 2:5-dimethylpyrazine; aconitine, atropine, cinchonidine, cinchonine, cocaine, morphine, narcotine, and their hydrochlorides. Curves are given in which the logarithm of the concentration at which extinction occurs is plotted as a function of the frequency. After a discussion of the procedure appropriate to the choice of a solution for use as a filter with a given transmitting power, the theory of the method employed is described and suggestions are made for improving the extinction-point method. R. W. LUNT.

Absorption of light in the ultra-violet by simple amino-acids. H. LEY and B. ARENDS (Ber., 1928, **61**, [*B*], 212—222; cf. A., 1926, 1080).—Contrary to the observations of Abderhalden and Haas (A., 1926, 959), a difference in optical behaviour of alanine and glycine is not detected when the substances are crystallised from water or precipitated from aqueous solution by alcohol. Further, the optical behaviour of alanine does not appear appreciably influenced by the presence of glycine as shown by direct observation and also by comparison of the effect of solutions of the mixed compounds with those of the components placed singly in series in the path of the rays. For each acid, the absorption is independent of the concentration (contrast Abderhalden and Haas, A., 1927, 451). Determinations of the f. p. of solutions of alanine and glycine fail to disclose any mutual influence of the components. Measurements are recorded of the absorption of glycine, alanine, α-amino-*n*-butyric acid, α-amino*iso*butyric acid, their hydrochlorides and sodium salts. Passage from the amino-acid to the salt or from the $\cdot NH_3\cdot R\cdot CO_2'$ ion to $NH_2\cdot R\cdot CO_2'$ causes in all cases marked displacement towards the red as observed previously (*loc. cit.*) with piperidinoacetic acid. The absorption curves of glycine hydrochloride and sodium aminoacetate appear to intersect at —0·2 (log ε); with increasing number of carbon atoms in the alkyl group R of the ions $NH_2\cdot R\cdot CO_2'$ and $\cdot NH_3\cdot R'\cdot CO_2H$, the point of intersection is displaced towards the region of greater values of ε. H. WREN.

Spectroscopical study of amino-acid anhydrides. II. Light absorptions of some amino-acids, their esters, peptides, and anhydrides. Y. SHIBATA and T. ASAHINA (Bull. Chem. Soc. Japan, 1927, **2**, 324—334).—Continuing previous work (A., 1926, 659) solutions of glycine, alanine, leucine, phenylalanine, tyrosine, glycine and tyrosine esters, glycyl-leucine, glycyl-*l*-phenylalanine, glycyl-*dl*-phenylalanine, and the anhydrides of glycyl-*l*-tyrosine, tyrosine, glycyl-*l*-leucine, leucine, glycyl-*l*-phenylalanine, and phenylalanine were examined spectroscopically. Of the above, only those compounds containing phenyl or hydroxyphenyl groups show selective absorption. Derivatives of tyrosine and phenylalanine absorb identically with the parent substances. The absorption of phenylalanine anhydride is, however, anomalous, end absorption only being observed. The anomalous absorption is possibly due to the mutual effect of the two symmetrically-situated phenyl groups. It is concluded that the substances examined exist only in the keto-form in solution. J. S. CARTER.

Absorption spectra of some triphenylmethane derivatives. L. C. ANDERSON (J. Amer. Chem. Soc., 1928, **50**, 208—212; cf. this vol., 285).—The absorption spectra of triphenylmethane and triphenylcarbinol in ethereal solution show only the four prominent bands of the ten reported for these compounds in alcohol by Orndorff, Gibbs, McNulty, and Shapiro (A., 1927, 764). The absorption spectra of ethereal and alcoholic solutions of triphenylmethyl ethyl ether differ only in intensity. The absorption spectrum of triphenylmethyl chloride in neutral ethyl alcohol is identical with that of triphenylmethyl ethyl ether, indicating that quantitative etherification takes place in the cold. F. G. WILLSON.

Effect of rhodamine on a line spectrum. F. R. TERROUX (Trans. Roy. Soc. Canada, 1927, [iii], **21**, III, 255—256).—The radiation from a quartz mercury lamp, after passage through a quartz absorption cell containing solutions of rhodamine *B* of different concentrations, has been examined spectrographically. Contrary to the observations of Rây (A., 1926, 1192), there was no shift in position of any of the lines, and no tendency for the line spectrum to become continuous. A few spectra taken with the sodium flame showed a widening of the lines on long exposure, but this was more pronounced when the absorbing solution was absent, and was probably due to creeping of the image on the plate. Rhodamine *B* has important qualities as a spectral filter. A 1% solution 1 cm. thick transmits a narrow band from 6500 to 6100 Å. A 0·05% solution transmits freely over a broad band from 7000 to 5300 Å., and less freely between 4500 and 3700 Å. Outside these limits the solutions appear to absorb completely. M. S. BURR.

Sterol group. I. Absorption spectra of cholesterol derivatives. I. M. HEILBRON, R. A. MORTON, and W. A. SEXTON (J.C.S., 1928, 47—51).—The absorption spectra of a number of cholesterol derivatives have been examined, with the view of determining the class of compound to which vitamin-*D* may be assigned. Selective absorption occurs only when at least two double linkings are present in the molecule. It is shown that the absorption spectrum of cholesterilene resembles that of ergosterol, and it seems probable that two of the three double linkings in the latter compound occupy the same positions as in cholesterilene. Cholestenone and vitamin-*D* also appear to be correlated (A., 1927, 948). W. A. RICHARDSON.

Absorption spectrum of antirachitic cholesterol. R. POHL (Nachr. Ges. Wiss. Göttingen, 1926, 142—145; Chem. Zentr., 1927, i, 2921).—The absorption coefficient at 280 mμ of cholesterol is reduced by half on irradiation, whereas analysis shows that at least 99·5% of the original cholesterol remains. Hence, the bands which disappear should be due to an impurity which in small concentrations absorbs in the ultra-violet to an extent corresponding with that of ordinary dyes in the visible part of the spectrum. A. A. ELDRIDGE.

Absorption spectrum of antirachitic provitamin and vitamin. R. POHL (Nachr. Ges. Wiss. Göttingen, 1926, 185—191; Chem. Zentr., 1927, i, 2921).—The ultra-violet absorption spectrum of ergosterol is essentially coincident with that of the provitamin, which is present in cholesterol to the extent of about 0·017%. The earlier designation "colouring matter" of the ergosterol is justified. A. A. ELDRIDGE.

Emission of phosphors. II. Transformation of constituent bands in the samarium–sulphide spectrum. R. TOMASCHEK and (FRAU) H. TOMASCHEK (Ann. Physik, 1927, [iv], **84**, 1047—1073; cf. A., 1927, 1125).—The spectra of calcium sulphide–samarium and strontium sulphide–samarium phosphors being already known, the mixed phosphors, prepared in various ways, have been further investigated. The method of comparing corresponding emission lines or bands has again been used. Two distinct mixed types are disclosed. A series of mixed phosphors has been examined at low temperatures. The CaS-*h* emission consists of 4 sharp lines (6058, 6007, 5697·7, and 5656·6 Å., designated 1, 2, 3, and 4, respectively). A mixed phosphor in which 6·5% of the calcium sulphide has been replaced by strontium sulphide shows 1 greatly broadened and exhibiting a satellite at 6061 Å., 2 unchanged in wave-length but with a satellite on each side, 3 slightly broadened, and 4 showing broadening and two satellites; the 18·8% phosphor is very similar. From 27·5 to 80·7%, the bands are all greatly broadened, and a gradual, uniform shift in the direction of shorter wave-lengths is apparent. The 87·5 and 94·5% phosphors are markedly different. A very definite resolution into lines is observed, and the wave-lengths approximate to those shown by the strontium sulphide phosphor. It is clear that the broad bands are due to the coexistence of two types of emission centres.

The lines in the strontium sulphide–samarium emission corresponding with 1, 2, 3, and 4, are identified as 6034·6, 5993·2 (or 5999·4), 5679·0, and 5642·8 Å., respectively.

The phosphorescence centres are regarded as adsorption compounds of heavy metal salts at the surface of complex aggregates. The constancy of the principal wave-lengths for small strontium sulphide percentages indicates that no change in the binding forces occurs, but that strong fields are set up, causing the resolution into components either by a Zeeman or Stark effect. The adsorption mechanism agrees with the results of *X*-ray investigations on the structure of phosphors and accounts for the observations throughout the range of calcium–strontium sulphide mixed phosphors.

R. A. Morton.

Determination of dielectric constants in intense electric fields. J. Malsch (Ann. Physik, 1927, [iv], **84**, 841—879).—Modifications in the technique of Wien (Physikal. Z., 1922, **23**, 399) are described which permit of the ready determination of dielectric constants of conducting liquids such as water as well as those of good insulators in intense electric fields. A very full discussion is given of the theory of the method and of the probable accuracy. Measurements on water, glycerol, and ethyl ether, using heavily damped oscillation at frequencies of the order of 10^3 kilocycles, indicate that, within the order of experimental error, no change can be observed in the dielectric constant with field strength; the maximum estimated field strength used was 10^5 volt $cm.^{-1}$ The effect of intense fields is discussed at length with reference to Debye's theory, on which, it is shown, an increase of the dielectric constant of from 10 to 20% is to be anticipated in the fields employed.

R. W. Lunt.

Scattering of light by gaseous and liquid chlorine. A. F. W. Cole (Trans. Roy. Soc. Canada, 1927, [iii], **21**, III, 267—268).—Data for the ratio of the intensities of light scattered by chlorine and ether, respectively, are given (cf. A., 1926, 559). The hypothesis that carefully dried chlorine re-radiates absorbed energy has been tested and is found to have no foundation, unless the re-emitted radiation is of frequencies entirely beyond the range of visual observation. The chlorine used contained 2% of carbon dioxide and traces of some other gas, probably carbon monoxide.

M. S. Burr.

Refraction and dispersion of air, oxygen, and gaseous chloroform. Gaseous refractivities of acetone, methyl ether, and ethyl ether. H. Lowery (Proc. Physical Soc., 1927, **40**, 23—28).—The refractivities of air, oxygen, and gaseous chloroform have been measured for the green mercury line 5461, and the dispersion determined over the range 4800—6700 Å. For air at *N.T.P.* $(\mu-1)=4{\cdot}8286\times10^{-7}/(16774\times10^{27}-\nu^2)$, and for oxygen $(\mu-1)=3{\cdot}4343\times10^{27}/(12970\times10^{27}-\nu^2)$, for chloroform $(\mu-1)_d=14{\cdot}622\times10^{-7}/(10659\times10^{27}-\nu^2)$, where ν is the frequency of the light, and $(\mu-1)_d$ refers to the same number of molecules as 1 c.c. of hydrogen contains at *N.T.P.* The values of $(\mu-1)_d$ for acetone, dimethyl ether, and diethyl ether were 1096×10^{-6}, 8876×10^{-7}, and 1509×10^{-6}, respectively.

C. J. Smithells.

Optical properties of arsenic. E. Grischkievitsch-Trochimovski and S. F. Sikorski (Bull. Soc. chim., 1927, [iv], **41**, 1570—1585; cf. A., 1927, 614). —Replacement of a chlorine atom or an alkyl group by an aryl group in an arsine in which the hydrogen atoms have been replaced by chlorine atoms and alkyl groups causes an increase in the atomic refraction of the arsenic, whereas substitution by a cyanide or an oxalate radical has the opposite effect, and replacement of chlorine by alkyl radicals scarcely changes the refraction at all. If a chlorine atom in each of two molecules is replaced by a single oxygen atom, the refraction is not altered, but if two chlorine atoms in the same molecule are replaced, it is reduced.

R. Cuthill.

Optical refraction of alkaline-earth compounds with oxygen, sulphur, selenium, and tellurium. K. Spangenberg [with M. Haase and W. H. Lehmann] (Naturwiss., 1927, **15**, 266; Chem. Zentr., 1927, i, 2710—2711).—The tabulated refractivities of the compounds of magnesium, calcium, strontium, and barium with oxygen, sulphur, selenium, and tellurium exhibit the same regularities as those of the alkali halides. The dispersion increased in the order oxide, sulphide, selenide, telluride; with oxides it increases with increasing mol. wt. Barium telluride has the rock salt structure, *d* 7·593, $2d_{100}$ 6·82±0·02 Å.

A. A. Eldridge.

Refractive index of quartz. W. R. C. Coode-Adams (Proc. Roy. Soc., 1927, **A**, **117**, 209—213; cf. Lowry and Coode-Adams, A., 1927, 813).—Theoretical. A new formula for the refractive index of quartz is obtained by making use of the ultra-violet frequencies calculated from the optical rotations (*loc. cit.*). Starting from the Ketteler–Helmholtz formula, $n^2=n^2_\infty+\Sigma M_m/(\lambda-\lambda^2_m)$, 18 values of n in the visible and ultra-violet regions are calculated from the equation: $n^2=3{\cdot}53445+0{\cdot}008067/(\lambda^2-0{\cdot}0127493)+0{\cdot}002682/(\lambda^2-0{\cdot}000974)+127{\cdot}2/(\lambda^2-108)$. The values are in excellent agreement with the experimental values of Gifford for the ordinary ray in dextro-quartz (Proc. Roy. Soc., 1902, **70**, 329), the average error being only ±0·00001. The new formula also provides an adequate representation of the most reliable data for the infra-red. The constant term 3·53445 should be equal to the specific inductive capacity of quartz.

L. L. Bircumshaw.

Refractive and natural rotatory dispersion. M. L. Pagliarulo (Atti R. Accad. Lincei, 1927, [vi], **6**, 157—159).—The rotatory dispersion of mono*iso*amyl aspartate is anomalous and of the same type as that of monoethyl aspartate (A., 1927, 610). In this case, also, the existence of a relationship between the rotatory and refractive dispersions is not apparent from the corresponding curves, but is rendered so by means of the curves connecting the differences of the refractive indices with successive changes in wave-length of 100 Å.

T. H. Pope.

Refractivity of normal saturated monobasic aliphatic acids. P. E. Verkade and J. Coops, jun. (Rec. trav. chim., 1928, **47**, 45—51).—The conclusions of Waterman and Bertram (A., 1927, 1167) with regard to oscillation in the product of the mol. wt. and refractive index, Mn_D, in the normal fatty acid series are not justified by their results, and when the same calculations are applied to their values for the *C*-, *E*-, and *G*-lines (*loc. cit.*), no similar regularities are obtained. The observed fluctuations of $\Delta(Mn)$ for all four wave-lengths lie, for the most part, within the limits of experimental error.

M. S. Burr.

Refractivity and dispersivity of normal saturated monobasic aliphatic acids. H. I. Waterman and S. H. Bertram (Rec. trav. chim., 1928, **47**, 52—54).—A reply to Verkade and Coops (cf. preceding abstract).

M. S. Burr.

Simultaneous effects of rod- and specific-double refraction. IV. H. Ambronn (Kolloid-Z., 1928, **44**, 1—5).—A posthumous theoretical paper, of date January, 1919, in which equations are derived to represent the changes in the rod- and specific-double refraction of cellulose and celloidin strips on drying. E. S. Hedges.

Optical activity and polarity of substituent groups. VII. *sec.*-β-Octyl esters of *o*-, *m*-, and *p*-substituted benzoic acids. H. G. Rule, W. Hay, (Miss) A. H. Numbers, and T. R. Paterson (J.C.S., 1928, 178—186).—A number of optically active *sec.*-β-octyl esters of substituted benzoic acids have been prepared and examined (A., 1926, 1038). Two effects are distinguished: (i) the general effect, irrespective of the position of the substituent group, in which the series $NO_2 > CO_2H >$ halogens $> OMe > H > Me$ can be observed for a number of properties, such as molecular rotatory power of the *l-sec.*-β-octyl esters of the substituted benzoic acids, and the dissociation constants of the benzoic acids and substituted acetic acids; (ii) a group effect represented by the series $NO_2 > CO_2H > Ac > H > Me > I > Br > Cl > OMe$, which indicates the relative influence of the substituents on the nitration of a mono-substituted benzene and on the optical activity of the menthyl and *sec*-β-octyl esters of the *o*-substituted benzoic acids. Groups which direct to the *m*-position increase the rotatory power of these esters and *p*-directing groups lower it. Iodine is a partial exception to this rule. On the electron-shift theory of the general effect the direction of the change in rotatory power following *p*-substitution can be predicted from a knowledge of the corresponding acetic esters. The rotatory power of *d*-octyl hydrogen phthalate in solutions at different concentrations at 20° and in the homogeneous state at 90·5° has been measured.

The following compounds are described: d-β-*octyl hydrogen terephthalate*, m. p. 95—96°, $[\alpha]_D^{19}$ +45·17° in acetone; d-β-*octyl* o-*chlorobenzoate*, b. p. 180°/14 mm., d_4^{20} 1·0473; d-β-*octyl* m-*chlorobenzoate*, b. p. 175°/12 mm., d_4^{20} 1·0425; d-β-*octyl* p-*chlorobenzoate*, b. p. 177—178°/12 mm., d_4^{20} 1·0403; d-β-*octyl* o-*bromobenzoate*, b. p. 175°/9 mm., $d_4^{18\cdot9}$ 1·1987; d-β-*octyl* o-*iodobenzoate*, b. p. 202°/12 mm., $d_4^{18\cdot9}$ 1·3522; d-β-*octyl* o-*toluate*, b. p. 154—155°/9 mm., $d_4^{[illegible]6}$ 0·9522; d-β-*octyl* m-*toluate*, b. p. 181·5—182°/17 mm., d_4^{20} 0·9492; d-β-*octyl* p-*toluate*, b. p. 184°/19 mm., d_4^{20} 0·9492. W. A. Richardson.

Crystal form and optical activity. E. Herlinger (Naturwiss., 1927, **15**, 289; Chem. Zentr., 1927, i, 3177).—With regard to van 't Hoff and Le Bel's view of the connexion between optical activity and crystallographic enantiomorphism it must be remembered that the rotation of the plane of polarisation of the light is effected by the rotation of a spatial distribution of polarisation electrons. Hence there follows the possibility of the existence of four optically active isomerides instead of two for a single centre of asymmetry, as is recognised with tartaric acid. On account of the unsymmetrical distribution of radicals about the stereochemical asymmetric centre, dipole-molecules, suitably approaching the dissolved optically active molecule, are able to effect an optical inversion. A. A. Eldridge.

Stereochemical inversions and cross-saturation processes. A. Lapworth and E. N. Mottram (Mem. Manchester Phil. Soc., 1926—1927, **71**, 63—73).—The evidence relating to cross-substitution, or simple stereochemical inversion, and cross-saturation processes is discussed. The former appears to be general when a linking between saturated carbon and halogen or oxygen is involved in a substitution process in aqueous or alcoholic solution. This is seen, for example, in Holmberg's experiments on halogenated succinic acid (A., 1926, 384, 937), or in the changes in optical rotatory effect observed when compounds of the acetochloroglucose type are used as "intermediates" in syntheses in the sugar group, or, finally, in the contrast between the reactions of esters of different types, *e.g.*, sulphonates as compared with carboxylates (Ferns and Lapworth, J.C.S., 1912, **101**, 273). When halogens, halogen hydrides, or hypohalogen acids are added to a pair of doubly-linked carbon atoms, cross-saturation usually takes place and does not necessarily mean that stereochemical inversion must have occurred at some stage in the reaction. Conversely, on elimination of the same elements, cross-desaturation results. It is suggested that in the series of reactions, *cyclo*hexene ⟶ *cyclo*hexene chloro- or bromo-hydrin ⟶ *cyclo*hexene oxide ⟶ *cyclo*hexanediol, each one is a cross-reaction, resulting finally in a *trans*-compound. Oxidation of *cyclo*hexene by permanganate, however, results in the formation of the *cis*-isomeride of *cyclo*hexanediol. It is possible that the latter case may be best explained by the intermediate formation of a ring compound with the manganese. M. S. Burr.

Electromagnetic rotation of the plane of polarisation by solutes. O. Schönrock (Z. Physik, 1928, **46**, 314—326).—In recent work (Pfleiderer, A., 1927, 8) the magnetic rotation of a solute has been calculated from the expression $\omega(q_1+q_2)=\omega_1q_1+\omega_2q_2$, ω, ω_1, and ω_2 being Verdet constants for solution, solvent, and solute respectively and q_1, q_2 the weights of solvent and solute per c.c. of solution. The expression $\omega=\Sigma_m\omega_m q_m/s_m$ (ω_m, q_m, and s_m being Verdet constants, volume contents per c.c., and densities, respectively, for the constituents of a solution) rests on a sound theoretical basis, and is supported by the degree of constancy obtained for ω_2, provided $\Sigma mq_m/s_m=1$ for the solution, within fairly narrow limits. Verdet's contention that determinations of magnetic rotation with only one type of solution suffice, for example, to decide whether a salt exists in the solution as a hydrate or in the anhydrous state, is shown to be erroneous. Krethlow's observations (A., 1925, ii, 1029) on camphor show that, correctly calculated, the Verdet constant for camphor dissolved in benzene is really constant, the values for three solutions being in agreement at four wave-lengths. Similarly for β-methylamyl bornylenecarboxylate, the new equation represents an accurate mixture law, judged by the constancy of ω_2. R. A. Morton.

Molecular symmetry in solutions. K. Weissenberg (Physikal. Z., 1927, **28**, 829—834).—A

review of the data referring to molecular symmetry with special reference to the electric moments of molecules and to the structure of the recently discovered compounds $C(CH_2\cdot OH)_4$ and $C(CH_2\cdot OAc)_4$.
R. W. Lunt.

Dipole moment and anisotropy in fluids. L. Ebert and H. von Hartel (Physikal. Z., 1927, **28**, 786—790).—The validity of Born's theory has been investigated by comparing the value of the orientation polarisation of *p*-azoxyanisole, *p*-azoxyphenetole, and *p*-azoxyethyl benzoate calculated from Born's theory, by substituting for the critical temperature the temperature at which the molten substance becomes clear, with the value obtained by taking the difference between the molecular polarisation and the polarisation calculated from the molecular refraction. The values so obtained are of the same order of magnitude and are thought to sustain the view that molecular forces can be calculated to a first approximation from the forces due to dipoles. R. W. Lunt.

Periodic table of the structure of atoms and its relation to ion formation and valency. A. A. Noyes and A. O. Beckmann (Proc. Nat. Acad. Sci., 1927, **13**, 737—743).—A preliminary account of an attempt to correlate the spectroscopic data relating to ion formation with valency from the point of view of the periodic law. R. W. Lunt.

Classification of metallic substances. W. Hume-Rothery (Phil. Mag., 1928, [vii], **5**, 173—178).—A classification of solid metallic phases is suggested as follows: metallic elements, which may be isotopically either simple or complex; primary metallic solid solutions, which form the end phases of the ordinary equilibrium diagrams and in which the crystal structure of the parent metal is retained; secondary solid solutions, in which the crystal structure is different from that of the parent metal, but in which there is no indication of the formation of compound molecules or electron exchange or transference; intermetallic compounds of fixed or variable composition, in which there is evidence either of electron transference and exchange or that a compound molecule is being formed. A. E. Mitchell.

Structure and dimensions of the benzene ring. J. K. Morse (Proc. Nat. Acad. Sci., 1927, **13**, 789—793).—A model of a benzene molecule is described which is thought to explain both the chemical properties and the *X*-ray spectrogram of benzene.
R. W. Lunt.

Influence of shape and polarity of molecules on the *X*-ray spectrum of liquids. II. Occurrence of two amorphous rings in substances, the molecules of which contain several equal groups or parts. J. R. Katz and J. Selman (Z. Physik, 1928, **46**, 393—405).—A large number of liquids exhibit one "amorphous ring" only, in their *X*-ray spectra (*ibid.*, **45**, 97). Provided the molecule can be considered as roughly spherical, the mean distance of separation between the centres of molecules may be calculated from the diameter of the ring. Many liquids, however, show two "amorphous" rings in the *X*-ray diagram, the appearance and diameter of the second ring being determined by the structure of the molecules of liquid. Possibly, the liquids showing two rings are made up of small aggregates of a few molecules, in which a certain regular orientation of groupings occurs.

Tertiary amines were studied because it was possible to obtain molecules in which three equal side-chains were grouped around a central atom. As an example, tripropylamine shows two rings of diameters $a_1=7\cdot9_5$, $a_2=5\cdot2$, whilst propyl alcohol shows one ring $a=5\cdot3$, and the distance separating the centres of molecules is calculated in the same units as $b=7\cdot6$ from the molecular volume. Similar results were obtained with compounds NR_3 in which R is Bu, Bu^{β}, and *iso*amyl. Ortho-esters of the following types gave similar results: $CH(OR)_3$ (R=Et, Bu^{β}, or *iso*amyl); $C(OEt)_4$; $Si(OR)_4$ (R=Et or Me); $B(OR)_3$ (R=Me, Et, and Bu^{β}, and $PO(OR)_3$ (R=Et or tolyl). The last case is interesting because three amorphous rings, $a_1=9\cdot6$, $a_2=6\cdot2$, $a_3=4\cdot5$, were shown, whilst b is $9\cdot1$ and the a values for toluene and methyl alcohol were $6\cdot0$ and $4\cdot5$, respectively. In general, it is found that the heavier the central atom, the greater is the relative intensity of the inner ring, and the heavier or the more numerous the side-chains the greater is the relative intensity of the outer ring. This result confirms the view that the inner ring indicates the mean distance between the centres of molecules, and the outer ring that between the side-chains.

Trisubstituted benzene and pyridine derivatives and ring hydrocarbons of the type methyl*cyclo*pentadecane also show two rings. The effect of polymerisation is exemplified by: liquid styrene $a=5\cdot9$, metastyrene, $a_1=12\cdot5$, $a_2=5\cdot8$, indene, coumarone, acetaldehyde, propaldehyde, etc.

For short side-chains good agreement obtains between a_1 and b, but for longer chains a_1 is often greater than b. This result appears to be due to departures from the approximately spherical shape of the molecules. Triglycerides and dialkylamines do not behave quite normally. R. A. Morton.

***X*-Ray spectra of aliphatic hydrocarbons, alcohols, and carboxylic acids.** G. W. Steward (Proc. Nat. Acad. Sci., 1927, **13**, 787—789).—A preliminary account is given of data shortly to be published on the *X*-ray spectra of aliphatic hydrocarbons, alcohols, and carboxylic acids which are thought to support an hypothesis of the structure of these substances on the basis of a molecular space array. R. W. Lunt.

Synthesis of molecules. H. Ludloff (Naturwiss., 1927, **15**, 409; Chem. Zentr., 1927, ii, 9—10).—Electron impulses in a molecule neutralise one another in pairs; all molecules with an even number of electrons are therefore diamagnetic. This explains the author's principle that even molecules exhibit absorption in the red and odd molecules in the violet.
A. A. Eldridge.

Effective cross-sectional area of gas molecules towards low-velocity ions of the alkali metals. C. Ramsauer (Physikal. Z., 1927, **28**, 858—864).—The effective target area of helium, neon, and argon to ions of lithium, sodium, potassium, and cæsium has been determined in the energy range 1—50 volts. The target area is a maximum for cæsium and diminishes along the series. In all cases it is large compared with the value deduced from kinetic theory at 1 volt and diminishes asymptotically to a value approximating to the "kinetic" value in the neighbourhood of 20 volts. R. W. LUNT.

Effective cross-sectional area of gas molecules. E. BRÜCHE (Naturwiss., 1927, **15**, 408—409; Chem. Zentr., 1927, ii, 12).—The effective cross-sectional area of molecules of methane, carbon monoxide, carbon dioxide, and nitrous oxide was determined by measuring the diminution of intensity of a stream of electrons of known velocity which was passed through the gas. The character of the curves is determined chiefly by the number of "valency" electrons of the constituent atoms. A. A. ELDRIDGE.

***X*-Ray spectrum of element 75.** O. BERG (Physikal. Z., 1927, **28**, 865—866).—*X*-Ray spectrograms of mixtures of principally tantalum and tungsten which exhibit the $L\alpha$ and $L\beta$ lines of element 75 are described and discussed. R. W. LUNT.

Calculation of crystal structure by means of Fourier's theorem. J. M. BIJVOET (Chem. Weekblad, 1928, **25**, 2—11).—A discussion of the methods by which structure may be calculated from the *X*-ray spectrum and measurements of the intensities of the diffracted rays. From each intensity a Fourier coefficient may be derived, the constant term being given by the total number of electrons in the cell. The history of this method of analysis is outlined, and the difficulties of the application are considered. S. I. LEVY.

Static methods and their application to the study of crystal habits. A. SHUBNIKOV and O. SHUBNIKOV (Bull. Acad. Sci. Petrograd, 1926, No. 6, 363—384).—The "normal" form of wiluite was ascertained by measurement of 335 crystals. CHEMICAL ABSTRACTS.

New kinds of mixed crystals. VII. D. BALAREV (Z. anorg. Chem., 1928, **168**, 292—296; cf. this vol., 110).—The inclusion of ferric chloride in ammonium chloride crystals is probably not a case of true mixed crystal formation, but is analogous rather to the inclusion of permanganates and other salts in the internal surface of barium sulphate crystals; *e.g.*, in both instances the amount of foreign salt in crystals separating from mother-liquor of a given composition is variable, and the crystals also contain free water. Ritzel's observation (A., 1916, ii, 568) that potassium sulphate or sodium nitrate present in the solution of ferric and ammonium chlorides does not appear in the crystals does not conflict with this view, since similar effects have been observed with barium sulphate. When barium chloride is precipitated with ammonium or lithium sulphate in presence of the corresponding chloride, the precipitate contains no chloride unless it has been formed so rapidly that the crystals contain cavities. If barium chloride and potassium sulphate diffuse into a solution of potassium and ammonium chlorides, the resulting precipitate contains potassium sulphate, but no ammonium sulphate is taken up unless the ammonium chloride concentration exceeds a certain limit. Finally, as with $NH_4Cl,FeCl_3,7H_2O$ crystals, some doubly refracting crystals have been found in the systems barium sulphate–alkali sulphate–water, and on warming these crystals become isotropic. R. CUTHILL.

Crystal structure of alkali metals. F. SIMON and E. VOHSEN [with C. VON SIMSON] (Naturwiss., 1927, **15**, 398; Chem. Zentr., 1927, ii, 10).—Sodium, potassium, rubidium, and cæsium are body-centred cubic; the lattice constants (90° Abs.) are 4·24, 5·25, 5·62, 6·05 Å., and *d* 0·996, 0·892, 1·59, 1·98, respectively. Values of *d* and atomic volume at 0° Abs. are calculated. A. A. ELDRIDGE.

Crystal structure of the isomorphous sulphates of potassium, ammonium, rubidium, and cæsium. A. OGG (Phil. Mag., 1928, [vii], **5**, 354—367).—The *X*-ray measurements of Ogg and Hopwood (A., 1916, ii, 594) with the $K\alpha$ radiation of palladium together with some further measurements on potassium and ammonium sulphates with the $K\alpha$ radiation of molybdenum have been systematically analysed. It is shown that the structures are all based on a simple orthorhombic lattice having 4 molecules to the unit cell. The space-group is V_h^{16}. The positions of the atoms have been determined and an explanation of the characteristic twinning of the crystals is given. A. E. MITCHELL.

Crystal structure of potassium, rubidium, and cæsium sulphates. F. P. GOEDER (Proc. Nat. Acad. Sci., 1927, **13**, 793—797).—An analysis of the *X*-ray spectra of the above sulphates indicates that in order to satisfy the internal symmetry of the molecule the only possible space-group is given by $2Di$—13 (V_h^{13}). R. W. LUNT.

Constitution of silver subfluoride. E. BRODY and T. MILLNER (Z. anorg. Chem., 1928, **168**, 349—355).—Assuming that silver subfluoride is formed, as Hettich has suggested (A., 1927, 1155), by introduction of neutral silver atoms into a distended silver fluoride lattice, and calculating the energy of lattice distension by Biltz and Grimm's method (A., 1925, ii, 842), the value −24·5 kg.-cal. is derived for the heat of formation from gaseous fluorine and solid silver, whereas if the fluoride is formed by the introduction of negative fluoride ions into a distended silver lattice the value would be +27·1 kg.-cal. The stability of the fluoride would agree with the latter structure, which is also in harmony with its considerable electrical conductivity, and the probable readiness with which it evolves fluorine. R. CUTHILL.

Crystal structure of silver chlorate. A. FERRARI and C. G. FONTANA (Atti R. Accad. Lincei, 1927, [vi], **6**, 312—314).—From *X*-ray measurements it is shown that the unit cell of silver chlorate is tetragonal and contains 8 molecules; the grating constants *a* and *c* are, respectively, 8·48 and 7·91 Å. R. W. LUNT.

***X*-Ray analysis and crystal structure of cadmium-silver alloys. I.** G. NATTA and M. FRERI (Atti R. Accad. Lincei, 1927, [vi], **6**, 422—428).—A first investigation has been made by *X*-ray methods of the series of solid solutions and compounds in the system Ag–Cd (cf. Petrenko and Fedorov, A., 1911, ii, 281). The results show that the alloys containing from 0 to 44 at.-% Cd (α-phase) consist of solid solutions of cadmium in the silver lattice in which the length of the unit cell varies linearly with the composition from 4·07 for pure silver to 4·14 Å. for 31 at.-% Cd. The alloys containing 47—51 at.-% Cd (β-phase) consist of the compound AgCd and solid solutions of cadmium in it, the structure being a cube-centred lattice of the cæsium chloride type. It is shown that the transformation which the β-phase undergoes at 460° is not a decomposition into the α- and γ-phases, but a polymorphous change of the compound AgCd to a hexagonal lattice having the structure Ag (0, 0, 0), Cd ($\frac{1}{3}$, $\frac{2}{3}$, $\frac{1}{2}$). O. J. WALKER.

Structure of smoke particles from a cadmium arc. H. P. WALMSLEY (Proc. Physical Soc., 1927, 40, 7—13).—Using the powder method of *X*-ray analysis, the particles dispersed in air from a cadmium arc were found to be isometric crystals of cadmium oxide. The primary particles in the smoke had *d* 8·16, which is normal for cadmium oxide. Photometric measurements gave dimensions for the primary crystals of about 5×10^{-6} cm. The particles grow by aggregation along binary axes of symmetry, uniting on their (110) faces. Models were constructed to show how the aggregates may be formed.

C. J. SMITHELLS.

Crystal structure of the double chloride of cadmium and cæsium, $CsCdCl_3$. A. FERRARI and A. BARONI (Atti R. Accad. Lincei, 1927, [vi], 6, 418—422).—*X*-Ray measurements of the above compound indicate that it has a cubic lattice of constant 5·20 Å. with the structure Cs (0, 0, 0), Cd ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$), Cl (0, $\frac{1}{2}$, $\frac{1}{2}$) ($\frac{1}{2}$, 0, $\frac{1}{2}$) ($\frac{1}{2}$, $\frac{1}{2}$, 0); $d_{\text{calc.}}$ 4·14, $d_{\text{obs.}}$ 3·75. The interatomic distance Cl—Cd is less than the sum of the radii of the chlorine and cæsium ions as given by Goldschmidt. The above structure, which is identical with that of cæsium mercuric chloride (A., 1927, 1128), is another example of the crystallographic similarities between cadmium and mercury. O. J. WALKER.

Crystal structure of modification *C* of sesquioxides of the rare earths, indium, and thallium. W. ZACHARIASEN (Norsk Geolisk Tidsskr., 1927, 9, No. 3—4; Chem. Zentr., 1927, ii, 11).—A consideration of the results of measurements for scandium, yttrium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutecium, indium, and thallium sesquioxides (cf. Goldschmidt, Barth, and Lunde, Norske Vidensk.-Akad. Oslo, Mat.-Nat. Kl., 1925, No. 7, 5). The space-group is T^5 and the disposition $12c+12c+8b$. The atomic distances for scandium—, yttrium—, and samarium—oxygen are 2·18, 2·36, 2·42 Å., respectively.

A. A. ELDRIDGE.

Crystal form of ψ-yohimbine. T. ITO (Z. Krist., 1927, 65, 303—305; Chem. Zentr., 1927, ii, 408).—ψ-Yohimbine is rhombic, apparently holohedral, $a:b:c=1·042:1:1·690$; $n_{\alpha D}$ 1·571±0·002, $n_{\beta D}$ 1·642±0·003, $n_{\gamma D}$ 1·655±0·002. A. A. ELDRIDGE.

Tetrahedral carbon atom and crystal structure of pentaerythritol. A. SCHLEEDE and E. SCHNEIDER (Z. anorg. Chem., 1928, 168, 313—321).—Pentaerythritol crystals with a polar tetragonal axis are imperfectly formed; properly grown crystals do not show such an axis, nor do etching experiments give any indication of its existence. It is therefore considered that the crystal class is S_4, and the space grouping S_4^2. This structure requires a tetrahedral, not a pyramidal, form for the carbon atom.

R. CUTHILL.

Space-group of dicyanodiamide and crystal structure of calcium cyanamide. U. DEHLINGER (Z. Krist., 1927, 65, 286—290; Chem. Zentr., 1927, ii, 541).—Dicyanodiamide, monoclinic, pseudo-rhombic, has *d* 1·40; *a* 13·8, *b* 4·4, *c* 6·2 Å., β 90° 35′; the elementary parallelepiped contains four molecules. The space group is C_s^3, C_2^3, or C_{2h}^3. The four nitrogen and four hydrogen atoms in the molecule are not equivalent. Calcium cyanamide is rhombohedral, *d* 2·20; *a* 5·11 Å., α 43° 50′. The corresponding trigonal prism has *a* 3·91, *c* 14·10 Å. There is one molecule in the elementary cell. The atomic co-ordinates are: Ca (0, 0, 0), C ($\frac{1}{2}$, $\frac{1}{2}$, $\frac{1}{2}$), N (u, u, u), ($\bar{u}$, $\bar{u}$, $\bar{u}$), where $u=0·37$, and the atomic distances Ca—Ca 3·91, Ca—C 3·26, C—N 1·59, Ca—N 2·40 Å.

A. A. ELDRIDGE.

Crystal form of methyl tetrathionoxalate. H. HIMMEL (Z. Krist., 1927, 65, 496—499; Chem. Zentr., 1927, ii, 1340).—The *cis*-form, m. p. 71·5°, is monoclinic holohedral, $a:b:c=0·8356:1:1·1684$, $\beta=124°\ 32'$; the *trans*-form, m. p. 101·5°, is also monoclinic holohedral, $a:b:c=0·7919:1:0·6059$, $\beta=99°\ 48'$. A. A. ELDRIDGE.

Scattering of *X*-rays and electron distribution in the atoms of crystals. R. J. HAVIGHURST (Physical Rev., 1928, [ii], 31, 16—26).—A critical examination of the method of obtaining the atomic structure factor and of the Fourier analysis method of determining electron distributions in crystals. If the method, as appears, is valid, any modification caused by the Compton effect in the intensity of regular reflexion of *X*-rays is negligible.

A. A. ELDRIDGE.

Diffraction of *X*-rays in liquid normal monobasic fatty acids. R. M. MORROW (Physical Rev., 1928, [ii], 31, 10—15).—The liquid normal fatty acids from formic to undecoic were investigated by the method previously employed (Stewart and Morrow, A., 1927, 1015). The spacing constants, d_2 and d, and the computed densities for the acids are: formic 3·65, 5·2, 1·42; acetic 4·17, 5·9, 1·25; propionic 4·39, 6·0, 1·36; butyric 4·64, 8·5, 1·03; valeric 4·54, 10·2, 1·03; hexoic 4·64, 12·8, 0·90; heptoic 4·54, 14·5, 0·93; octoic 4·54, 17·0, 0·88; nonoic 4·54, 18·4, 0·89; decoic 4·59, 20·3, 0·86; undecoic 4·54, 22·0, 0·88. The arrangement of molecules in the cybotactic state is not that found in the crystalline state.

A. A. ELDRIDGE.

***X*-Ray diffraction in liquids. Comparison of certain primary normal alcohols and their isomerides.** G. W. STEWART and E. W. SKINNER (Physical Rev., 1928, [ii], 31, 1—9).—*X*-Ray diffraction curves were obtained for *iso*-, *sec*.-, and *tert*.-amyl and *tert*.-butyl alcohols, diethyl-, methyl-*n*-butyl-, *sec*.-butyl-, and triethyl-carbinols. The attachment of a methyl group at the side of a chain increases the mean diameter of the chain molecule by 0·6 Å., and that of a hydroxyl group by 0·4 Å., whereas the attachment of both groups to the same carbon atom increases the diameter by only 0·65 Å. The attachment of three ethyl chains to the same carbon atom increases the diameter by 1·35 Å. With di-*n*-propylcarbinol the side attachment of a hydroxyl group is shown to increase the diameter in one direction by 0·45 Å. and in the other not at all. Associated polar groups give two molecules in a continuous chain for each longitudinal spacing, but when the hydroxyl group is not attached to the last or penultimate atom in the chain this association disappears.

A. A. Eldridge.

[Magnetic transformation of iron.] F. Wever (Z. anorg. Chem., 1928, **168**, 327—328; cf. A., 1927, 627).—A reply to Ruer's criticism (*ibid.*, 925).

R. Cuthill.

Transformation of β-brass and the demagnetisation process of ferromagnetic metals. C. H. Johansson (Ann. Physik, 1927, [iv], **84**, 976—1008).—The transformation of β-brass and the transformations occurring in ferromagnetic metals with loss of magnetic properties resemble each other in showing anomalous behaviour when various tests are applied. The idea is advanced that the transformations occur with lattice structures permitting rotational vibrations of the atoms, a phenomenon which does not obtain in normal lattices of metals and alloys. There is reason to regard the sphere of influence of the zinc atoms in β-brass as ellipsoidal rather than spherical, and as the lattice is probably of the cæsium chloride type (Cu : Zn=1 : 1) the copper may be expected to retain the spherical sphere of influence. On this basis, arguments are advanced in favour of the view that the transformation of β-brass in the solid state arises from heat vibrations about the inertia axes, vertically to the symmetry axes of the zinc atoms. A similar mechanism is put forward for the demagnetisation processes, the heat oscillations occurring about the inertia axes and at right angles to the magnetic axes. Possible objections to the view are considered in detail. The magnetic properties are constitutive to the atom (or molecule) concerned and the magnetic moment is independent of thermal oscillations. Phase transformations or chemical reactions bound up with changes in electron configurations, can, however, effect discontinuous changes in magnetic moments. Mixed crystals of weakly magnetic metals and a smaller amount of a ferromagnetic metal must, on account of Larmor's (precessional motion) theorem, be themselves weakly magnetisable, even if the ferromagnetic atom is able to retain its moment unchanged. Weiss' theory is discussed in relation to this kinetic-lattice theory; there is no necessary opposition between the two.

R. A. Morton.

Evolution of nickel sulphide and cobalt sulphide in contact with water. (Mlle.) S. Veil (Compt. rend., 1928, **186**, 80—81; cf. A., 1926, 567).—Nickel sulphide prepared by precipitation in the cold is less magnetic than the hydroxide obtained under the same conditions. The use of warm water renders it less oxidisable and reduces its magnetism. The magnetic properties of the oxide derived from the sulphide prepared in the cold are of the same order as that from the hydroxide prepared in the cold, and show variations with temperature analogous to those observed for nickelous hydroxide and the hydrate of nickel sesquioxide (A., 1925, ii, 183). In general, cobalt sulphide yielded the same results, except that cobalt sulphide was more magnetic than the hydrate of cobalt sesquioxide, both prepared in the cold, although their coefficients of magnetisation are of the same order (cf. A., 1927, 614).

J. Grant.

Deformation structures of aluminium crystals and crystal masses and their reciprocal relations. E. Schiebold (Fortschr. Min. Kryst. Pet., 1927, **11**, 25—28; Chem. Zentr., 1927, i, 2707—2708).—The deformation structures of aluminium crystals and crystal masses on crushing, drawing, rolling, and torsion were studied.

A. A. Eldridge.

Diffusion in crystals with overgrowths. E. Dittler (Z. anorg. Chem., 1928, **168**, 309—312).—Examination of various natural specimens of crystals with overgrowths and also of similar crystals prepared artificially about 50 years ago has failed to yield any decisive evidence of the occurrence of diffusion between the crystal layers.

R. Cuthill.

***X*-Ray study of the heat motion of the atoms in a rock-salt crystal.** R. W. James and E. M. Firth (Proc. Roy. Soc., 1927, **A**, **117**, 62—87).—The ratio of the intensity of reflexion of *X*-rays by rock-salt crystals at the temperature of liquid air to that at the ordinary temperature has been measured for a number of spectra. The temperature factor is of the form exp. $\{-bf(T)\sin^2\theta_T/\lambda^2\}$, where $f(T)$ is some function of the temperature Abs., and the constant b will in general differ for atoms of different kinds. The experimental results, combined with data obtained previously at high temperatures (Phil. Mag., 1925, [vi], 49, 585), are compared with the theoretical formulæ of Debye and Waller for the temperature factor of *X*-ray reflexion. Up to about 500° Abs. fairly good agreement is obtained with Waller's theory, but at high temperatures the experimental curve deviates widely from the theoretical. This is to be expected, because the assumptions on which the theory is based need modification at such temperatures. The fact that, for corresponding angles of reflexion, the temperature factor is considerably larger for spectra of the type Cl+Na than for those of the type Cl—Na, is discussed. It is possible that the temperature factor may be a function of the direction of the rays relative to the crystal axes. The absolute value of the integrated reflexion for the (200) spectrum from a rock-salt crystal has been redetermined and found to be 0·000492 for molybdenum $K\alpha$, and 0·000544 for rhodium. An estimate of the "extinction" for this crystal for molybdenum has been made. The reflexions from a number of faces of the rock-salt crystal have been determined in absolute measure by comparison with the (200) spectrum, and from these, the *F*-factors, or atomic scattering factors, have been deduced at 0, 86, 290, and 900° Abs. An attempt has been made to get some idea of the actual amplitude of the heat-motions of the atoms in the rock-salt lattice, by analysing the curves showing the variation of the atomic scattering power with the angle of scattering, using the method of Fourier analysis so as to obtain the distribution of electrons in the crystal unit at different temperatures.

From the broadening of the peaks in the distribution curves, the mean amplitudes of the atomic vibrations have been estimated. Mean amplitudes of about 0·20 Å. at 290° Abs., and of 0·58 Å. at 900° Abs., explain the observed changes in the distribution curves. This estimate of the amplitudes is checked by means of a rough calculation, which gives results of the same order. L. L. Bircumshaw.

Structure of liquids and vitreous solids. H. Jeffreys (Proc. Camb. Phil. Soc., 1928, **24**, 19—31).—Whilst the kinetic theory and the ionic lattice theory present a consistent picture of the gaseous and crystalline solid states, no adequate theory is available for the liquid and amorphous states. The description of vitreous solids as supercooled liquids is open to objection. The three states of matter are regarded as gaseous, crystalline, and vitreous. In the typical gas, single molecules move freely at intervals much greater than their own dimensions; the crystal is built according to a regular repeating pattern, and the vitreous solid is held together by the same kind of forces as the crystal, but the structure is less regular. It is probably comparable in stability with the crystal except near the m. p. The liquid is a compromise between the vitreous and gaseous states, the clots of molecules in a liquid resembling small pieces of vitreous solid, whilst themselves playing a part similar to molecules of a gas in producing viscosity. Migration of molecules from one clot to another will occur. This point of view is in harmony with the rigidity, density, strength, cleavage, conductivity, and other properties of vitreous solids. R. A. Morton.

Electrical conductivity of silicon. H. J. Seemann (Physikal. Z., 1927, **28**, 765—766).—The electrical conductivity of a number of single crystals of silicon has been determined in the range −180° to −80°; the mean value of the coefficient α is approximately +0·002. R. W. Lunt.

Electrical conductivity of crystalline zinc oxide. R. Bach (Arch. Sci. phys. nat., 1927, [v], **9**, 426—430).—The specific resistance of crystalline zinc oxide has been investigated over the temperature range −183° to +297°. The specific resistance is minimal (0·1 ohm cm.) at −100° and 0·14 ohm cm. at the ordinary temperature. Over the temperature range investigated the conductivity is entirely metallic, although it is probable that, at temperatures of the order of 1000°, conductivity of the ionic type is superposed. Neither polarity nor variation of resistance with axial direction was observed.

J. S. Carter.

Effect of magnetic, electric, and mechanical forces on "mesophases." H. Zocher (Physikal. Z., 1927, **28**, 790—796).—A mathematical analysis of the effect of magnetic, electric, and mechanical forces on "mesophases," of which anisotropic liquids are considered as typical examples. R. W. Lunt.

Susceptibility of ozone. O. R. Wulf (Proc. Nat. Acad. Sci., 1927, **13**, 744—748).—The volume susceptibility of ozone and ozone–oxygen mixtures has been determined by a modification of Gouy's method in the range 11,000—16,000 gauss. The results show, in contradistinction to Becquerel's measurements, that ozone is not more paramagnetic than oxygen, and suggest that ozone is diamagnetic. R. W. Lunt.

Diamagnetic susceptibilities of gases at low pressures. V. I. Vaidyanathan (Phil. Mag., 1928, [vii], **5**, 380—386).—A susceptibility balance capable of measuring changes in volume susceptibility of 6×10^{-12} in a field of 1400 gauss is described. Examination of nitrogen, argon, and carbon dioxide, at pressures up to 544 mm., showed strict proportionality between pressure and volume susceptibility. The values obtained for the volume susceptibilities of carbon dioxide, argon, and nitrogen were $-9{\cdot}2\times10^{-10}$, $-11{\cdot}3\times10^{-9}$, and $-5{\cdot}8\times10^{-10}$, respectively. The values for nitrogen and carbon dioxide are in fair agreement with those of Hector (Physical Rev., 1926, [ii], **24**, 418) and of Lehrer (A., 1926, 1086), respectively. The value for argon is 40% higher than that of Hector and 28% higher than that of Lehrer. The mean atomic radius of argon calculated from the author's value is in close agreement with that determined from *X*-ray and viscosity measurements, whilst the gram atomic susceptibility of $25{\cdot}3\times10^{-6}$ approximates to the calculated value of Pauling (Proc. Roy. Soc., 1927, **A**, **114**, 181), viz., $21{\cdot}5\times10^{-6}$. The direct linear relationship between pressure and susceptibility is in agreement with the results of Hamar (Proc. Nat. Acad. Sci., 1926, **12**, 594) and Lehrer (*loc. cit.*). A. E. Mitchell.

Photometric determination of the permeability of olive oil towards ultra-violet light. E. Rousseau (Compt. rend. Soc. Biol., 1927, **96**, 611—612; Chem. Zentr., 1927, i, 2711).

Optical properties of selenium in the conducting form. (Miss) P. M. Nicol (J. Proc. Roy. Soc. New South Wales, 1926, **60**, 60—72).—The extinction coefficient, κ, and refractive index, n, of selenium for wave-lengths of 4400—7100 Å., determined from measurements with selenium mirrors, are independent of the temperature at which the selenium was transformed into the conducting variety, and alter little, if at all, with exposure to light and with increasing age. With increasing wave-length, κ decreases and n increases. R. Cuthill.

Heterochromic photometry of body colour. K. Schaum (Z. physikal. Chem., 1928, **131**, 226—236).—The problem of the analysis of colour from the physical and physiological point of view is discussed, and a method is described for determining quantitatively the degree of contrast between coloured bodies with an error of less than 2%, and for measuring the degree of brightness compared with a standard white substance such as magnesium oxide.

H. F. Gillbe.

True temperature scale of carbon. C. H. Prescott, jun., and W. B. Hincke (Physical Rev., 1928, [ii], **31**, 130—134).—Measurements of the spectral emissive power of Acheson graphite for 0·660 μ at 1250—2700° Abs. are summarised by the relation $\varepsilon=0{\cdot}984-5{\cdot}8\times10^{-5}T$. A. A. Eldridge.

Specific heat of hydrogen at high temperatures. W. H. McCrea (Proc. Camb. Phil. Soc., 1928, **24**, 80—84).—The specific heat of hydrogen has been recalculated on the basis of empirical values for the energy levels involved in the production of ultraviolet bands of the hydrogen molecule, as determined by Hori (A., 1927, 1005). It would appear that a simultaneous confirmation of Hori's work and of the expression $C_v=4{\cdot}659+0{\cdot}00070T$, proposed by Partington and Shilling, has been obtained. For other gases, the same statistical methods applied to vibrational frequencies deduced from band spectra lead to erroneous results. R. A. Morton.

Latent heat of fusion and heat of transformation of some metals [manganese, thallium, iron, and steel]. S. Umino (Sci. Rep. Tôhoku Imp. Univ., 1927, **16**, 775—798).—The total heat content and specific heat at different temperatures up to the m. p., the heat of transformation, and the latent heat of fusion of manganese, thallium, pig iron, and various plain carbon steels have been determined by a differential calorimetric method and the results are shown in tables and graphs. The heat of transformation in g.-cal./g. of thallium at 232° is 0·6 and of manganese 2·88 at 835° and 4·43 at 1044°. The latent heat of fusion of thallium is 3·67, of manganese 64·8, and of pig iron containing 4·31% C 46·63 g.-cal./g. The heat of the A0-transformation of carbon steel at 215° increases with the carbon content, being 0·86, 1·38, and 1·63 g.-cal./g. with 0·57, 0·94, and 1·16% C, respectively; hence the heat of magnetic transformation of cementite is 9·72 g.-cal./g. The true specific heat of carbon steels rises sharply in a smooth curve to a maximum, which is greater the higher the carbon content, at 215°, then falls abruptly to little more than the value at 20°; at higher temperatures, the rise is relatively small and the curve is almost a straight line. The true specific heat of thallium falls abruptly at the transformation point and that of manganese is erratic between the two transformation points. Redeterminations of the m. p. of thallium and manganese gave 303° and 1221°, respectively.
A. R. Powell.

Heats of vaporisation of *iso*propyl alcohol and ethyl alcohol. G. S. Parks and W. K. Nelson (J. Physical Chem., 1928, **32**, 61—66).—The heats of vaporisation of these alcohols have been determined in an apparatus of the type described by Awbery and Griffiths (A., 1924, ii, 541) in which the weight of alcohol vaporised at its b. p. by a measured amount of electrically supplied energy is found. The values are for *iso*propyl alcohol at 82·2°, 161·7 g.-cal./g., and for ethyl alcohol at 78·4°, 208·7 g.-cal./g. After a consideration of the values found by Brown (J.C.S., 1903, **83**, 991) and by Mathews (A., 1926, 462), the best value for *iso*propyl alcohol is suggested to be 161·0±1·5 g.-cal./g. The value now determined for ethyl alcohol lies between those found by these workers. L. S. Theobald.

Thermal magnitudes. W. Herz (Z. anorg. Chem., 1927, **168**, 86—88).—Division of the product of the cryoscopic constant and the latent heat of fusion by that of the ebullioscopic constant and the latent heat of evaporation yields an approximately constant value for all substances. H. F. Gillbe.

M. p. of benzene derivatives. T. Beacall (Rec. trav. chim., 1928, **47**, 37—44).—Examination of the m.-p. data for a large number of halogen-substituted benzene derivatives brings to light the following regularities: (i) The introduction of a pair of chlorine (or bromine) atoms in the *p*-position increases the m. p. in an approximately constant ratio, viz., by about 23% for two chlorine atoms, 26% for one chlorine and one bromine atom, and 30% for two bromine atoms. When two iodine atoms, however, are introduced, the increase in m. p. becomes progressively less as the complexity of the molecule increases. (ii) The introduction of a single asymmetric halogen atom into benzene or a symmetrically-substituted halogenobenzene, lowers the m. p. in an approximately constant ratio, *i.e.*, by about 22%. The bearing of these regularities on the structure of the molecule is discussed. Similar relationships may also be recognised between m. p. and molecular volume, but the available data are scanty.
M. S. Burr.

Thermal and electrical conductivity of fused quartz as a function of temperature. H. E. Seemann (Physical Rev., 1928, [ii], **31**, 119—129).—The thermal conductivity of clear fused quartz between 235° and 1225° Abs. is represented by the equation $K=3{\cdot}83\times10^{-6}T+0{\cdot}00163$. There is an abrupt change in the thermal conductivity in the vicinity of 1140° Abs. Interpolated values of the specific resistance (ohms/cm.^{3}) are: 550° Abs., $4{\cdot}46\times10^9$; 750° Abs., $2{\cdot}09\times10^7$; 950° Abs., $1{\cdot}35\times10^6$; 1150° Abs., $2{\cdot}69\times10^5$. A. A. Eldridge.

Hydrogen cyanide. H. Sinozaki and R. Hara (Proc. Imp. Acad. Tokyo, 1927, **3**, 590—594).—The vapour pressure of hydrogen cyanide has been determined over the temperature range 0—190°, and the pressure range 100—830 mm. The data agree well with equations of the type $PV/WT=R-bP-CP^2$ and $PV/WT=R-bP$, the former being valid for lower and the latter for higher temperatures. On the basis of an equation of state proposed by Keyes, the molar fraction of double molecules formed by association may be calculated. The fraction varies from 0·00040 to 0·0655.

The density of liquid hydrogen cyanide has been determined by the dilatometric method at approximate intervals of 5° from 0° to 30°. The results agree well with the empirical equation $V_t=V_0(1+0{\cdot}00200201t-10^{-7}\times6{\cdot}175t^2)$, where V_0 is 1·39588 c.c./g. R. A. Morton.

Determination of the vapour pressure of arsenic tri-iodide. S. Horiba and R. Inouye (Sexagint [Osaka celebration], Kyoto, 1927, 279—287).—The vapour pressure of the orange form of arsenic tri-iodide has been determined from 11° to 182°. The T–$T.\log p$ curve shows the m. p. to be about 144°; the molar heat of vaporisation is 19·2 kg.-cal. Experiments are described on the vapour pressure of the yellow modification, which is stable at low temperatures. H. F. Gillbe.

Vapour pressure, dissociation, and transition point of mercuric sulphide. J. Rinse (Rec. trav. chim., 1928, **47**, 28—32).—The vapour pressure of mercuric sulphide has been determined between 333° and 651° using a glass spring indicator. On plotting vapour pressure against temperature two curves are obtained, intersecting at 386°±2° and 0·8 cm. of mercury. Below this temperature the red sulphide is the stable form and above it the black. This is confirmed by the change in colour and density on heating. The ($T \log p$–T) graph is not straight, indicating a change in the heat of vaporisation. This has been shown to be due to the dissociation of the sulphide, which is complete at least up to 530°. The abnormal behaviour is a result of the changing degree of association of the sulphur vapour. Changes in colour and density below the transition temperature have been observed. These are explained on Smits' theory of allotropy. Under certain conditions a high vapour pressure may be observed at temperatures at which the vapour pressure of mercuric sulphide should be very small. This may indicate the presence of an unstable mercurous sulphide, Hg_2S. M. S. Burr.

Vapour pressure and dissociation of mercuric iodide. J. Rinse (Rec. trav. chim., 1928, **47**, 33—36).—The vapour pressure of mercuric iodide has been determined between 130° and 347° by a statical method using a glass spring indicator. When $T \log p$ is plotted against T the graphs are nearly straight and intersect at the m. p., 255·5°. The heat of sublimation of the solid salt, calculated from the vapour pressure, is 20·0 kg.-cal., and the heat of vaporisation of the liquid is 15·1 kg.-cal. The difference, 4·9 kg.-cal., represents the latent heat of fusion. The degree of dissociation at 500°, 550°, and 600° has also been determined by vapour-pressure measurements. The average values of $K=(P_{Hg}\times P_{I_2})/P_{HgI_2}$ at these temperatures are, respectively, 0·01, 0·05, and 0·14. At 400° the vapour is colourless, but at 500° a slight brown colour, due to free iodine, is visible.

M. S. Burr.

Vapour pressures of *iso*propyl and *tert.*-butyl alcohols. G. S. Parks and B. Barton (J. Amer. Chem. Soc., 1928, **50**, 24—26).—The vapour pressures of the above alcohols, measured by static methods, are recorded between 0° and 90°. The heats of vaporisation are calculated for three temperatures; the molal entropies of evaporation indicate that these alcohols are associated. S. K. Tweedy.

Internal pressure of pure and mixed liquids. W. Westwater, H. W. Frantz, and J. H. Hildebrand (Physical Rev., 1928, [ii], **31**, 135—144).—The change in pressure with temperature at constant volume, γ, was determined for heptane, acetone, carbon tetrachloride, benzene, carbon disulphide, ethylene chloride, ethylene bromide, and bromoform, and for 12 50 mol.-% mixtures of these substances. The results are tabulated together with derived values for the compressibilities. γ is a function of the specific or molal volume only. For each pure liquid $v^2T_1\gamma=a$ (where v is the molal volume, and T_1 the temperature at which the pressure is 1 atm.) is constant. The values for the mixtures are less than additive, and less than those calculated from Biron's equation, but generally accord with the expression $a=(a_1a_2)^{1/2}$; still better agreement is obtained by considering that γv is additive. A. A. Eldridge.

New additive property of liquids. I. N. Longinescu (Compt. rend., 1927, **185**, 1472—1474).—The formula $a^{1/2}V^{1/6}=KT^{1/2}V^{2/3}$, where K is a constant, a the van der Waals coefficient, T the critical temperature, and V the critical volume, respectively, expresses the additive character of the property more exactly than that of van Laar. From this, generalised forms of the equations of G. G. Longinescu and of Walden are obtained, and also an expression from which the critical temperature of a compound may be calculated from the critical data of its components.

J. Grant.

One-component system SiO_2. I. Dilatometric measurements on tridymite and cristobalite. C. J. van Nieuwenburg and H. I. Zijlstra (Rec. trav. chim., 1928, **47**, 1—12).—An apparatus is described for the measurement of changes in the rate of linear expansion with increase of temperature of small quantities (less than 1 g.) of powdered materials. It has been used for the determination of the following transition points: α- → β-cristobalite, 220°±5°; α- → β-tridymite, 100°±7°; β- → γ-tridymite, 141°±7°. The values for tridymite are considerably lower than those found by Fenner (cf. B., 1913, 22). Certain irregularities in the behaviour of tridymite have also been observed in the neighbourhood of 440°. A semi-quantitative estimation of the composition of mixtures of tridymite and cristobalite can be made by observing the amount of expansion at the transition points relative to that of the pure constituents. The alterations in length are due to changes of crystalline form and bear no simple relation to the variations in density. Although it is possible to determine the transition point of cristobalite by the change in density, as indicated by a liquid dilatometer, this method cannot be employed for tridymite, of which the changes in density at the transition point must be less than 0·2%. M. S. Burr.

Entropy of hydrogen chloride. Heat capacity from 16° Abs. to b. p. Heat of vaporisation. Vapour pressures of solid and liquid. W. F. Giauque and R. Wiebe (J. Amer. Chem. Soc., 1928, **50**, 101—122).—The vapour pressures of solid hydrogen chloride, in international cm. of mercury, are given by $\log p=-1114/T-1{\cdot}285\log T-0{\cdot}0_4 9467T+11{\cdot}005$, in agreement with the single observation of Henning and Stock (Z. Physik, 1921, **4**, 226), but in slight disagreement with the values of Henglein (A., 1923, ii, 124) and Karwat (A., 1924, ii, 822). Karwat's equation for p does not reproduce that observer's own values. The vapour pressures of the liquid acid are well represented by Henning and Stock's equation. The heat capacity of hydrogen chloride between 17·29° and 188·07° Abs. (b. p.) is recorded; a transition occurs at 98·36° Abs. and the m. p. at 158·91° Abs. The observed latent heats of transition, fusion, and evaporation are 284·3, 476, and 3860 g.-cal. per mol., respectively. The entropy of hydrogen chloride gas at the b. p. is 41·2 g.-cal./1° per mol. or 44·5 at 25°, in agreement with the values calculated from spectroscopic data, using the Lewis and the Tetrode equations. The same values, within experimental error, are calculated using the third law of thermodynamics, thus confirming the validity of this law. A pink form of hydrogen chloride, possibly a third crystalline modification, was observed. The

entropy of a gas obeying Berthelot's equation of state is lower than that of an ideal gas by $27RT_c^3p/32T^3p_c$.
S. K. Tweedy.

Internal friction and number of molecules [per unit volume]. W. Herz (Z. anorg. Chem., 1927, **168**, 89—92).—The variation with temperature of the internal friction between the molecules of any normal liquid is such that the sixth root of the viscosity η is proportional to the number of molecules N per unit volume. For associated liquids $N\eta^{1/6}$ increases with rise of temperature.
H. F. Gillbe.

Hagenbach correction in the determination of viscosity by the efflux method. W. Rieman III (J. Amer. Chem. Soc., 1928, **50**, 46—55).—The Hagenbach correction was calculated from determinations of the viscosity of water and of methyl alcohol in a viscosimeter of the Bingham type having a uniform, nearly circular, bore (cf. Knibbs, J. Proc. Roy. Soc. New South Wales, 1895, **29**, 77). The value $1·124 \pm 0·006$ was obtained (neglecting the Couette correction), in agreement with the theoretical value of Bousinesq (Compt. rend., 1891, **113**, 49). The data do not support the view that the correction decreases when the Reynolds' number exceeds 700.
S. K. Tweedy.

Measurement of diffusion constants in liquids. G. von Békésy (Physikal. Z., 1927, **28**, 812—814).—An interferometric method is described for the measurement of diffusion constants of liquids; data are cited relating to aqueous $0·25N$-carbamide and water, and of aqueous $0·25N$-potassium chloride and water, which show that the accuracy of the method is approximately 0·7%.
R. W. Lunt.

Deviations of gaseous mixtures from Dalton's law of partial pressures due to chemical causes. I. Hydrogen chloride and water. J. Shidei (Sexagint [Osaka celebration], Kyoto, 1927, 143—169).—Observed values of the vapour pressure of a mixture of hydrogen chloride and water in the neighbourhood of 100° are smaller than the theoretical values, but with rise of temperature approach the latter; the two values become identical at about 150°. The equilibrium constant K_c $(\times 10^6)$ for the equilibrium $HCl + H_2O \rightleftharpoons H_2O,HCl$ at constant volume is 1026 at 110°, 1193 at 120°, 1406 at 130°, and 1898 at 150°.
H. F. Gillbe.

Dielectric constants of binary mixtures. V. Electric moments of certain organic molecules in carbon disulphide and hexane solution. J. W. Williams and E. F. Ogg (J. Amer. Chem. Soc., 1928, **50**, 94—101; cf. A., 1927, 819).—Dielectric constant and density data for 25° are recorded for carbon disulphide solutions of phenol, cinnamic acid, iodine, anthracene, and hexane, and for both carbon disulphide and hexane solutions of benzoic acid, naphthalene, benzene, nitrobenzene, and chlorobenzene. The polarisation, and therefore the electric moment, of a solute molecule is independent of the non-polar solvent; benzene and the above two solvents are non-polar. The electric moment of naphthalene is in agreement with the known difference between the chemical behaviour of the two benzene rings in the molecule.
S. K. Tweedy.

Dielectric properties of aqueous-alcoholic mixtures. P. Brun and J. Granier (Compt. rend., 1928, **186**, 77—80).—If the critical miscibility of aqueous-alcoholic mixtures is accompanied by changes in the molecular condition of the liquids, variations in their dielectric capacity should also be evident. A study of mixtures of water and ethyl alcohol with *iso*butyl or *iso*amyl alcohol has shown these variations to exist and to be similar in nature to those observed for the other physical properties of such mixtures. Maxwell's rule connecting refractivity and specific inductive capacity holds for the pure liquids, but for the mixtures the dielectric capacity increases as the refractive index falls (cf. A., 1926, 683).
J. Grant.

Binary azeotropes. VIII. M. Lecat (Rec. trav. chim., 1927, **47**, 13—18).—In continuation of previous work (A., 1927, 617, 1133), data for 154 binary mixtures are given. A number of these are azeotropes, positive or negative, some of which form two phases, either liquid or solid, at temperatures very near the constant b. p. Ten new negative azeotropes are included, eleven eutectics, and twenty-four non-azeotropic mixtures for some of which the isobars are practically rectilinear.
M. S. Burr.

Chemical affinity in metallic alloys, especially solid solutions. Compressibility. R. F. Mehl and B. J. Mair (J. Amer. Chem. Soc., 1928, **50**, 55—73).—The compressibility data for alloys are discussed and new measurements on sixteen alloys of copper, iron, and aluminium (including "constantan") are recorded. In all cases the compressibility was less than that calculated by the rule of mixtures, the divergence being greater the greater the chemical dissimilarity of the two metals. The difference between the measured and calculated compressibility is an indication of the intensity of the chemical affinity between the unlike metal atoms. This affinity results in an increase in the lattice rigidity, so that compressibility is a measure of "chemical hardness" as distinct from "physical hardness" (slip resistance). The experimental results are correlated with the mechanical properties of the alloys. The quenching hardness in steels is not caused by increase in the cohesive forces. Attempts to measure the heat of formation of alloys of aluminium with magnesium and zinc by determining the heat of dissolution in hydrochloric acid are recorded.
S. K. Tweedy.

Solubility of hydrogen in silver. E. W. R. Steacie and F. M. G. Johnson (Proc. Roy. Soc., 1928, **A**, **117**, 662—679; cf. A., 1926, 1089).—The apparatus and experimental procedure have previously been described (*loc. cit.*). A containing vessel of fused silica was used, and corrections were made for the diffusion of hydrogen through silica. This was measured separately at temperatures from 200° to 900° and at pressures from 5 to 80 cm. The ratio P/D, where P is the pressure and D the rate of diffusion, is constant at constant temperature. This is in agreement with the results of previous investigators and indicates that the gas diffuses through silica as molecular hydrogen. The solubility of hydrogen in silver, in the form of foil (0·40 and 0·12 mm. thick), was measured over the same range of temperature and pressure. Below 400° the solubility is extremely small; it increases rapidly with rising temperature and the values of log absorption/temperature are practically constant. At constant temperature the ratio $\sqrt{P}/Q$, where Q is the absorption, is constant. It follows from Henry's law that the dissolved gas must be dissociated into atoms, or else it must exist in the form of a dissolved hydride containing one atom of hydrogen to the molecule. The influence of extent of surface was found to be negligible. The absorption of hydrogen is compared with that of oxygen, the chief difference being that the solubility minimum for oxygen at 400° does not occur with hydrogen. The diffusion of gases through metals is discussed on the basis of Langmuir's theory of the mechanism of adsorption, and the connexion between absorption, adsorption, and diffusion is considered.

L. L. Bircumshaw.

Distribution and solubility of gases in fats. S. Schmidt-Nielsen (Annal. Acad. Sci. Fennicæ, 1927, **A**, **29**, No. 12).—Cod-liver oil, herring oil, linseed oil, olive oil, and mineral (transformer) oil, saturated with air at 20°, evolve the following volumes of gas per 100 g. of oil (measured at N.T.P.) when heated at 100° in a vacuum: 9·6, 5·9, 10·1, 5·0, 8·4 c.c., respectively, containing separately 21·8, 10·8, 19·1, 15·7, and 30·6% of oxygen. The amount of air absorbed at 50° is almost the same, but the oxygen contents are approximately halved in every case except that of the mineral oil, where it is practically unaltered. The lower oxygen values are probably due to the increased rate of oxidation. The four first-named oils absorb in a similar manner 13·5, 13·4, 160, and 117 c.c. of carbon dioxide per 100 g. of oil. G. A. C. Gough.

Di-, tri-, and tetra-chloroethylene as solvents in ebullioscopy. P. Walden (Annal. Acad. Sci. Fennicæ, 1927, **A**, **29**, No. 23).—These solvents are suitable for use in the determination of the mol. wt. of many organic compounds; carboxylic acids, however, give results corresponding with double molecules. It is suggested that this is due to the combination of pairs of intramolecularly ionised molecules. The following values for the molecular elevation of b. p. are given by the data for hydrocarbons, amines, ketones, and esters on extrapolation to infinite dilution of the solute: di-, 34·4°; tri-, 44·3°; tetra-chloroethylene, 55·0°. G. A. C. Gough.

Solubility of cellulose esters. I. II. G. Kita, I. Sakurada, and T. Nakashima (Cellulosechem., 1928, 9, 13—17, 27—29).—See this vol., 124.

Effect of impurities on the consolute temperature of the system water–phenol. G. MacKinney (Trans. Roy. Soc. Canada, 1927, [iii], **21**, III, 265—266).—The discrepancy between Hill and Malisoff's value, 65·85±0·15°, for the consolute temperature of the system water–phenol (A., 1926, 571) and Rothmund's value, 68·4° (A., 1898, ii, 503), is probably due to the presence of small traces of impurities in the latter case. Experiments have been made with four different samples of phenol giving values ranging from 65·75° to 68·3°. After purification by the method of Rhodes and Markley (A., 1922, i, 135), all the values lay between 65·65° and 65·85°. By the addition of 0·85% of *o*-cresol the temperature was raised to 68·4°. Since benzoquinone, produced by oxidation of phenol, is a likely impurity, 0·17% was added, and the consolute temperature was raised from 65·75° to 66·0°, whilst 0·8% gave 66·5°. To check the shape of the solubility curve near the critical solution temperature, 29% and 35% phenol solutions were examined. They gave miscibility temperatures of 65·65° and 65·75°, respectively, in close agreement with the results of Hill and Malisoff (*loc. cit.*). The consolute temperature is probably a better test of the purity of phenol than the m. p. or b. p. M. S. Burr.

Separation of binary liquid mixtures by silica gel. I. H. G. Grimm and H. Wolff. **II.** H. G. Grimm, W. Raudenbusch, and H. Wolff (Z. angew. Chem., 1928, **41**, 98—103, 104—107).—I. An investigation of the efficiency of processes involving silica gel in effecting a separation of binary liquid mixtures which cannot be separated by fractional distillation. Three methods have been investigated. The first consists in allowing the liquid mixture to percolate through a column of gel. In the second method the liquids are boiled and the vapours passed into a fractionating column packed with gel. In the third method the fractionating column is surrounded by a vapour jacket, so that both substances are maintained in the vapour phase. Liquid retained by the gel is recovered by heating to about 250° and collecting various fractions. The gel is regenerated by heating at 250—300° in a vacuum. The present measurements have reference to the mixture of ethyl alcohol (15·85%) and carbon tetrachloride (84·15%) of minimum b. p. The composition of the various fractions was determined refractometrically. In all cases the first fractions consist almost entirely of carbon tetrachloride. The degree of separation increases with decreasing grain size, decreasing size of pores, and increasing diameter of the column used. Using a gel of fine grain and having narrow pores, about 60% of pure carbon tetrachloride was obtained by the percolation method. The separations effected under comparable conditions by the three methods are roughly the same. On account of its simplicity the first method is to be preferred.

II. The separations effected when certain binary mixtures of various organic liquids are allowed to percolate through a column of silica gel have been investigated. When the heat changes produced by wetting silica gels with the components of the binary mixtures are compared with the results of the percolation experiments it is found that the component producing the greater heat effect is most strongly adsorbed and that the degree of separation increases with increasing difference between the heats of wetting.

The heat of wetting is influenced by various factors, *e.g.*, grain size, size of pores The following values (g.-cal./g. of gel) refer to a gel of grain size 0·2—0·5 mm. having very narrow pores: *cyclo*hexane, 6·25; hexane, 6·5; carbon tetrachloride, 7·3; chloroform, 10·9; toluene, 11·3; benzene, 11·3; propyl alcohol, 20·8; water, 20·95; methyl alcohol, 22·95; ethyl alcohol, 23·7. A gel having much wider pores gave values about 50% smaller. Addition of small quantities of ethyl alcohol to carbon tetrachloride produces a remarkable increase in the heat of wetting, addition of 0·125% of alcohol raising the heat of wetting to a value which is approximately the arithmetic mean of the values for the two components.

J. S. CARTER.

Adsorption of substances dissolved in water by inactive and active carbon. K. SKUMBURDIS (Kolloid-Z., 1928, **44**, 127—133).—Measurements of the adsorption of a number of non-colloidal and colloidal substances by five different samples of carbon show that for all the substances investigated the samples of carbon retain the same order of effectiveness. The best adsorbents were "supra-norit 5X," "supra-norit 4X," and "carboraffin." Among the non-colloidal substances the adsorption of *iso*amyl alcohol, *iso*valeric acid, diethylamine, and sodium *iso*valerate was followed stalagmometrically by comparing the drop number with a curve relating this value to the concentration. The adsorption of sucrose was followed polarimetrically, and that of *d*-tartaric acid and quinine hydrochloride by titration. In the latter case, the solution was titrated with 0·1*N*-potassium hydroxide solution, using cresol-red as an indicator. Surface-active substances such as *iso*amyl alcohol can displace sugar from the adsorption surface to an extent depending on the nature of the carbon. The importance of this in the sugar industry is pointed out as a means of preventing loss through adsorption in the decolorisation of sugar by carbon. E. S. HEDGES.

Sorptive power of lignin. E. WEDEKIND and G. GARRE (Z. angew. Chem., 1928, **41**, 107—112).—Lignin is a gel carrying a negative charge capable of adsorbing alkalis, ammonia, and basic dyes. The sorption is irreversible and hence indicative of subsequent formation of compounds, probably of a molecular type. The quantity of substance taken up depends on various factors (water content of the lignin, duration of the process, etc.). Sulphurous and hydrochloric acids are also fixed, the latter acid by moist lignin only, formation of solid solutions being followed by a chemical combination. Lignin takes up considerable quantities of iodine. Of the amount taken up only a fraction can be removed by thiosulphate. The fact that the solution of iodine acquires no measurable acidity, even on long keeping in contact with lignin, indicates that there is no substitution of hydrogen in the lignin molecule by iodine, but rather the saturation of some unsaturated linking. Neutral salts are not adsorbed, although there is considerable sorption of potassium hydrogen sulphite. Three types of lignin were used, obtained by Willstätter's method from oak, beech, and a wood of Japanese origin, respectively. The sorptive powers were, in general, very similar. J. S. CARTER.

Configuration of polymethylenedicarboxylic acid. II. Adsorption of the hexahydrophthalic acids. R. KUHN and A. WASSERMANN (Helv. Chim. Acta, 1928, **11**, 70—79).—The proportion of acid adsorbed by animal charcoal under the same conditions, viz., water 5 c.c., acid 4·170 mg., and animal charcoal 5·300 mg., has been determined for all the hexahydrophthalic acids. For the *o*-, *m*-, and *p*-derivatives of the *cis*-acids the percentage amounts adsorbed were 29, 24, and 24, respectively, and for the corresponding *trans*-acids, 24, 27, and 33. The relative adsorptions of *cis*- and *trans*-acids in the *m*- and *p*-series are, qualitatively, in accordance with the solubility relationships. The greater dissociation constant of the *trans*-*p*-acid reinforces the effect of the smaller solubility, hence the large difference in adsorption between the *cis*- and *trans*-acids. In the *m*-acids the two factors oppose one another, however, and the difference in adsorbability is only small. In the case of the *o*-acids, both on account of the smaller solubility and the larger dissociation constant, the *trans*-acid might be expected to be more readily adsorbed than the *cis*-acid. That this is not so is probably due to configurative influence, the directive influence of the water on the carboxyl groups (cf. Langmuir, A., 1917, ii, 525) making it more difficult for the remainder of the molecule of the *trans*-*o*-acid to accommodate itself to the adsorbing surface than will be the case for any of the other acids. The adsorption experiments lead to the same views as to configuration as the dissociation constants (cf. this vol., 240), and since the former refer chiefly to undissociated acid and the latter to ions, it may be concluded that ionisation is not accompanied by any marked change in configuration. The adsorption isotherms for the *cis*- and *trans*-*o*-acids have been determined at 21°; the adsorption exponents of the two are almost identical, *i.e.*, $1/n=0{\cdot}42$. The adsorption isotherm of benzoic acid has also been determined at 20° M. S. BURR.

Adsorption on barium sulphate and ultramicroscopical examination. M. N. CHAKRAVARTI and N. R. DHAR (Kolloid-Z., 1928, **44**, 63—68).—Barium sulphate for adsorption experiments was prepared by mixing solutions of barium chloride and potassium sulphate, this method giving smaller particles than the employment of solutions of barium hydroxide and sulphuric acid of equivalent concentration. The size of the particles was determined by observation of the velocity of fall in a liquid of known viscosity. Particles of radius down to $2{\cdot}5\times10^{-3}$ cm. could be followed with the unaided eye, and the ultramicroscope was used for the finer particles. Counting the particles under the ultramicroscope gave values for the size in agreement with those obtained by determining the velocity of fall under gravity. The phenomena of adsorption depend not only on the surface of the adsorbing substance, but also on the nature of the solution. A parallelism was observed between the adsorption and the water content of the barium sulphate particles. The results support Langmuir's view of a unimolecular adsorption layer. E. S. HEDGES.

Absorption velocity of carbon dioxide by the still surface of sodium hydroxide solution. S. MITSUKURI and Y. SAKAMOTO (J. Chem. Soc. Japan, 1927, **48**, 495—500).—The absorption velocity of carbon dioxide by a still surface of 1—8*N*-sodium hydroxide solution at about 20° has been obtained from the rate of change of the partial pressure of the dioxide. When the concentration of the solution is 1—3N, the absorption velocity is proportional to the partial pressure of the gas, which is expressed as follows: $-\Delta m/\Delta t=kp$, where $-\Delta m$ is the quantity of the dioxide absorbed during time Δt, p the partial pressure of the gas, and k a constant depending only on the concentration of the solution. For 4—8N-solutions of sodium hydroxide, the absorption velocity increases rapidly, which is said to be due to the auto-catalytic action of carbon dioxide which exists in the solution. The maximum absorption velocity at about 20° is obtained when the concentration of the solution is 3 or 4N. K. Kashima.

Capillarity. IX. K. Schultze (Kolloid-Z., 1928, 44, 120—127; cf. A., 1927, 625).—Theoretical. A series of symbols is proposed for use in dealing with capillary phenomena. E. S. Hedges.

Structure of surface films. X. Phenols and monoglycerides. N. K. Adam, W. A. Berry, and H. A. Turner (Proc. Roy. Soc., 1928, A, **117**, 532—541; cf. A., 1926, 1002).—Two series of compounds have been found in which the areas of the liquid expanded films, at no compression, differ widely from 48 Å.^{2}, and the hypothesis of coiled chains, previously advanced (*loc. cit.*), must be abandoned. The areas at no compression of the expanded liquid films of dodecylphenol, nonylphenol, α-monomyristin, and α-monopalmitin, respectively, are 37, 39, 70±3, and 70±3 Å.^{2} The possibilities of tilted molecules are discussed, but from the evidence available it is only possible to say that there is either a definite and uniform angle of tilt at each stage of compression of the expanded films, or a motion of the molecules through various angles of tilt. Langmuir's view that the chains hold the films together against a disruptive force exerted by the heads appears to be incorrect, since the heads seem to make a considerable contribution to the lateral attraction between molecules, both in the condensed and expanded states. The monoglycerides form condensed liquid films of the close-packed head variety, the area at no compression being 26·3±0·5 Å.^{2} Müller's suggestion (A., 1927, 503) that the chains are tilted is not incompatible with the theory of close-packed heads. The condensed film of dodecylphenol shows hysteresis, or "elastic after-working," on compression and decompression. L. L. Bircumshaw.

Films of oil inside a small bubble of gas in water. H. A. McTaggart (Trans. Roy. Soc. Canada, 1927, [iii], 21, III, 242—254).—By a method previously described (A., 1925, ii, 509) the behaviour of minute traces of different oils on the inner surface of air bubbles in water has been observed. The following liquids with a positive spreading coefficient against pure water, viz., benzene, chloroform, oleic acid, typewriter oil, xylol, aniseed, cedarwood, castor, olive, and lavender oils, form small globules in Brownian movement on the inner surface of the bubbles. When the bubble is absorbed these are dispersed in the water, but still retain their identity. After repeated formation of these bubbles an emulsion of oil in water is ultimately obtained. If a minute trace of thorium nitrate is present there are no globules showing Brownian movement, and no dispersion of oil in water takes place. As previously shown (Phil. Mag., 1924, [vi], 27, 297), the sign of the electric charge at the surface of the air bubble is annulled or reversed. Three liquids with negative spreading coefficients, carbon disulphide, acetylene bromide, and methylene iodide have been examined. They do not spread over the surface of the bubble, but form a pool round the edges of which globules in Brownian movement collect. This Brownian movement persists, even in the presence of thorium nitrate solution, but it may be reduced to some extent. The globules finally unite without giving an oil dispersion in water. M. S. Burr.

Laws governing molecular collisions at a surface reacting with the gas. A. Predvoditelev (Z. Physik, 1928, 46, 406—419)—Cantor (Ann. Physik, 1897, 62, 482) investigated the reaction between chlorine and a copper surface, with the view of testing the validity of the Maxwell distribution law for the gaseous pressure in a system involving collisions at a reactive surface. Cantor's results are regarded as erroneous. The question has been investigated theoretically and the equations have been tested by means of the hydration of anhydrous oxalic acid; the experimental work involved the use of a sensitive torsion balance and a microbalance; results in agreement with the theory were obtained. R. A. Morton.

Diffusion of gaseous mixtures through membranes. D. Alexejev and V. Matalski (J. Chim. phys., 1927, 24, 737—741).—Previous work on the diffusion of air through rubber and cellulose (Bull. Inst. Rech. biol. Univ. Perm, 1923, 2, 165) indicated that the solubility of the gas in the membrane is a determining factor in the coefficient of diffusion obtained. This has now been definitely demonstrated by using a membrane of water supported by cellulose which, when dry, was impervious to the gas. Atmospheric air was first dissolved by the water and then emitted in the vacuum on the other side of the membrane. In the same apparatus, which is described, the coefficients of diffusion of carbon dioxide, oxygen, acetylene, and nitrogen through a rubber membrane have been determined at different temperatures. The coefficient of diffusion $q=0{\cdot}4343\,.\,1/t\times v/PS\,.\log P/(P-p)$, where P is the external pressure of the gas, S the surface of the membrane, and t is the time during which the pressure on the other side of the membrane passes from 0 to p. The ratios of the diffusion coefficients are $Na : O_2 : C_2H_2 : CO_2 = 1 : 2{\cdot}29 : 9{\cdot}85 : 13{\cdot}7$, whilst Graham found $N_2 : O_2 : CO_2 = 1 : 2{\cdot}56 : 13{\cdot}59$. A study of the rates of diffusion of mixtures of these gases confirms the view that the velocity of diffusion of a gaseous mixture is equal to the sum of the velocities of diffusion of the components, in spite of considerable differences between these velocities and between the relative quantities of the components. M. S. Burr.

Effect of temperature on rate of osmosis. R. N. Traxler (J. Physical Chem., 1928, 32, 127—141).—The influence of temperature on the rate of establishment of equilibrium between pyridine and water separated by a thin rubber membrane and between an aqueous solution of sodium chloride

(0·5M) and water separated by a membrane of collodion has been investigated. For 10° rise of temperature in the first case, the rate increases 100% between 5° and 25°, 50% between 25° and 45°, 33% between 45° and 65°, and from 33 to 25% between 65° and 85°. In the second case, the initial rate of passage of sodium chloride through collodion is greater the higher the temperature, but at the end of 30 min. dialysis, the rate becomes practically uniform for all temperatures between 25° and 65°. The results obtained in the system pyridine–rubber–water are discussed in relation to the theory that water is an equilibrium mixture of hydrol and its polymerides.

L. S. Theobald.

Osmosis of ternary liquids. General considerations. I. F. A. H. Schreinemakers (Proc. K. Akad. Wetensch. Amsterdam, 1927, **30**, 761—768).—The osmosis occurring with membranes permeable to the solvent and to each of two solutes contained in it has been examined. The theory of the process is discussed, with graphical illustrations. Experimental measurements on the progress of osmosis necessitate the removal of small quantities of liquid for analysis from time to time, and it is shown that with appropriate sampling the theoretical and experimental osmosis paths should be nearly coincident.

L. F. Gilbert.

Permeability of artificial colloidal membranes. I. Action of acid-base swelling on the permeability of gelatin and agar membranes. K. J. Anselmino (Biochem. Z., 1928, **192**, 390—425).—Increased swelling of gelatin membranes, brought about by change of $p_{\rm H}$, results in an increase of permeability to dextrose and surface-inactive non-electrolytes, the minimum permeability being in the neighbourhood of the isoelectric point. The swelling and permeability curves are similar. The absolute increase in permeability is, however, compensated for by increase in thickness. If a series of membranes is used such that all have the same thickness when swelling at the respective $p_{\rm H}$ values is completed, an apparent maximum permeability is obtained at the isoelectric point. From diffusion experiments it is inferred that the greater part of the water absorbed during swelling by gelatin is bound in such a way that it can no longer serve as a diffusion medium. The diffusion of a number of acid and basic dyes through gelatin and agar membranes at different $p_{\rm H}$ values has been investigated, the results being summarised in the form of curves.

P. W. Clutterbuck.

Cellulose nitrate membranes of graded permeability. H. F. Pierce (J. Biol. Chem., 1927, **75**, 795—815).—The conditions affecting the permeability of collodion membranes are discussed. The preparation of such membranes of reproducible permeability is described (*a*) by a method involving the drying of the membrane for definite times under constant physical conditions and (*b*) by complete evaporation of solutions of collodion in alcohol and ether to which varying amounts of ethylene glycol have been added.

C. H. Harington.

Solution volume of a solute in liquid mixtures. G. J. Burrows (J. Proc. Roy. Soc. New South Wales, 1926, **60**, 197—207).—The specific solution volume of acetamide in solution in a mixture of water and acetone is greater than it is in either solvent alone, and the same is true for carbamide dissolved in a mixture of methyl alcohol and water. Since in both cases the formation of the solvent mixture from its components is accompanied by a considerable diminution in volume, it might appear that the apparent solution volume of a solute is determined by the amount of contraction which the solvent can undergo, *i.e.*, its compressibility, the addition of a third substance to a binary solvent mixture which shows the maximum contraction having no effect on the volume. It is not possible, however, to give a complete explanation of the volume changes on this basis. The density of solutions of methyl alcohol and of pyridine in water, acetone, and a mixture of the two has also been measured, the specific contractions for solute in solvent being found to pass through a maximum value, whilst the quotient of the total contraction by the total volume of the three components decreases regularly with the amount of solute added. The specific volume–composition curve of methyl alcohol–acetone mixtures and pyridine–water mixtures shows a minimum, but with methyl alcohol–water mixtures the maximum divergence of the curve from a straight line is not large enough to appear as a minimum on the curve. No satisfactory explanation of these various volume effects can be given, either on the assumption that decreases in volume are a consequence of closer packing resulting from the admixture of molecules of different sizes or on the basis of changes in the molecular complexity of the solvent.

R. Cuthill.

Ebullioscopic determination of the molecular state of resorcinol in aqueous solutions of sodium chloride. F. Bourion and E. Rouyer (Compt. rend., 1928, **186**, 82—84).—The authors' experiments (A., 1927, 515) are extended to solutions of resorcinol in 0·5M- and 1·225M-solutions of sodium chloride. In both cases there is evidence of an equilibrium between simple and double or triple molecules of resorcinol. Association is greater in sodium chloride than in potassium chloride solutions. The results obtained are in disagreement with the authors' view that aqueous solutions of alkali chlorides containing resorcinol should have ebullioscopic properties similar to those of water, but the deviation may be explained by the fixation of water on the salt either in the form of ions or of complete molecules.

J. Grant.

Viscosity and hydration. II. S. Liepatov (J. Russ. Phys. Chem. Soc., 1927, **59**, 465—476).—See A., 1927, 413.

Variation in rotation and conductivity of certain sugars in aqueous solution with and without boric acid. I. R. Verschuur (Rec. trav. chim., 1928, **47**, 123—152).—According to Böeseken and Couvert (A., 1921, i, 497), the rise in specific rotation shown by certain sugars in the presence of boric acid is always accompanied by a marked increase in electrical conductivity. It is probable that there is a particular configuration of the terminal hydrogen atoms and hydroxyl groups which favours the formation of compounds with boric acid. Most sugars, on dissolution in water, undergo a transformation which can be followed with the polarimeter, and is due to the transition from the α- to the β-form, or the reverse, until equilibrium is attained. Such a change may involve an increase or a decrease in the power to combine with boric acid, and hence a corresponding change in conductivity. The behaviour of α- and β-lactose in solution, in the presence and absence respectively of boric acid, has been examined. The effect of boric acid on the rate of change of rotation of both forms is practically negligible. Although, from the structure of lactose, which resembles that of dextrose already examined by Böeseken (*loc. cit.*), an increase in the equilibrium value of the conductivity of the sugar solution, apart from that due to boric acid alone, might be expected, there is, on the contrary, a slight decrease. This suggests that the behaviour of lactose is due to the galactose, and not to the dextrose portion of the molecule. In addition, the equilibrium values for the two forms are not identical. The conductivity of α-lactose alone, after dissolution, first increases and then decreases to the equilibrium point, but in the presence of boric acid there is a continuous decrease. The conductivity of β-lactose alone remains constant at first and then decreases. In the presence of boric acid it increases continuously. In no case is the change unimolecular. The presence of a minute trace of impurity greatly affects the result. Experiments have been made at 12·9°, 15·5°, 20·0°, and 25°. A few experiments have been carried out with melibiose. In this case also there appears to be no increase in conductivity in the presence of boric acid. Methods for the preparation of pure α- and β-lactose are given.

M. S. Burr.

Aqueous solutions of sodium silicates. VIII. General summary and theory of constitution. Sodium silicates as colloidal electrolytes. R. W. Harman (J. Physical Chem., 1928, 32, 44—60; cf. A., 1927, 519; Cann and Gilmore, this vol., 243).—The results and conclusions of preceding papers are summarised. The data previously presented are correlated and the constitution and behaviour of aqueous solutions of sodium silicate explained. The only definite salts are those represented by Na_2SiO_3 and $NaHSiO_3$, and their hydrolysis and ionisation are in agreement with the various measurements made. Above the ratio $Na_2O : SiO_2 = 1 : 2$, colloidal silica is in evidence and its proportion increases with concentration and with the ratio $SiO_2 : Na_2O$. In dilute solutions of ratio $Na_2O : SiO_2$ greater than 1 : 2, crystalloidal, uncharged silica, probably metasilicic acid, occurs, and these solutions show properties characteristic of colloidal electrolytes with a micelle of complex composition (cf. A., 1927, 415). Silicic acid is an acid stronger than is usually supposed (cf. A., 1927, 519).

L. S. Theobald.

Blue colour of the cuprammonium complex. S. S. Bhatnagar, D. N. Goyle, and M. Prasad (Kolloid-Z., 1928, 44, 79—82).—The deep blue colour of ammoniacal solutions of cupric salts is believed to be due mainly to the presence of copper hydroxide in colloidal solution. The dissolution by excess of reagent of the greenish precipitate first obtained on adding ammonia to a solution of a cupric salt is analogous to the peptisation of the similar precipitate obtained when sodium hydroxide is added to a copper salt solution in presence of sugar, gum arabic, etc. Further evidence was sought by comparing the physical properties of a cuprammonium sulphate solution with those of a sol of cupric hydroxide prepared by electrolysing a potassium chloride solution with a copper anode in presence of 1·5% of gelatin. The absorption spectra of the two solutions were examined and found to be similar, and a similar behaviour was also observed in cataphoretic experiments, both solutions depositing a greenish precipitate on the anode. On dialysis, no molecularly disperse cuprammonium compound could be found in the outer liquid, but a cuprammonium sulphate solution deposited a greenish precipitate.

E. S. Hedges.

Preparation of readily reproducible red gold sols by means of aqueous extracts of flowers. N. von Weimarn (Kolloid-Z., 1928, 44, 41—42).—Extracts of a number of flowers (bean, pink, azalea, peony, rose, chrysanthemum) were prepared by boiling the washed petals with water and passing the infusion through a hard filter. Red gold sols of high dispersity were obtained in a few seconds when these extracts were boiled with a dilute solution of chloroauric acid. The colours of the sols produced are characteristic for each extract and are quite reproducible if the same manipulation is followed.

E. S. Hedges.

Preparation of red gold sols by reduction with extracts of fresh leaves and plants. E. Iwase (Kolloid-Z., 1928, 44, 42—43).—Easily reproducible gold sols of a ruby colour have been prepared by adding the aqueous extracts of leaves to a boiling dilute solution of chloroauric acid. The extracts were prepared by cutting up the leaves (cherry, pine, maple, bamboo, and camellia), boiling in water, and passing through a hard filter. The most stable sols were those prepared from the camellia extract.

E. S. Hedges.

Preparation of colloidal gold solutions. Detection and determination of small amounts of gold. D. Nider (Kolloid-Z., 1928, 44, 139—140).—Sols of colloidal gold may be prepared rapidly by reduction of an alkaline gold salt by means of a solution of mercuric iodide in excess of potassium iodide. The colour of the sol produced depends on the concentration of the solutions, but red sols are formed if the gold solution contains less than 0·0002 g. of gold per 10 c.c. The method can be applied to the gravimetric determination of small quantities of gold by precipitating the gold by addition of hydrochloric acid and warming at 80°, filtering, and weighing. The results are compared with those of other methods. A colorimetric method of determining gold in small quantities is also devised, depending on the colour of the sol produced. Examination of the gold precipitates showed that, as long as an excess of potassium iodide is used, the precipitate contains no mercury.

E. S. Hedges.

"Solid-phase" rule in the production of coarsely disperse systems. Wo. Ostwald, W. Steinbach, and R. Köhler (Kolloid-Z., 1927, 43, 227—232).—The rule that in the direct dispersion of a substance to form a colloidal system the amount of substance peptised at first increases, passes through a maximum, and subsequently decreases with the amount of the solid phase present also holds for the production of coarsely disperse suspensions and emulsions. Results in accordance with the rule were obtained in the emulsification of olive oil and water (with or without the addition of an emulsifier) and in the stabilisation of suspensions of charcoal by picric acid, aniline, and pyridine. It is shown that picric acid not only has a stabilising effect on a suspension of charcoal, but also causes partial dispersion.

E. S. HEDGES.

" Solid-phase " rule. WO. OSTWALD (Kolloid-Z., 1927, **43**, 249—267).—An attempt is made to classify the various types of peptisation under the following headings: adsorption-peptisation (*e.g.*, carbon in picric acid), dissolution-peptisation (metal hydroxides in acids), peptisation of swelling substances (gelatin), spontaneous colloidal dissolution (colloidal dyes), peptisation with chemical reaction (formation of basic bismuth nitrate sol by hydrolysis of the neutral salt). The " solid-phase " rule, according to which the amount of peptised colloid is not independent of the amount of solid phase present, can be explained by the principles of adsorption. If the amount of solid phase is small, adsorption is great and the substance tends to be precipitated; on the other hand, with a large excess of solid phase adsorption is so small that little colloid-chemical effect is produced. Consequently, peptisation is greatest for medium amounts of the solid phase. This view explains why the solid-phase rule applies also to the production of coarse suspensions and emulsions.

E. S. HEDGES.

Ultramicroscopical method for determining the charge on colloid particles. P. TUORILA (Kolloid-Z., 1928, **44**, 11—22).—A direct method of determining quantitatively the velocity of migration of colloid particles under an electric potential gradient is described. The measurements were carried out with the help of a slit ultramicroscope, which is more serviceable for this purpose than the cardioid and paraboloid ultramicroscopes which have been employed formerly. A special type of cuvette for the work is described. The variations in the observed velocities of migration can be expressed by Gauss' error distribution curve. The use of relatively thick cells (3—4 mm.) is recommended, and it is shown experimentally that the formula of von Smoluchowski for the electro-endosmotic velocity of the liquid stream in parallelepipedal cells is valid for the cuvette used. An open type of cell is described, which can be refilled repeatedly during the observations, thus obviating the disturbing effects of degradation products due to the electrolysis. This permits a sufficient number of observations to be made to represent the true cataphoretic velocity of the colloid particles.

E. S. HEDGES.

Nephelometric investigation of starch sols. Nephelometric law of dilution. F. H. RITTER (Biochem. Z., 1928, **192**, 337—350).—A method is described for the preparation of starch sols of high dispersion for nephelometric purposes. With these solutions, deviations from the Kleinmann rule follow a law analogous to the so-called nephelometric law of dilution, suggesting that deviations are due to changes in the particles during dilution.

P. W. CLUTTERBUCK.

Thermodynamics of dispersed systems. A. MARCH (Ann. Physik, 1927, [iv], **84**, 605—623).—From a thermodynamic analysis of dispersed systems it is shown that for particles of radius less than 10^{-7} cm. the degree of dispersion decreases with increasing concentration and increases with rise of temperature, and that the conditions governing the stability of such systems are not to be sought in the thermal agitation nor in the electrical charge of the particles.

R. W. LUNT.

Hydrodynamics of systems of variable viscosity. II. Streaming in the capillary. M. REINER and R. RIVLIN (Kolloid-Z., 1928, **44**, 9—10; cf. A., 1927, 1138).—The following equation for the resistance value of the capillary viscosimeter is derived from the specialised Einstein–Hatschek formula for the viscosity of a sol: $w=(\eta_0-\eta_\infty)e^{-0\cdot4c_1Rp/\eta_0l}+\eta_\infty$, where η_0 and η_∞ are respectively the coefficients of viscosity of the sol at rest and under extreme shearing, R is the inner radius of the capillary, l its length, p the driving pressure, and c_1 is a constant for the sol. E. S. HEDGES.

Complete solutions of Fourier's partial differential equation for given surface conditions, and application to colloid-chemical problems. E. L. LEDERER (Kolloid-Z., 1928, **44**, 108—120).—Mathematical. The equation is applied to the conductivity of heat, diffusion, swelling, and drying.

E. S. HEDGES.

Flocculation produced by mixing two colloidal solutions having particles with opposite signs. A. BOUTARIC and (MLLE.) M. DUPIN (Bull. Soc. chim., 1928, [iv], **43**, 44—48).—Experiments in which ferric hydroxide sols of varying concentration were added to an arsenious sulphide sol of fixed concentration and *vice versa* show that precipitation occurs only when the concentration of the added sol lies between certain limits. These limits are dependent on a number of factors, *e.g.*, concentration of the sol concerned, duration of previous dialysis, particle size, presence of foreign substances. The stability of each sol is, however, diminished on addition of the other in quantity insufficient to cause actual precipitation. Comparison of the velocity of cataphoresis v_0 of an arsenious sulphide sol with the velocity v of the same sol containing ferric hydroxide shows that the value of v/v_0 decreases with increasing concentration of ferric hydroxide. In the converse case the variation of v/v_0 is not so pronounced. J. S. CARTER.

Relations between hydration and stability of a sol and the anomalous coagulating influence of fluorine ions on some hydrosols. S. GHOSH and N. R. DHAR (Kolloid-Z., 1928, **44**, 149—156).—Hydrosols of cerium hydroxide, thorium hydroxide, ferric hydroxide, and stannic hydroxide prepared at the ordinary temperature were found to be more strongly hydrated than those prepared at the b. p. The coagulating power of chlorine, bromine, and iodine ions was identical for both sets of sols in the case of cerium hydroxide and thorium hydroxide. The coagulating effect of these univalent ions was, however, greater for a ferric hydroxide sol prepared in the hot way than for such a sol prepared in the cold. For stannic hydroxide sol, the coagulating power of lithium, sodium, potassium, rubidium, and cæsium ions was the same for the sols prepared at the different temperatures. The fluorine ion is 100 times as powerful as the other halogen ions, being very close to the sulphate ion in this respect, and it is suggested that it acts as a bivalent ion F_2''. The cerium hydroxide sol prepared in the cold is of a lyophilic nature, but shows no ion-antagonism, and objections are therefore raised against the explanation of ion-antagonism given by Freundlich and Scholz (A., 1922, ii, 828). The difference between the coagulating powers of ions with the same valency cannot be related to the degree of hydration of the colloid particles or of the coagulating ions, but a high coagulating power may be due to combination of the coagulating ion with an ion already present, which is necessary for the stability of the sol, to form a non-ionised compound. E. S. Hedges.

Flocculation of agar sols by salt mixtures. E. H. Büchner and D. Kleijn (Proc. K. Akad. Wetensch. Amsterdam, 1927, 30, 740—742).—The flocculating power of binary solutions of sodium sulphate and other salts has been determined. The resultant effect follows the simple mixture rule in the case of mixtures of disodium hydrogen phosphate, sodium ferrocyanide, citrate, tartrate, thiosulphate, tungstate, molybdate, formate, acetate, and bromate, which all have positive flocculating power. For mixed solutions of sodium sulphate with sodium chlorate, bromide, iodide, dichromate, nitrate, and nitrite which appear to have negative flocculating power at most concentrations, the mixture rule is also applicable, except in the case of very small concentrations of sodium dichromate, bromide, and iodide, which act positively. Sodium chloride has little influence. These results are correlated with the opposing effects of salts on the swelling, gelatinisation, and viscosity of colloids (cf. A., 1927, 825). L. F. Gilbert.

Dependence of the velocity of coagulation of sols of ferric hydroxide and sulphur on the concentration of the sol and of the coagulator. A. Fodor and R. Rivlin (Kolloid-Z., 1928, 44, 69—76).—The course of the coagulation of sols of ferric hydroxide and sulphur on addition of potassium chloride was followed continuously in an "extinctiometer," which records automatically and continuously the degree of turbidity of the sol. In the precipitation of ferric hydroxide sols by means of potassium chloride, the turbidity increases with time, at first linearly and then more rapidly, then reaches a constant value, and later falls as precipitation commences. The angle which the first, linear portion of the curve makes with the time axis was taken as a measure of the velocity of coagulation. It was found that, with sols of ferric hydroxide and of sulphur, the velocity of coagulation increases greatly with the concentration of the coagulator, the effect being greater for increasing concentrations of the sol. It is considered that with progressive dilution of a strongly solvated sol, the effect of the increase in dispersity of the solid phase becomes evident, but not the change in the number of impacts per unit time, for the particles are *a priori* protected by the sheath of molecules of solvate. E. S. Hedges.

Coagulation of hæmoglobin in presence of alcohols. III. B. Jirgensons (Kolloid-Z., 1928, 44, 76—79).—In the coagulation of hæmoglobin by potassium chloride or magnesium chloride, the presence of ethylene glycol has a sensitising influence, whilst glycerol has a stabilising effect. Measurements were made of the viscosity of water–alcohol mixtures in presence of potassium chloride and of magnesium chloride, and the viscosity of mixtures of coagulating hæmoglobin and alcohol was also measured. Hæmoglobin is more readily brought into solution by high concentrations of propyl alcohol and magnesium chloride than by low concentrations of these reagents. It is concluded that the general sensitising effect of alcohols in small concentrations is due to dehydration, but the stabilising effect observed at higher concentrations is due to the peptising influence of the salt present. This takes effect in the presence of alcohols which can increase the viscosity of the dispersion medium and lower the dielectric constant. E. S. Hedges.

"Acclimatisation phenomenon" in the coagulation of arsenious sulphide sols by barium chloride. W. Krestinskaja and W. Jakovleva (Kolloid-Z., 1928, 44, 141—148).—When sols of arsenious sulphide are coagulated by addition of barium chloride solution, the amount of barium chloride required depends on the rate at which it is added, more being required if the electrolyte is added in small quantities at long intervals. This "acclimatisation phenomenon" has been studied and the experimental results suggest the following explanation. When barium chloride solution is added gradually, the barium ions react with the hydrolysis products of arsenious sulphide, so quickening the hydrolysis. The barium sulphide produced is adsorbed by the colloid, and consequently the barium-ion concentration of the solution is diminished, so raising the critical amount of barium chloride required for coagulation. The explanation given is supported by the fact that hydrochloric acid, which cannot promote the hydrolysis of arsenious sulphide, does not show the acclimatisation phenomenon. E. S. Hedges.

Dispersing action of concentrated aqueous solutions of lithium thiocyanate and lithium iodide. P. P. von Weimarn (Kolloid-Z., 1928, 44, 39).—In regard to the dispersion of natural silk in concentrated solutions of very soluble salts, the author's original observations (A., 1926, 576) led to the conclusion that lithium thiocyanate has a stronger dispersing effect than lithium iodide. This was later corrected to the reverse order. Re-investigation has shown that the order of influence depends on the conditions of preparation of the lithium thiocyanate solution. The dispersing power of lithium thiocyanate is less than that of lithium iodide if the solution has been heated at a temperature of 150° or higher, and is greater if the thiocyanate solution has been concentrated under reduced pressure at 110° or under. At high temperatures a solution of lithium thiocyanate may lose the property of dispersing silk in the cold. This effect may be due to the formation of an oxidation product. E. S. Hedges.

Time effect of the dispersion medium in spontaneous colloidal dissolution. P. P. von Weimarn (Kolloid-Z., 1928, **44**, 39—40).—Natural silk dissolves completely at the ordinary temperature in saturated solutions of manganese thiocyanate or calcium thiocyanate to give a 2% solution if sufficient time (about 5 weeks) is allowed. This time effect makes it difficult to estimate the tendency of a substance towards spontaneous dispersion. The case is analogous to the extremely slow dissolution of magnesium sulphate monohydrate and of anhydrous chromic chloride in cold water. It is considered that hydration precedes dissolution. E. S. Hedges.

Kinetics of peptisation. A. von Buzágh (Kolloid-Z., 1928, **44**, 156—162).—The velocity of peptisation of ferric hydroxide gel by hydrochloric acid, of humic acid by sodium hydroxide, and of Prussian blue by potassium oxalate has been measured. The time curves obtained are autocatalytic in nature and can be expressed by the relation $dx/dt=k(1+cx)(1-x)$, where x is the amount peptised in the time t, c and k are constants, and the total amount of peptisation is made equal to 1. With increasing concentration of the peptising agent, the value of k increases and that of c decreases rapidly, so that at higher concentrations of the peptiser the course of the peptisation can be represented by the simple form $dx/dt=k(1-x)$. A study was made also of the change in the viscosity of the system during peptisation. The viscosity first rises to a maximum, then falls suddenly, and approaches a limiting value asymptotically. The maximum is reached earlier the more concentrated the solution of the peptising agent. E. S. Hedges.

Proteins and the lyotropic series. R. A. Gortner, W. F. Hoffman, and W. B. Sinclair (Kolloid-Z., 1928, **44**, 97—108).—A study has been made of the peptising influence of 21 inorganic salt solutions on wheat flour, the salt solutions being used at concentrations of $0{\cdot}5N$ to $2{\cdot}0N$. The results show that the effect of the anion increases according to the following series: $F<SO_4<Cl<\text{tartrate}<Br<I$, and that the peptising effect of the cation increases thus: $Na<K<Li<Ba<Sr<Mg<Ca$. Differences in hydrogen-ion concentration are not responsible for these results. With increasing concentration of the salt solution, the peptising power of the alkali halides decreases, but with the alkaline-earth halides the peptising effect increases with concentration, especially in the case of magnesium chloride and bromide, strontium chloride, and calcium bromide solutions. The peptisation is not due to hydrolysis, for the peptised material is no richer in amino- or carboxyl groups. The definition of "globulin" as a protein which is soluble in dilute solutions of salts of strong acids and bases is questioned, since equivalent solutions of different salts dissolve very different amounts of protein from wheat flour. E. S. Hedges.

Influence of volume of solution on degree of swelling of disperse systems. P. N. Pavlov (Kolloid-Z., 1928, **44**, 134—139).—Experiments were made on the swelling of hide in hydrochloric acid, sodium hydroxide, and some tanning agents, ferric hydroxide in sodium hydroxide, and animal charcoal in acetic acid. In all cases, stronger swelling took place when a large volume of solution was used than in presence of a small volume. The behaviour of ferric hydroxide varied according to its method of preparation, some forms not showing this effect. It is considered that the swelling is brought about by the attraction of the dipolar water molecules by the ions in the surface layer of the solid phase, and an explanation of the observed phenomena is advanced on these lines. E. S. Hedges.

Relations of the solid phase in the swelling and dissolution of gelatin. Wo. Ostwald and R. Köhler (Kolloid-Z., 1927, 43, 233—240).—The swelling of gelatin is influenced by the ratio of the solid phase to the volume of liquid, the relative swelling falling as this ratio increases. The numerical values obtained by Küntzel (A., 1927, 19) for the swelling of gelatin in hydrochloric acid are plotted and lead to a quantitative statement of this relation. This takes the form $q/m=kv^n$, where q is the degree of swelling, m the amount of gelatin, v the relative amount of liquid, and k and n are constants. It is shown that these results are not due to the liquid being impoverished of hydrogen ions through the presence of large amounts of the solid phase. Also, similar effects were observed with three different types of gelatin in pure water. The spontaneous dissolution of gelatin in pure water increases with increasing amount of the solid phase. It is possible to obtain in this way at 20° a weakly viscous, non-gelatinising solution containing 2·5%. The influence of the amount of the solid phase on both the relative swelling and the spontaneous dissolution of gelatin is markedly less at lower temperatures. The curves are similar to those obtained by von Neuenstein (cf. B., 1927, 327) for the spontaneous dissolution of cellulose derivatives, and it is therefore considered that gelatin is a mixture of "state-isomerides" having different spontaneous dissolution tendencies. E. S. Hedges.

Adsorption and swelling of cellulose in sodium hydroxide solutions. P. N. Pavlov (Kolloid-Z., 1928, **44**, 44—63).—In order to examine the nature of the equilibrium between cellulose and sodium hydroxide, the adsorption and swelling of ash-free filter paper were measured in solutions of sodium hydroxide, particularly as regards the influence of the volume of solution and amount of cellulose on the adsorption isotherm. It was found that the coefficient of adsorption of sodium hydroxide by cellulose is independent of the volume of the solution or the amount of cellulose. The isotherm of true adsorption has to be differentiated from that of apparent adsorption. The swelling isotherms exhibit a maximum and a minimum. Simultaneous measurements of swelling and adsorption isotherms were undertaken. At the swelling maximum, the true adsorption isotherm shows the taking up of 1 molecule of sodium hydroxide for each molecule of cellulose.

The apparent adsorption isotherm cannot be used for ascertaining the chemical relations between cellulose and sodium hydroxide. It is further shown from the true adsorption isotherm that the compounds $C_6H_9O_5Na$, $C_6H_8O_5Na_2$, $C_6H_7O_5Na_3$, and $C_6H_6O_5Na_4$ exist in a state of electrolytic dissociation in sodium hydroxide solutions of various concentrations. The relations between cellulose and sodium hydroxide do not follow the laws of heterogeneous chemical equilibria. The reaction takes place on the surface of ultramicro-crystals of the solid phase, and the active mass of the molecules on the surface of the insoluble phase is a variable value. A thermodynamic theory is developed for surface chemical equilibria in reactions of combination, hydrolysis, and double decomposition in systems where the solid phase has a variable active mass. A theory of swelling in relation to the electrical double layer on the surface of the micelles is put forward which explains the effect of the volume of the swelling medium on the degree of swelling. E. S. Hedges.

Electrical phenomena in colloidal solutions. G. Génin (Rev. gén. Colloid., 1927, **5**, 691—696, 723—729).

Diffusion of methylene-blue in gelatin gels. S. G. Mokruschin (Kolloid-Z., 1928, **44**, 32—38).—When a solution of methylene-blue is allowed to diffuse into a gelatin gel for a long period of time, the following phenomena occur. Normal diffusion takes place during the first 24 hrs. During the following 24 hrs. a marked increase in concentration of the dye occurs at the boundary of the gel and the solution. After 5 days, the boundary becomes quite colourless, whilst the colour of the liquid layer above has become lighter. The extent of the colourless zone increases with time, and the colour of the upper liquid diminishes in intensity until, after 50 days, the whole is colourless. Simultaneously, the gelatin gel shrinks. It is considered that the blank space at the boundary of the gel is analogous to the spaces between the bands of precipitate in the Liesegang phenomenon, and an explanation is advanced which is based on Ostwald's "diffusion wave" theory of Liesegang rings. Two independent processes have to be considered: adsorption of methylene-blue by the gelatin, and the decomposition of the dye. In this case, the phenomenon is due to the interference of two waves of diffusion set up by the methylene-blue and the more highly dispersed of the gelatin particles, respectively. This latter process is believed to account for the phenomenon of syneresis.

E. S. Hedges.

Thixotropy of gelatin solution. H. Freundlich and H. A. Abramson (Z. physikal. Chem., 1928, **131**, 278—284).—Although gelatin gels exhibit thixotropy, the phenomenon cannot be observed easily owing to the great velocity of the reverse transformation, but is rendered more apparent by the considerable decrease of elasticity which is found after a highly elastic gel has passed through a capillary tube. The motion of coarse particles of, *e.g.*, quartz, in a gel undergoing cataphoresis indicates that the cataphoretic movement is also capable of producing thixotropic softening of the gel. H. F. Gillbe.

Viscosity and hydration. Fluids separated by syneresis and the theory of syneresis. S. Liepatov (Biochem. Z., 1928, **192**, 91—104).—The solutions formed from dried gelatin, agar, or geranin vary with the conditions of temperature, medium, and content of electrolytes. When a solution of geranin at 50° is cooled to 18°, a sol or gel is obtained according to the concentration. Such a system consists of a saturated solution in the molecular or ionic form and hydrated colloidal particles. Phase separation does not coincide with gelatinisation, but is present already in sol and gel. Such separation increases gradually and leads to syneresis. The concentrated colloidal phase may contain a larger amount of water than the dilute phase and the latter may not exist at all, the whole of the water being necessary for hydration. During gelatinisation, the particles which separate from the saturated solution gradually coalesce and precipitate as hydrated complexes, the velocity of the process depending on the distance between the particles, being greater the greater the gel concentration. A 0·4% gel shows syneresis after 30 days and a 0·8% gel after 2 days.

P. W. Clutterbuck.

Measurement of cataphoresis in suspensoids. H. R. Kruyt and P. C. van der Willigen (Kolloid-Z., 1928, **44**, 22—32).—Macroscopical methods for the determination of the cataphoretic velocity of colloid particles are discussed and the various sources of error are pointed out, both for sols of high electrolyte content and for sols poor in electrolytes. It is essential to have a layer of the intermicellar liquid covering the sol. In the ordinary method of determination with the Burton apparatus, electrolytes collect at the electrodes and the potential gradient is therefore not even throughout the tube. Further, the electrolytes generally fall to the boundary of the sol, where they may undergo chemical reaction or cause other disturbances. An improved form of Burton's apparatus is described in which these and other difficulties are overcome. Some microscopical methods are discussed, and a new type of cuvette, suitable for this work, is described. E. S. Hedges.

Thermotropism and constants of colpoids. A. L. Herrera (Atti R. Accad. Lincei, 1927, [vi], **6**, 131—137).—The amœboid forms, termed colpoids, obtained on addition of sodium hydroxide solution to a petroleum solution of olive oil (A., 1926, 244, 435) exhibit distinct positive thermotropism, owing to increased osmosis and to the enhanced intensity of the currents prevailing at the membrane and of the chemical reactions at the hotter side. The influence of lactose, gum arabic, and egg-albumin on the magnitudes and movements of the colpoids is described.

T. H. Pope.

Weigert effect as a more general characteristic of certain colloidal systems. I. S. Horiba and T. Kondo (Sexagint [Osaka celebration], Kyoto, 1927, 61—71).—The Weigert effect produced by the action of plane polarised light on a silver–gelatin gel has been studied, and the nature of the effect is discussed. H. F. Gillbe.

Weigert effect as a more general characteristic of certain colloidal systems. S. Horiba and T.

Kondo (Sexagint [Osaka celebration], Kyoto, 1927, 271—272; cf. preceding abstract). By washing gelatin with conductivity water until, after addition of silver nitrate solution to the sol, no Tyndall effect due to silver chloride could be observed, it was found that the formation of colloidal silver proceeds extremely slowly even when the gelatin–silver nitrate sol is exposed to sunlight; addition of a trace of tap-water accelerates the reduction enormously. This catalytic influence of the chloride ion furnishes one of the most sensitive reactions for its detection. Bromide and iodide ions act in a similar manner, but their influence is much smaller. H. F. Gillbe.

Constant of mass action. R. D. Kleeman (Phil. Mag., 1928, [vii], 5, 263—271).—Molecules are divided into two classes, those which do not dissociate on isolation termed "sepro-stable" molecules and those which dissociate on isolation termed "sepro-unstable" molecules. Sepro-stable molecules obey the classical gas law, whilst sepro-unstable molecules obey a gas law of the form $v=RT/p+\Sigma A_n/p_n$, where A_n is a function of T. On this hypothesis it is shown that the constant of mass action is not a constant but is a function of the volume of the reacting mixture, its temperature, and the masses of the elementary constituents. The thermodynamic deduction is supported by kinetic considerations.

A. E. Mitchell.

Osmotic pressures of concentrated solutions. W. D. Bancroft and H. L. Davis (J. Physical Chem., 1928, **32**, 1—43; cf. this vol., 14).—The following, equivalent expressions have been derived for the relation between vapour pressure and osmotic pressure: (*a*) $PV_m=RT\log_e p_0/p_1$ and (*b*) $PV_1=(RTN/n)\,.\log_e p_0/p_1$, where V_m is the volume in the solution of 1 g.-mol. of the solvent in the state of vapour, and V_1 is the volume in the solution of the solvent containing 1 g.-mol. of the solute. Osmotic pressures cannot be accurately represented by the equation $PV=RT$, but if V be defined as V_1, the data of Morse and Frazer show that the equation $PV_1=RT$ is more applicable than $PV=RT$, where V is the volume of the solution. The heat of dilution represents a work term (not yet evaluated), which invalidates any equation of this form, but for ideal solutions, $PV_1=RT$ holds with an error not greater than 5% when the solute is 10 mol.-% of the solution. From (*b*), and in so far as $PV_1=RT$ is valid, $n/N=\log p_0/p_1$ is a general equation for the calculation of mol. wt. Raoult's law and Henry's law are said to be essentially different. The objections to van 't Hoff's relation raised by other authors have rested on incorrect definitions of the contained terms, especially of V in the expression $PV=RT$. Further, it is shown that compressibility of the solvent is not a factor in measurements of osmotic pressure. Previous methods of finding the volumes of the components of a solution are discussed and it is shown that the specific volume of the solvent can be calculated from (*a*) rewritten as $V_g=RT(\log p_0/p_1)/PM$, where V_g is the volume of 1 g. in the solution and M is the mol. wt. of the solvent in the condition of vapour. The value of V_g for either component can be determined from density relationships, subject to a correction, probably insignificant for solutions of moderate concentration, for possible hydrates of varying composition, thus making possible a calculation of osmotic pressures from a knowledge of densities and partial pressures. The osmotic pressures of ideal solutions of benzene and toluene are calculated from (*a*) and (*b*) and these values are satisfactorily expressed by an equation of the van der Waals type.

L. S. Theobald.

Formation of complexes between substances dissolved in non-associated solvents. B. von Szyszkowski (Z. physikal. Chem., 1928, **131**, 175—188).—On account of hydration the solubility of compounds containing hydroxyl and carboxyl groups in a non-associated solvent is much greater when the latter is saturated with water. The partition coefficients of salicylic, benzoic, and *o*- and *m*-nitrobenzoic acids between water and benzene at 25° are 0·3575, 0·530, 1·71, and 0·590, respectively. The following solubilities in dry benzene and in benzene saturated with water have been measured: benzoic acid $8{\cdot}946\times10^{-1}$ and $9{\cdot}222\times10^{-1}$, salicylic acid $5{\cdot}616\times10^{-2}$ and $7{\cdot}370\times10^{-2}$, *o*-nitrobenzoic acid $1{\cdot}656\times10^{-2}$ and $2{\cdot}650\times10^{-2}$, *m*-nitrobenzoic acid $1{\cdot}073\times10^{-1}$ and $1{\cdot}359\times10^{-1}$, 3 : 5-dinitrobenzoic acid $4{\cdot}880\times10^{-3}$ and $8{\cdot}676\times10^{-3}$. The association and hydration coefficients of the five acids in benzene have been calculated. The simultaneous solubility in dry benzene of various pairs of these acids is about 50% greater than the sum of the separate solubilities, and the dissociation constants of the suggested complex acids have been calculated. Measurements of the simultaneous solubility of two, three, and four different acids in dry benzene and in benzene saturated with water indicate the existence of complexes containing up to five molecules. From partition and solubility data conclusions may be reached regarding hydration in the non-associated, but not in the associated, phase. H. F. Gillbe.

Polarity of substituents in the benzene nucleus. R. Kuhn and A. Wassermann (Helv. Chim. Acta, 1928, **11**, 3—30).—The dissociation constants in water or 50% methyl alcohol of benzoic acid, phenol, and aniline, and also of the *o*-, *m*-, and *p*-forms of dihydroxybenzene, hydroxybenzoic acid, aminophenol, chlorophenol, and chloroaniline, have been determined. Measurements were made by the hydrogen electrode or the quinhydrone electrode. In some cases the vacuum hydrogen electrode had to be employed (Kuhn and Zumstein, A., 1926, 513). It was not possible to use the hydrogen electrode for aniline and the chloroanilines, and the quinhydrone electrode could be employed only in very dilute solutions. Neither the quinhydrone electrode nor the hydrogen electrode in any form gave satisfactory results with nitroanilines. Conductivity measurements were made on these at comparable concentrations. According to Flürscheim (Chem. and Ind., 1925, **44**, 246), the general polarity effect of a substituting group may be deduced from the dissociation constants of the *p*- and *m*-substitution products by the formula $p=(K_m+K_p)/2K_u$, where K_m, K_p, and K_u are the dissociation constants of the *m*-, *p*-, and unsubstituted compounds, respectively. From the data obtained experimentally, and the data of Farmer and Warth for nitroanilines (J.C.S., 1904, 85, 1726) the effect of different substituents on the polarity of benzoic acid, phenol, and aniline has been calculated. In the polarity series for substituents in benzoic acid (cf. Flürscheim, *loc. cit.*), the electronegative action of the different groups diminishes in the order NO_2, CO_2H, Cl, OH, Me, and NH_2. The phenol and aniline series are almost identical. It is evident, however, that the polarity of an atom or atomic group is not, as has been stated (cf. Flürscheim, *loc. cit.*), a characteristic and constant quantity, but that it depends, to a very large extent, on the nature of the compound into which the group is introduced. The effect of the *o*-substituent is a steric one, and its value, s, may be deduced from the formula $s=(K_o+K_m)/(K_m+K_p)$, where K_o is the dissociation constant of the *o*-substituted compound. In no case is s less than 1, *i.e.*, in all the compounds studied, the effect of *o*-substitution has been to raise the acidity of the compound, whether in acids, phenols, or amines. It is further evident that the *o*-effect of any given group depends to a remarkable extent on the nature of the ionising compound, and the relative effects of the different groups are not the same in the three series. The results cannot be reconciled with the supposition that the influence exercised by *o*-substituents on the dissociation constant depends in any simple manner on their atomic or ionic radii. M. S. Burr.

Dissociation constants of *o*-halogenobenzoic acids. R. Kuhn and A. Wassermann (Helv. Chim. Acta, 1928, **11**, 31—44).—To determine the influence of the nature and position of the halogen on the affinity constants of aromatic compounds, the dissociation constants of *o*-, *m*-, and *p*-fluorobenzoic acids in water have been obtained and compared with the data of other investigators for the corresponding chlorobenzoic acids and the *o*- and *p*-bromo- and iodo-derivatives. The dissociation constants of all the monohalogen-substituted derivatives of benzoic acid have been determined in 50% methyl alcohol. The quinhydrone electrode was used and the solutions contained 0·12 g.-mol. of potassium chloride per litre, which prevented changes in the activity of the hydrogen ion through variations in the concentration of the acid and its salt. Within the limits of experimental error, the dissociation constant is practically unaffected by the nature of the halogen substituent. It depends, however, on position, *o*-, *m*-, and *p*-representing the order of diminishing dissociation constants. M. S. Burr.

Dissociation constants of phthalic acids. R. Kuhn and A. Wassermann (Helv. Chim. Acta, 1928, **11**, 44—50).—The second dissociation constant of terephthalic acid in water has been determined, using the quinhydrone electrode, and from this, and the data of earlier investigators, it is shown that the ratios of K_1 to K_2 for phthalic, *iso*phthalic, and terephthalic acids are, respectively, 320, 12, and 20. Determinations of the two dissociation constants of all three acids have been made in 50% methyl alcohol, and the ratios are 1000, 31, and 50, respectively. That is, in both solutions, the influence of the two groups on one another is greater in the *p*- than in the *m*-position. This is comparable with the behaviour of the phenylenediamines (Kuhn and Zumstein, A., 1926, 513) and is, perhaps, related to the position of the *p*-substituent at the end of a system of conjugated double linkings. In addition, the first dissociation constant of *iso*phthalic acid is greater than that of terephthalic acid. M. S. Burr.

Configuration of polymethylenedicarboxylic acids. I. Dissociation constants of *cyclo*hexanedicarboxylic acid. R. Kuhn and A. Wassermann (Helv. Chim. Acta, 1928, **11**, 50—70).—The two dissociation constants, K_1 and K_2, of the *cis*- and *trans*-forms of the *o*-, *m*-, and *p*-hexahydrophthalic acids have been determined in water and in 50% methyl alcohol. The extent of the influence of the two carboxyl groups on one another may be measured by the ratio K_1/K_2. The values for this ratio in water for the *o*-, *m*-, and *p*-*cis*-acids are 267, 23, and 22, and for the *trans*-acids 56, 26, and 17, respectively. In 50% methyl alcohol the values are 885, 38, and 36 for the *cis*-acids, and 85, 83, and 30 for the *trans*-acids, respectively. The regular decrease from the *o*- to the *p*-hexahydrophthalic acids appears to confirm the view that the smaller value obtained for the ratio K_1/K_2 for the *m*-compound in the phthalic acid series and the phenylenediamines is due to the conjugated double linkings of the benzene nucleus (cf. this vol., 231). The difference between the ratio for the *cis*-*m*- and the *cis*-*p*-acid is very small, being practically within the range of the experimental error. This is because, in the *cis*-compounds, owing to a screening effect of the rest of the molecule, the carboxyl groups are more independent of one another than corresponds with their relative positions in space. The *cis*-hexahydroterephthalic acid has a smaller value for K_2 than the *trans*-compound, corresponding with the difference between maleic and fumaric acids. The hydrogenated *iso*phthalic acids are the first example of *cis*-carboxyl groups which have a smaller influence on one another than the *trans*-carboxyl groups, and this difference is especially great in 50% methyl alcohol. This difference between the influence of the two solvents is greater than appears to correspond with the difference in dielectric constant and is observed also in the case of the other hexahydrophthalic acids, as well as *o*-phthalic acid. The data obtained are discussed with reference to the space models of Sachse. The same configuration cannot be given to *trans*-*o*-hexahydrophthalic acid as that deduced by Baeyer from anhydride formation unless the molecule of the *trans*-acid is not rigid. It is therefore not possible to reach conclusions as to configuration from the ability to form a ring. Similar considerations apply also to the configuration of the hydrogenated *iso*phthalic acids. The configuration of the hexahydrophthalic acids may, therefore, be best explained by the flexibility of the *cyclo*hexane residue, and by the tendency of the carboxyl groups to lie as far from one another as possible. M. S. Burr.

Conjugation relationships in naphthalene. R. Kuhn and A. Wassermann (Helv. Chim. Acta, 1928, **11**, 79—87).—The dissociation constants of the naphthylenediamines, except the second dissociation constants of the 1 : 4-, 1 : 8-, and 2 : 3-derivatives, which were too small to measure potentiometrically, have been determined (cf. this vol., 240). The greatest reciprocal action of the two amino-groups is observed for the 1 : 4-position. The 1 : 8-compound is about 50 times more basic than the 2 : 3-compound. Within the limits of experimental error, the ratio of the dissociation constants of the 1 : 5- and 2 : 7-compounds agree, whilst the reciprocal action between the 2- and 6-positions is double the former. The types of formulæ for benzene and naphthalene are discussed on the basis of these results. M. S. Burr.

Mol. wt. and association of chlorophyll in solution. N. Marinesco (Compt. rend., 1928, **186**, 315—318).—By means of the expression which is obtained by combining the diffusion and Einstein viscosity equations (A., 1927, 17) the mol. wt. of chlorophyll in solutions of acetone has been found to be 816. Its coefficient of association exceeds 5·6 for 0·1—0·3% solutions, and it is deposited from 3% solutions by centrifuging. In photochemical reactions involving the use of chlorophyll, dilute solutions should be used or the associated molecules de-activate one another by molecular induction, and the reactivity is not proportional to the amount of the activating light. The extraction of chlorophyll from leaves by acetone, followed by light petroleum and methyl alcohol, and adsorption on talc is described, and yields a mixture of α- and β-chlorophylls. J. Grant.

Behaviour of sodium and barium amalgam electrodes in solutions of amphoteric substances. P. L. Kirk and C. L. A. Schmidt (J. Biol. Chem., 1928, **76**, 115—136).—Measurements with sodium and barium amalgam electrodes indicate that the sodium and barium salts of glycine, aspartic acid, and glutamic acid behave as typical strong electrolytes. The curve obtained by plotting the square root of the ionic strength against the activity coefficient plus a constant is practically identical with that obtained with sodium chloride. Similarly, sodium caseinogenate behaves as a strong electrolyte, the caseinogen ion being univalent over the range of reaction investigated. Barium caseinogenate, however, behaves abnormally, owing to formation of complex ions.

C. R. Harington.

Theory of binary mixtures and its application to calculating the association degrees of liquids. T. Ishikawa (Sexagint [Osaka celebration], Kyoto, 1927, 103—141).—The volume change which occurs when two indifferent liquids are mixed isothermally at constant pressure has been investigated mathematically and a formula derived whereby, if the degree of association of one component be known, that of the other may be calculated. Consistent results are obtained when the method is applied to data in the literature. H. F. Gillbe.

Null point [absolute zero] **state.** W. Jazyna (Physikal. Z., 1927, **28**, 908—911).—Theoretical. The thermodynamical implications of a distinction between the "quasi-permanent" equilibrium state, corresponding with the expression $Q_{T_2}/Q_{T_1}=T_2/T_1$, and the "permanent" equilibrium state corresponding with $Q_T=ST$ are discussed. R. A. Morton.

Entropy of a perfect gas at 0° Abs. N. von Kolosovski (J. Chim. phys., 1927, **24**, 621—622).—Theoretical. Planck's demonstration that the entropy of an ideal, not degenerated gas approaches infinity at 0° Abs., is disputed. Experimentally it is known that the vapour-pressure curve of a liquid touches the axis of temperature near 0° Abs., and it follows, using the Clapeyron equation, that λ, λ/T, and λ/T^2 have the limiting value 0 at $T=0$ (λ is the latent heat of vaporisation). Using Nernst's heat theorem and the relation $S_g-S_l=\lambda/T$, where S_g and S_l are the entropies of the gas and liquid, respectively, the result is obtained that the entropy of the gas vanishes at 0° Abs. It follows also that the specific heat of the saturated vapour and the specific heat at constant pressure become identical at this temperature.

G. A. Elliott.

Pseudo-constant of integration of Kirchhoff's formula. N. von Kolosovski (J. Chim. phys., 1927, **24**, 723—726).—Theoretical. An apparent discrepancy between the limiting values for λ at absolute zero, as deduced from the Clapeyron–Clausius equation (A., 1927, 936) and Kirchhoff's formula, respectively (cf. Bennewitz, A., 1925, ii, 97), is explained. M. S. Burr.

Thermodynamics of mixtures. V. Fischer (Z. Physik, 1928, **46**, 427—443).—A general mathematical treatment is given for various equilibrium states in two-component systems. The equations deduced are applied to gold–copper alloys. Mixtures containing three constituents are also discussed.

R. A. Morton.

Theory of the Ludwig–Soret effect. M. Ballay (Compt. rend., 1928, **186**, 232—234; cf. A., 1926, 1199).—A thermodynamical expression for the available energy of an unequally-heated solution in terms of the molecular heat of dilution and vapour pressure of the dissolved substance is obtained on the assumption that the phenomena involved are reversible, and this is shown to correspond with a series of curves of anisothermal equilibria. The expression provides an explanation of the Ludwig–Soret effect more in accordance with experimental facts than that which is based on the theory of osmosis.

J. Grant.

Activity and free energy of dilution of some salts of cadmium. F. H. Getman (J. Physical Chem., 1928, **32**, 91—102; cf. Horsch, A., 1920, ii, 8).—The activity coefficients of the chloride, bromide, and sulphate of cadmium at concentrations ranging from 0·001*M* to saturation have been calculated from the *E.M.F.* of the cells $Cd|CdCl_2(M)|Hg_2Cl_2|Hg$, $Cd|CdBr_2(M)|Hg_2Br_2|Hg$, $Cd|CdSO_4(M)|Hg_2SO_4|Hg$, measured at 25°, and compared with the corresponding values calculated from conductivity and f.-p. data. The free energy of dilution for each salt has also been calculated. The heats of formation of cadmium chloride and bromide derived from the cell data by means of the Gibbs–Helmholtz relation are 93,710 and 74,759 g.-cal., respectively, the latter agreeing well with the value obtained by Oblata (A., 1922, ii, 343). L. S. Theobald.

Relation between activity of metallic ions and that of hydrogen ions in the hydrolysis of heavy metal salts. M. Quintin (J. Chim. phys., 1927, **24**, 712—721).—See A., 1927, 729.

Ebullioscopic paradox. A. Berthoud, E. Briner, and A. Schidlof (J. Chim. phys., 1927, **24**, 587—592).—See A., 1927, 1029.

Dissociation pressure of sodium sulphate decahydrate. II. M. Matsui, S. Fukushima, and S. Nakada (J. Soc. Chem. Ind. Japan, 1927, **30**, 330—341).—The vapour pressure of sodium sulphate decahydrate and of the products of its transition have been measured with an improved form of static isoteniscope. The results agree fairly well with those obtained statically by Wuite (A., 1914, ii, 203), but are lower than those furnished by dynamic methods. From the data, the following vapour-pressure equations are derived: $\log p = -2837{\cdot}83/T + 10{\cdot}7866$ (below 32·4°) and $-2360{\cdot}58/T + 9{\cdot}2254$ (above 32·4°). The transition point thus indicated is 32·6°.

S. Oka.

Equilibrium diagram of the zinc–antimony system. T. Takei (Sci. Rep. Tôhoku, 1927, **16**, 1031—1056).—The system zinc–antimony has been re-investigated by thermal, micrographic, dilatometric, and röntgenographic analysis and by the electrical resistance method, and the accepted diagram is very considerably modified. The existence of the compounds Zn_3Sb_2 and ZnSb is confirmed; in addition the compound Zn_4Sb_3 has been found in alloys containing 35—45% Zn. All the compounds form very limited solid solutions α, β, and ε, which undergo transformation between 400° and 500°. The solid solution of Zn_3Sb_2 contains 45—46% Zn and solidifies as the η phase, which is transformed into ξ at 437—455° according to the composition, and into ε at 405°. The γ solid solution of Zn_4Sb_3 in Zn_3Sb_2 is stable only above 493°, and undergoes a change at 527—530°, the nature of which is not apparent. The α solid solution exists together with free antimony in the form of a eutectic in all alloys containing up to 42% Sb and undergoes an allotropic change at 300°. The compound Zn_3Sb_2 forms a eutectic with zinc melting at 411° and containing 97% Zn. The polymorphic change at 405° occurs in all alloys containing more than 45% Zn and that at 455° in alloys containing 45—90% Zn. The antimony–ZnSb eutectic melts at 505° and contains 21% Zn. The unstable phase observed by previous investigators in alloys containing 35—42% Zn is really the γ phase supercooled below the peritectic line at 546°.

A. R. Powell.

Determination of the heterogeneous field in the system iron–nickel. K. Honda and S. Miura (Sci. Rep. Tôhoku, 1927, **16**, 745—753).—Dilatometric analysis of the system iron–nickel shows that the Ac3 transformation takes place between 860° and 905° in pure iron and between 440° and 557° in the 28% Ni alloy, the temperatures of the beginning and ending of the change falling regularly on smooth curves convex to the temperature axis between these points; these curves therefore define the $\alpha+\gamma$ field in iron–nickel alloys during heating. The boundaries of this field are entirely different when the metal changes from the γ condition. On cooling the change to α starts at 889° and is completed at 850° in pure iron; it starts at 215° and is completed at 0° in the 19% Ni alloy, whilst for the 29% and 33% Ni alloys the starting temperatures are 0° and −78°, respectively. For iron containing only small quantities of nickel the lowering of the A3 transformation follows the law of depression of the f. p. in dilute solutions.

A. R. Powell.

Relationship between liquidus curves and breaks due to liquid mixtures (Fe–FeS ; Fe–Cu). Rational expressions for heterogeneous equilibria. C. Benedicks (Z. physikal. Chem., 1928, **131**, 285—296).—Breaks in a binary liquidus curve may be produced by the presence of a third component which is more soluble in one of the pure components than in the mixed mass. Such a break is produced in the liquidus curve of the Fe–FeS system, of which the components are normally totally miscible, by the presence of silicon, which although soluble in molten iron is only very sparingly soluble in molten ferrous sulphide. The small quantity of silicon necessary to produce this effect may easily be introduced into the mass from the glaze of a porcelain vessel. Discrepancies between the liquidus curves of the system Fe–Cu which have been found by a number of observers are attributable to the type of disturbance described, and a diagram is described which is in agreement with the phase rule.

A number of new terms are proposed, such as "eutectol" for a fused mixture of eutectic composition.

H. F. Gillbe.

Thermal dissociation of manganese dioxide. C. Drucker and R. Hüttner (Z. physikal. Chem., 1928, **131**, 237—266).—The thermal decomposition of manganese dioxide into the sesquioxide and oxygen has been studied by a number of methods. Both oxygen pressure curves and *X*-ray diagrams fail to indicate the presence of either intermediate oxides or manganous oxide during the reaction. The pressure–temperature curves are greatly influenced by the physical condition of the specimen; *e.g.*, a compact form of the oxide has an oxygen pressure of 125 mm. at 530°, whereas a finely-divided form attains the same pressure at 450°. By the static method higher pressures are recorded than by the dynamic, since in the former case the film of manganese sesquioxide produced on the surface of the particles hinders the diffusion of oxygen from the interior. The reaction is practically irreversible. Manganese dioxide and sesquioxide form solid solutions, but since neither the isotherms nor the pressure curves indicate any simple relationship between the pressure and the degree of dissociation, the formation of solid solutions must take place very slowly and in a thin layer inside the particles. As usually observed, the system is therefore in false equilibrium. The heat of decomposition is about −26 kg.-cal.

H. F. Gillbe.

Cooling curves in the binary systems *p*-toluidine–salicylic acid, and *p*-toluidine–benzoic acid. (Miss) E. M. Bartholomew and I. W. Wark (J. Proc. Roy. Soc. New South Wales, 1926, **60**, 388—391).—Cooling curves of fused binary mixtures of *p*-toluidine with salicylic or benzoic acid resemble the curve obtained by Philip for the mixture of the amine with α-naphthol (J.C.S., 1903, **83**, 814), and indicate in each case the existence of a compound containing the two components in equimolecular proportions. R. Cuthill.

Distillation of water-soluble organic compounds in a current of steam. A. I. Virtanen and L. Pulkki [Annal. Acad. Sci. Fennicæ, 1927, **A**, 29, No. 25].—A large number of experiments have been made to test the validity of Wiegner's equation $(\log y_1 - \log y_2)/(\log x_1 - \log x_2) = k$. Consistent results are obtained for typical volatile acids, amines, phenols, aldehydes, and alcohols under constant conditions. Increase in the rate of distillation in general raises the value of k. From the values obtained it is possible to calculate the ratio of two mutually neutral substances in a distillate from their aqueous solution to within 1% of that actually obtained by experiment. The result of adding salt to the aqueous solutions is to raise the value of k. This effect is explained by the absorption of a part of the water by the salt; it is apparently not due to the elevation of the b. p. produced, since the addition of glycerol or other similar substances which raise the b. p. has no influence on the value of k.

G. A. C. Gough.

System: water and the sulphates of sodium and magnesium. W. C. Blasdale and H. L. Robson (J. Amer. Chem. Soc., 1928, **50**, 35—46).—New data are given for the temperature range 67—210°. A complete temperature–composition diagram is given for the interval −5° to 210°. The invariant point löwite–hexahydrate–astrakhanite–solution is 59·5° and that represented by löwite–kieserite–van'thoffite–solution is between 180° and 210°, probably 190°. An apparatus is described which enables equilibrium measurements to be carried out in systems composed of two salts and water at temperatures above the b. p. of the solution.

S. K. Tweedy.

Salting-out effect. Influence of electrolytes on solubility of *m*-cresol in water. J. S. Carter and R. K. Hardy (J.C.S., 1928, 127—129).—Measurements were made of the solubility of *m*-cresol in electrolyte solutions, and it is shown that for solutions of sodium and magnesium chloride and sulphate the relation between the solubility s of the *m*-cresol and the concentration c of the salt is given by $s = s_0 l^{-kc}$ where s_0 has a value approximately that of the solubility in pure water and k is a constant, characteristic of each salt, which measures the salting-out effect of the salt. k is greater for the sulphates than for the chlorides. The solubility is depressed to a smaller extent in solutions of the corresponding acids, and the logarithmic relation does not hold. Measurements with phosphoric acid solutions show that the salting-out power of phosphoric acid increases in a regular manner when the dissociable hydrogen atoms are replaced by sodium, so long as the solution remains acid or neutral. W. A. Richardson.

Chemical equilibrium between iron, carbon, and oxygen. Theoretical considerations of the reduction of iron ores. K. Iwase and T. Watase (Sexagint [Osaka celebration], Kyoto, 1927, 185—201).—Equilibria in the system Fe–C–O are derived theoretically from earlier experimental data, and the mechanism of the reduction of iron ores by carbon is explained. H. F. Gillbe.

Causticisation of sodium carbonate by ferric oxide. VIII. Thermal decomposition of sodium carbonate in presence of ferric oxide and some empirical equations for the decomposition pressure. M. Matsui (J. Soc. Chem. Ind. Japan, 1927, **30**, 180—189).—The decomposition pressure of sodium carbonate in the presence of ferric oxide at various temperatures may be represented by $\log p = A/T + B \log T + CT + D$, and numerical values have been obtained for the various constants in this equation. The molecular heat of sodium ferrite calculated from the author's data is 44·28—44·66 g.-cal., which is greater than that indicated by the law of Neumann and Kopp. The decomposition pressure reaches 760 mm. at 1121·4° Abs.; the heat of reaction is 30,038 g.-cal. and the entropy change 26·8 g.-cal. per degree at that temperature. The entropy change per degree at the ordinary temperature is 33·2 g.-cal.

S. Oka.

Causticisation of sodium carbonate by ferric oxide. X. Thermal change of a mixture of sodium carbonate and ferric oxide in an atmosphere of carbon dioxide and the use of Nernst's micro-torsion balance. M. Matsui and K. Hayashi (J. Soc. Chem. Ind. Japan, 1927, **30**, 633—641).—About 2 mg. of a mixture of 1 part of sodium carbonate and 1·8 parts of ferric oxide was heated for 10 min. in a small platinum vessel in an atmosphere of carbon dioxide, and the loss of weight measured by means of a Nernst balance after cooling. The temperature of heating was raised in regular steps, and the temperature at which the loss of weight suddenly increased was taken as an indication that the decomposition pressure had reached 1 atm. The temperature 787·3° was obtained as the mean of 17 values in the range of 774·5—820·2°. This value is lower than that obtained by the authors in previous measurements. S. Oka.

"Saccharate" process and the phase rule. II. System, sucrose–barium oxide–water, at 75°. Y. Hachihama (J. Soc. Chem. Ind. Japan, 1927, **30**, 435—438).—The composition of solutions and solid phases in equilibrium at 75° has been determined. Comparison with the data for 25° and 45° shows that the solubility of "barium saccharate" in the sugar or baryta solution decreases as the temperature rises. The solid phases at 75° are $C_{12}H_{22}O_{11},BaO$ and $C_{12}H_{22}O_{11},3BaO$. The latter compound is new. Y. Nagai.

System sodium oxide–silica–water. II. Relationship between composition and b. p. of aqueous solutions of sodium silicate. (Miss) J. Y. Cann and K. E. Gilmore (J. Physical Chem., 1928, **32**, 72—90; Cann and Cheek, B., 1925, 498; Harman, this vol., 234).—The b.-p. elevations of sodium silicate solutions of ratios $Na_2O : SiO_2$ 1 : 1·995, 1 : 2·874, 1 : 3·154, and 1 : 3·753 at various concentrations have been measured by the Cottrell–Washburn method, and the activity coefficients calculated. The degree of dissociation of the solute is considered to decrease with the concentration, since the percentage elevation of the b. p. diminishes as the concentration increases. Dilute solutions of the last ratio show elevations which are abnormally high, whilst those of concentrated solutions are abnormally low, indicating micelle formation in this ratio.

L. S. THEOBALD.

Heat of mixing of molten metals. M. KAWAKAMI (Sci. Rep. Tôhoku Imp. Univ., 1927, **16**, 915—935).—See this vol., 21.

Heats of combustion and formation of calcium cyanamide. N. KAMEYAMA and S. OKA (J. Soc. Chem. Ind. Japan, 1927, **30**, 317—323).—Calcium cyanamide was prepared by the repeated calcination of calcium oxide with dicyanodiamide in a current of nitrogen (B., 1920, 818A). The cyanamide used contained $CaCN_2$ 98·25%, $CaCO_3$ 0·81%, CaO 0·94%. The heat of combustion was measured by a bomb calorimeter, benzoic acid being used to assist ignition. Special experiments were made to ascertain the amount of benzoic acid which sufficed for this purpose. The mean of eight determinations gave $CaCN_2+1{\cdot}5O_2=CaO+CO_2+N_2+161{,}170\pm240$ g.-cal. From this are derived: $Ca+C(\text{diamond})+N_2=CaCN_2+86{,}010$ g.-cal., $CaC_2+N_2=CaCN_2+C(\text{graphite})+72{,}700$ g.-cal.

S. OKA.

Conductivities of some dilute amalgams at various temperatures. A. L. JOHNS and E. J. EVANS (Phil. Mag., 1928, [vii], **5**, 271—289).—The electrical conductivities of dilute germanium, gallium, and copper amalgams of different concentrations have been measured at about 300°. The conductivities at infinite dilution were, respectively, $4{\cdot}7\times10^{-2}$, $5{\cdot}5\times10^{-2}$, and $6{\cdot}5\times10^{-2}$. The corresponding conductivities of silver amalgams have been measured between 15° and 300°. With an amalgam of concentration 0·186% the temperature coefficient of resistivity was found to increase with increasing temperature. The values are always less than those for pure mercury. Between 15° and 100° the temperature coefficient of resistivity of silver amalgams decreases with increasing concentration. For all the amalgams examined, except those of silver at 300°, the increase of conductivity relative to that of mercury at the same temperature is approximately proportional to the concentration, and the ratio of this relative conductivity to the concentration is nearly constant so long as the concentration is small.

A. E. MITCHELL.

Equivalent conductivity of strong electrolytes at infinite dilution. II. Methyl-alcoholic solutions. Effect of temperature on the constants in the equation $\Lambda_0=\Lambda+BC^n$. I. VOGEL (Phil. Mag., 1928, [vii], **5**, 199—204).—Data for solutions of a number of uni-univalent salts in methyl alcohol have been used to show that the equation $\Lambda_0=\Lambda+BC^n$ is more directly applicable than that given by the complete-ionisation theory of Debye and Hückel. For solutions of potassium iodide in nitromethane both the constants B and n increase steadily with temperature up to 55° and then pass through a maximum between 55° and 70°.

A. E. MITCHELL.

Electrical conductivity of beryllium chloride and bromide in some anhydrous organic solvents. J. M. SCHMIDT (Bull. Soc. chim., 1928, [iv], **43**, 49—62).—The solubilities of beryllium chloride at the ordinary temperature in methyl, ethyl, and amyl alcohols and pyridine are 257, 151, 154, and 133 g./litre, respectively. Measurements of the electrical conductivities of solutions of beryllium chloride in the above solvents show that the conductivities vary with concentration in a very complex manner. The molecular conductivity–dilution curves show maxima and minima in two instances and in no case can the value of μ_∞ be calculated from the customary Kohlrausch relation $\mu_\infty-\mu_r=K\sqrt{C}$. The measurements are interpreted as indicating the existence of two molecular complexes, one of which exists only in dilute solutions. The solubility of beryllium bromide in ethyl bromide at the ordinary temperature is of the order of 1 g./litre. The degree of ionisation is probably small.

J. S. CARTER.

Electrolytic transference of water in aqueous hydrogen bromide solutions. G. BABOROVSKY and A. WAGNER (Z. physikal. Chem., 1928, **131**, 129—133).—Application of Baborovsky's method for the determination of electrolytic transference of water to solutions of hydrogen bromide yields for the true transport number of the cation 0·878, and for the total water transference 0·50. During the electrolysis transference of water takes place towards the cathode. On the assumption that electro-osmotic effects are negligible and that the hydrogen ion is associated with one molecule of water, each bromine ion is attached to three water molecules.

H. F. GILLBE.

Variation of electrical conductivity of solutions with field strength. M. WIEN (Physikal. Z., 1927, **28**, 834—836).—Data are given for the following solutions: potassium ferrocyanide, cerium trichloride, potassium ferricyanide, magnesium sulphate, copper sulphate, aluminium sulphate, calcium ferrocyanide, barium ferrocyanide, calcium nitrate, sodium chloride, cobalt chloride, and cadmium iodide. For aqueous and acetone solutions it has been found that the increase in conductivity with the strength of the field can be resolved into two components: a thermal effect proportional to the square of the force and a potential effect proportional to the force.

R. W. LUNT.

Behaviour of Debye electrolytes in intense fields. G. JOOS and M. BLUMENTRITT (Physikal. Z., 1927, **28**, 836—838).—It follows from Debye's theory that the conductivity of an electrolyte should increase as a function of the square of the field strength. For solutions of specific conductance 0·0002 in a field of 4×10^4 volt $cm.^{-1}$ the calculated values agree well with Wien's experimental data (cf. preceding abstract) in the case of sodium and barium chlorides and potassium sulphate; qualitative agreement is obtained for copper sulphate, aluminium chloride, and potassium ferrocyanide. It is further shown that, in accordance with theory, the observed increase in conductivity varies inversely as the square root of the dielectric constant of the solvent.

R. W. LUNT.

Free space-charges in electrolytes. A. COEHN and R. SCHNURMANN (Z. Physik, 1928, **46**, 354—373).—Free space-charges occur when a current is passed through a gas, *i.e.*, accumulations of charged carriers occur around the electrodes. A similar phenomenon in solutions of electrolytes would involve the breakdown of the Hittorf mechanism of ionic migration. In order to obtain such an effect, highly dilute solutions of electrolytes are necessary in order to preserve the analogy with rarified gases. It has been found possible by the use of point electrodes and the investigation of electrostatic charges of gas bubbles in the liquids to demonstrate free space-charges. A recoil stream of gas bubbles is observed and is most marked when the electrode potential is small, the ionic concentration small, and the difference between the mobilities of the two ions great.

R. A. Morton.

Electrochemical behaviour of glass. M. J. Mulligan and J. B. Ferguson (Trans. Roy. Soc. Canada, 1927, [iii], 21, III, 263—264).—The coloration or deposit obtained when soda–lime glass is electrolysed, with mercury first as anode and then as cathode (Ferguson and Ellis, A., 1926, 31), is formed at places at which the high apparent resistance of the anode glass layer has been markedly reduced by current reversal. When glasses are electrolysed at 300—400°, with an anode such as mercury or carbon, soluble with difficulty, the current decreases with time, apparently due to the setting up of a large counter-*E.M.F.* nearly equal to the applied voltages. This counter-*E.M.F.* is a function of the applied voltage, but nearly constant at the higher voltages. This has made it possible to determine the true ohmic resistance of the anode layer. The resistance varies with temperature, in agreement with the rule of Rasch and Hinrichsen. The small temperature coefficient of the apparent resistance of the whole glass sample, for temperatures below 100°, may be traced to the counter-*E.M.F.*, and not to the true ohmic resistance of the anode layers. M. S. Burr.

Alternating-current electrolysis. Relation of frequency. J. W. Shipley and C. F. Goodeve (Trans. Roy. Soc. Canada, 1927, [iii], 21, III, 393—409).—The relation to current density of the rate of generation of electrolytic gases by an alternating current of frequency varying from 5 to 300 cycles has been determined for platinum, copper, and silver electrodes. As previously shown (B., 1927, 633), there is a critical current density above which alternating-current electrolysis follows the laws of direct current electrolysis, and may be made coincident with it by subtracting the critical current density from that actually used. Alternating-current electrolysis is dependent on the "electrolytic capacity" of the electrode, *i.e.*, on the average storage capacity (in coulombs) for electrolytic gases of 1 sq. cm. of electrode surface. The electrolytic capacity, at constant frequency but varying current density, is constant for copper but varies with the quarter-wave area for platinum and silver electrodes. The quarter-wave area refers to the quantity of electricity that has passed before reversal of the current. The relation of the electrolytic capacity to the quarter-wave area at all frequencies is represented by the equation $Q_0=Aq_1^n$, where A and n are electrolytic absorption constants, Q_0 is the electrolytic capacity, and q_1 is the quarter-wave area. For copper n is zero, so that the electrolytic capacity equals the quarter-wave area. For platinum, n is constant at 0·62 for all frequencies when q_1 is less than 10 millicoulombs, whilst A varies from 1·53 at 20 cycles to 1·34 at 120, above which it remains constant. For silver n is constant at 0·53 up to 150 cycles, but increases to 0·66 at 200 and 0·77 at 250. A is constant at 1·92 below 150 cycles, but decreases to 1·55 at 200 cycles and 1·29 at 250 cycles. Electrolytic capacity decreases to a minimum with increase of frequency, and then remains constant for copper and platinum, but in the case of silver there is a definite rise again. The mechanism of alternating-current electrolysis is discussed. In the case of platinum the electrolytic capacity is probably due to absorption of the gases at the surface. The electrolytic capacities of copper and silver, however, are more likely to be due to the formation of oxides and possibly hydrides. An amount of hydrogen is liberated which is in excess of that required to reduce the oxide previously formed, and conversely for the oxygen. The volume R_1 of electrolytic gas liberated from one electrode per min. per sq. cm. is $4{\cdot}71[I_1-A(4{\cdot}44f/1000)^{1-n}I_1^n]$, where I_1 is the current density and f the frequency. The critical current density I_c, when $R_1=0$, is $A^{1/(1-n)}$ $(4{\cdot}44f/1000)$. These equations agree closely with the experimental results for platinum, copper, and silver. M. S. Burr.

Electrocapillary properties of mercury in contact with air. G. Colange (Compt. rend., 1928, 186, 74—75).—When a gradually increasing negative potential is applied to pure mercury in a clean vertical tube (more than 0·1 mm. in diameter), the air–mercury meniscus rises to a maximum (at 15,000—20,000 volts) and then falls below its original level. When the apparatus is slowly discharged, the meniscus rises to the maximum level again and then returns to its original position. J. Grant.

Diffusion potential of hydrochloric acid. A. Bühl (Physikal. Z., 1927, 28, 767—770).—From measurements of the diffusion potential of hydrochloric acid at various dilutions and from a comparison of these results with the author's earlier data in sodium, potassium, and lithium chlorides it appears that the initial fall in the conductivity of a solution of hydrochloric acid which is observed when the concentration is gradually increased is due to a decrease in the velocity of agitation of the ions and not to a diminution of the degree of ionic dissociation.

R. W. Lunt.

***P.D.* at the boundary between two liquid phases.** L. W. J. Holleman and J. P. Werre (Rec. trav. chim., 1928, 47, 105—110).—If two immiscible solvents containing the same electrolyte in solution are in equilibrium with one another, there is a definite difference of potential at their surface of separation. This has been determined for solutions of potassium chloride, hydrogen chloride, and sodium salicylate in amyl alcohol and water by means of the following cell, in which all diffusion potentials are practically eliminated: normal calomel electrode| saturated potassium chloride|2*N*-ammonium nitrate in methyl alcohol|MA in amyl alcohol|MA in water| saturated potassium chloride|normal calomel electrode. The values obtained are in good agreement with those of Baur (A., 1925, ii, 1164; 1927, 23). They also show that, contrary to the conclusions of Abel (Z. physikal. Chem., 1924, **110**, 587), the value of the *P.D.* is influenced by concentration; *e.g.*, for a concentration of 0·1*M*-hydrogen chloride in the aqueous phase the *E.M.F.* is 54 millivolts, whilst for a 0·04*M*-solution it is 62 millivolts. The theory of the phenomenon is discussed and earlier investigations are critically considered. M. S. Burr.

Boundary potential of textile fibres in water. P. Karrer and P. Schubert (Helv. Chim. Acta, 1928, **11**, 221—229).—An apparatus is described for the determination of the *P.D.* between water and a material in the form of fibres, such as wool, silk, cotton, viscose, acetate silk, and so on. Under the influence of an applied difference of potential, E, water was allowed to pass through a tube packed with the fibres. The boundary potential, ζ, was calculated from two different formulæ. In the first the volume of water V, in mm.³ per min., passing through the tube, is equal to $q\zeta ED/4\pi\eta a$, where D is the dielectric constant of water $=81$, η is the viscosity coefficient, a the distance apart of the electrodes, and q the total cross-section of the capillaries of the fibres calculated by dividing the volume of the dry fibres by the length of the cylinder containing them. According to Smoluchowski's formula, $V=I\sigma\zeta D/4\pi\eta$, where I is the current strength and σ the specific resistance of the liquid. The second formula gives somewhat larger numerical values than the first, but of the same order. The difference may be partly ascribed to the uncertainty in the value of q in the first formula. Natural silk acquires only a very slight negative charge, $-0{\cdot}0005$ or $-0{\cdot}0008$ volt. Mercerised cotton becomes less acid than cotton wool, but more so than the artificial silks, except acetate silk, which is strongly negative, $-0{\cdot}021$ or $-0{\cdot}036$ volt. Wool is also strongly negative, $-0{\cdot}028$ or 0·048 volt. The results are reproducible. The values obtained for the artificial silks depend on the extent to which they have been purified from adhering grease. Cotton treated with pyridine acquires a positive charge of the same order as that observed for zinc oxide, $+0{\cdot}01$ to 0·02 volt. Under the same conditions, viscose also takes up a positive charge of smaller value. M. S. Burr.

Influence of current on solution potential of hydrogen. E. Dennino and G. Ferraro (Gazzetta, 1927, **58**, 881—899).—The solution potential of hydrogen in sulphuric acid of *d* 1·22 is a function of the current density passing through the acid between electrodes of nickel and of copper, and of the time of passage of the current. The initial solution potential increases rapidly in the neighbourhood of 0·05 amp. cm.$^{-2}$ and becomes linear at about 0·5 amp. cm.$^{-2}$; when the time of passage of the current is increased to 1000 hrs. this relation persists, but the value of the solution potential, at any given current density, diminishes. R. W. Lunt.

Cuprous chloride electrodes. R. F. Nielsen and D. J. Brown (J. Amer. Chem. Soc., 1928, **50**, 9—19).—The *E.M.F.* at 25° of the following cells are recorded: Cu (2-phase amalgam), $CuCl(s)|xM\text{-}HCl|H_2$; H_2(700 mm.)$|HCl,0{\cdot}0478M\text{-soln.}|Cl_2(p)$; and $CuCl(s)|CuCl_2,yM|\text{soln.}|Cl_2(p)$, where x ranges from 0·02029 to 0·03564, y from 0·01 to 5·82, and p has some low value. In each case the cuprous chloride was prepared *in situ* in complete absence of oxygen. The standard potential of the copper amalgam–cuprous chloride electrode is $-0{\cdot}1298$ volt, and $\Delta F^0_{298}=2995$ g.-cal. The values for the cuprous chloride–cupric chloride electrode are $-0{\cdot}5758$ volt and 13,285 g.-cal., respectively. The standard free energy of solid cuprous chloride is $-28{,}370$ g.-cal. and of cupric chloride dihydrate, $-44{,}100$ g.-cal. The activity coefficients of cupric chloride over a limited range are recorded. S. K. Tweedy.

Structure of the platinicyanides. Potential of the platino-platinicyanide electrode. H. Terrey (J.C.S., 1928, 202—206).—Measurements were made of the potential of the platino-platinicyanide electrode. Putting the value $n=2$ in the equation $E=E_0+RT/nF\log i/o$ (where i and o are respectively the concentrations of platinic and platinous ion), leads to a constant value of E_0 for a range of values of i/o, and it is concluded that in the conversion of the platinocyanide into the platinicyanide there is a valency change from 2 to 4, and that the formula for the so-called platinicyanides is more correctly represented by $K_2Pt^{IV}(CN)_4{\cdot}Pt^{II}(CN)_4$ than by the formula $KPt^{III}(CN)_4$. W. A. Richardson.

Potential of solutions containing ferrous, ferric, and iodide ions and free iodine. N. Sasaki and K. Nakamura (Sexagint [Osaka celebration], Kyoto, 1927, 241—248).—A new method is described of measuring the potential of solutions which undergo change with time. The potential of solutions containing iron salts and iodide is influenced solely by the concentration of iodide and free iodine. H. F. Gillbe.

Thermodynamic studies of cuprous and mercuric oxides. F. Ishikawa and G. Kimura (Sexagint [Osaka celebration], Kyoto, 1927, 255—269).—The *E.M.F.* of the cells $H_2|N\text{-}NaOH,HgO|Hg$ and $Cu|Cu_2O,N\text{-}NaOH,HgO|Hg$ have been determined, and the influence of various forms of mercuric oxide in the former case has been studied. Only the red form gives a constant *E.M.F.*, which is independent of the method of preparation of the oxide. The free energy changes for the reactions involved have been calculated. H. F. Gillbe.

Cells with unchanged electrodes [*K* cells] and Carnot's principle. V. Karpen (Compt. rend., 1928, **186**, 230—232; cf. this vol., 23).—A cell formed from a platinum–platinum-black cathode and an Acheson graphite anode immersed in a saturated solution of sodium hydroxide was maintained at 95—100° for 16 hrs. The *E.M.F.* on open circuit was 0·5 volt, and after the passage of a quantity of electricity which would correspond with the dissolution of 5·5 mg. of quadrivalent platinum, the actual loss in weight of the platinum electrode was only 0·1 mg., part of which was due to mechanical losses during the washing and drying processes. The experiment, which cannot be explained by a reaction at the anode and is reproducible with slightly varied conditions, is said to be incompatible with the second law of thermodynamics. J. Grant.

Becquerel effect. I. C. Winther (Z. physikal. Chem., 1928, **131**, 205—213).—The term Becquerel effect should be restricted to photogalvanic effects at the electrodes. Substances which are effective as Becquerel electrodes have a large surface, considerable power of adsorption, and are rendered better conductors by irradiation. The Becquerel effect is ascribed to a primary ionisation followed by a change in the adsorption equilibria, whilst the chemical processes which often occur are secondary side reactions. H. F. Gillbe.

Theory of passivity. I. Theory of polarisation by anodic deposition and passivation of metals. W. J. Müller and K. Konopicky (Monatsh., 1927, **48**, 711—725; cf. A., 1924, ii, 743; 1927, 735, 942, 1145).—Electrometric investigations of the passivity of certain metals in acid media have led to the conclusion that the observed effects are most readily explained by assuming the existence of a sparingly conducting film on the metal anode. The formation of such a film, which probably consists of metal salt or basic salt, causes a progressive diminution of the effective surface of the electrode and a consequent increase in current density. Postulating the existence of such a film, an equation is derived which represents the variation of current strength with time. The equation in its abbreviated form is $t=C+A[-1/(i_0-i)+2{\cdot}3/i_0\,.\log\{(i_0-i)/(i-i_r)\}]$, where t represents the time elapsed, i the current strength after time t, i_0 the original and i_r the residual current strengths. The quantities C and A are functions of various physical and electrochemical quantities, but may be considered as constants characteristic of the metal concerned. The equation represents in a very satisfactory manner the behaviour of copper, nickel, and iron in solutions of sulphuric acid. The behaviour of chromium is, however, anomalous, the values of A increasing with time. Calculations of the conductivity of the liquid in the pores of the anode sheath show that with iron and copper, but not with nickel, the constituent salts are probably the stable hydrated sulphates. During the deposition the potential of the metal does not change, the observed variation in potential being due to the change in resistance consequent on the growth of the deposit. The similarity between the current–time curves for copper, where no passivation occurs, and iron, which becomes actually passive, shows that passivation is due to a change in the metal and that this change occurs only at the high current densities resulting from the deposition. The present data are not sufficiently comprehensive to permit the precise evaluation of the current density necessary for passivation. Previous values of the order 10 amp./cm.^{2} are now held to be too low, the true values being probably 5—7 times as great. J. S. Carter.

Electrochemistry of solutions of aluminium bromide in nitrobenzene. V. A. Plotnikov and M. A. Bendetzki (J. Russ. Phys. Chem. Soc., 1927, **59**, 493—507).—See A., 1927, 832.

Kinetics of simultaneous reactions. A. Skrabal (Ann. Physik, 1927, [iv], **84**, 624—638).—A mathematical discussion of the kinetics of simultaneous reactions in reply to the criticisms of the author's theory (A., 1927, 188) by Bodenstein (*ibid.*, 492). R. W. Lunt.

Reaction velocities. II. W. F. Brandsma (Rec. trav. chim., 1928, **47**, 94—104; cf. A., 1926, 913).—Theoretical. Scheffer's formula for reaction velocities deduced thermodynamically is $\log k=(\varepsilon_I-\varepsilon_t)/RT-(\eta_{I_{t-1}}-\eta_t)/R+C$, where k is the velocity coefficient, C a constant independent of the nature of the reacting substances, ε_I is the sum of the molecular energies, $\eta_{I_{t-1}}$ the sum of the concentration-free molecular entropies, and ε_t and η_t are an energy and entropy respectively of the "intermediate state." The latter refers to the condition of those molecules which will react in the next unit of time. A further investigation has been made of the physical significance of ε_t and η_t. With this object two examples of unimolecular reaction mechanism are discussed, one based on the classical theory and the other on the quantum theory. By calculating the energy and entropy terms for these examples, and substituting the calculated values in Scheffer's formula, the same value for the reaction constant is obtained as can be calculated directly by the method of statistical mechanics. It has been shown that η_t has a physical meaning, just like the entropy under normal conditions, and the value depends on the unit of time. The constant C, which must be a universal constant, is apparently zero for the examples considered. M. S. Burr.

Velocity of the explosion wave. P. Laffitte and P. Dumanois (Compt. rend., 1928, **186**, 146—147).—The author's method (A., 1925, ii, 135) has been used for the determination of the rates of propagation of explosion waves in various mixtures of oxygen with hydrogen, with nitrogen and hydrogen, and with methane, under initial pressures of 1—7 atm. The results have an accuracy of 2%, and show that the velocities are unaltered by the presence of lead tetraethyl (1 in 1000). J. Grant.

Combustion of carbon monoxide. I. J. P. Baxter (Phil. Mag., 1928, [vii], **5**, 82—96).—An account is given of preliminary experiments to compare the action of hydrogen, in combination with different elements, on the combustion of carbon monoxide. The methods are similar to those described by Harrison and Baxter (A., 1927, 211). Effects of water vapour on the combustion of carbon monoxide with air at 1 atm. original pressure have been examined. There is no apparent relationship between flame velocity and moisture content, the relationship varying with the composition of the mixture. The addition of moisture to the gas mixture caused a steady reduction in the time taken to reach the maximum temperature. Violent temperature fluctuations observed in some cases have been shown to be accompanied by corresponding pressure fluctuations. The addition of moisture reduces the time taken for the attainment of the maximum pressure and as this time decreases the rate of the subsequent cooling tends to increase. As the moisture content is increased the amounts of oxides of nitrogen produced decrease considerably. A. E. Mitchell.

Gaseous combustion at high pressures. IX. Influence of pressure on the "explosion limits" of inflammable gas–air etc. mixtures. W. A. Bone, D. M. Newitt, and C. M. Smith (Proc. Roy. Soc., 1928, A, **117**, 553—576).—Observations have been made on the "explosion-ranges" at the ordinary temperature of hydrogen–air, methane–air, and carbon monoxide–air mixtures at varying pressures between 1 and 250 atm. In the first two cases, whilst the composition of the lower-limit mixture giving 100% combustion remains practically unchanged, the range of explosibility is progressively widened by successive increases in the initial pressure, particularly in the case of methane–air mixtures. The results on the whole confirm those of Berl and Werner (cf. B. 1927, 546). The narrowing of the limits at 10—30 atm. found by these investigators may be ascribed to the fact that they used spark ignition, instead of the electrical fusion of a platinum wire. In the case of carbon monoxide–air mixtures, the explosion range narrows considerably as the initial pressure rises. The same phenomenon is observed when the nitrogen of the air is replaced by argon or, to a much slighter extent, by helium. It is predicted that at some very high initial pressure carbon monoxide–"air" mixtures will become non-explosive at ordinary temperatures.

L. L. Bircumshaw.

Pressures produced on inflammation of mixtures of carbon monoxide and air and of hydrogen and air in a closed vessel. G. B. Maxwell and R. V. Wheeler (J.C.S., 1928, 15—21; cf. A., 1927, 317, 1036).—The authors, having had indications that the values for the dissociation of carbon dioxide found by Nernst and Bjerrum were over-estimated, applied the "maximum pressure mixture" method used by Fenning and Tizard (cf. A., 1927, 826). A mixture containing 35·5% of moist carbon monoxide gave the maximum pressure of 6·72 atm. Using Fenning and Tizard's method of calculation, the values of K_p at 2543° Abs. obtained were: Maxwell and Wheeler $1{\cdot}35\times10^{-2}$, Fenning and Tizard $1{\cdot}66\times10^{-3}$, Bjerrum $6{\cdot}4\times10^{-3}$. Expressed as % at 1 atm. the results are, respectively, 30·1%, 14·9%, and 23·4%.

In view of this result the authors criticise the method of determining the dissociation, the more particularly as it is based on the assumption that the gases are in chemical equilibrium at the moment of attainment of maximum pressure. Ellis and Wheeler have observed the phenomenon of "after burning" on exploding mixtures of carbon monoxide and air.

Similar discrepancies in the values of K_p for steam deduced by this method were observed. By repressing the dissociation with an excess of hydrogen, mean values for C_v for steam from 15° to 2120° were obtained. Details of the method of calculation are given. The value 10·8 g.-cal./g.-mol. does not alter appreciably over the range 1400—2120°. The results obtained agree well with those of Womersley (B., 1922, 163A).

H. Ingleson.

Propagation of combustion in hydrocarbon mixtures. R. Duchêne (Compt. rend., 1928, **186**, 220—223).—The rates of propagation of the explosion-wave fronts in mixtures of C_6-hydrocarbons with air, which were exploded by means of an electric spark following an adiabatic compression (volumetric coefficient 4·2), rise rapidly to maxima and then fall slowly to constant values. The highest initial and maximum speeds attained correspond with an air–gas mixture richer than that required for complete combustion (cf. Pignot, B., 1926, 260), and having an air/hydrocarbon ratio of 6 (approx.). The intensity of the light emitted increases during the propagation of the flame progressively (*e.g.*, with benzene), or discontinuously (*e.g.*, with *cyclo*hexane). The second type is more usual, and since the luminosity often occurs in both the burnt and unburnt portions of the gas mixture, the combustion of the gas in two phases is indicated. The addition of lead tetraethyl (1—2%) inhibits the appearance of the second phase and this confirms the opinion of Aubert, Pignot, and Villey (cf. B., 1928, 5) that this substance reacts during a prelimiary phase of the combustion.

J. Grant.

Theory of anti-detonants. P. Dumanois (Compt. rend., 1928, **186**, 292—293; cf. B., 1926, 619).—The experiments of Moureu, Dufraisse, and others (this vol., 180) and of the author have shown that the theory in which anti-detonants act as accelerators of the rate of combustion is not correct. The theory of the former authors, however, that the formation of unstable peroxide in the liquid phase during the compression period is inhibited by anti-detonators, explains the behaviour of hydrocarbons giving rise to detonation in high-compression motors, and also the phenomena associated with self-ignition. The temperature of ignition of the normal hydrocarbon mixture is of more importance than the actual proportion of anti-detonant present. J. Grant.

Thermal decomposition of nitrogen pentoxide. F. O. Rice and (Miss) D. Getz (J. Physical Chem., 1927, **31**, 1572—1580).—The decomposition of nitrogen pentoxide is not a dust reaction, since removal of phosphorus pentoxide dust by an asbestos or by an electrical filter left the velocity unchanged. Phosphorus pentoxide is apparently not a catalyst for the reaction since the velocity coefficients are unchanged when material obtained from different sources is used or when its use in the preparation of the pentoxide is eliminated. Attempts to demonstrate catalytic activity of nitric acid also failed. Nitrogen pentoxide is apparently more stable in 100% nitric acid than it is in the gaseous state or when dissolved in organic solvents. The results of Lueck (A., 1922, ii, 433) for the decomposition of the pentoxide in solutions of carbon tetrachloride have been confirmed by an independent method. L. S. Theobald.

Velocity of ionic reactions. I. R. N. J. Saal (Rec. trav. chim., 1928, 47, 73—93).—Hartridge and Roughton's method for the determination of large velocity coefficients (A., 1923, ii, 744; 1925, ii, 47) by allowing the reacting liquids to flow together at constant velocity through a tube, and measuring various physical constants at different points, has been applied to the determination of the velocity of a number of ionic reactions. For this purpose, variations of electrical conductivity and potential with time have been measured. The possibility of using hydrogen, quinhydrone, copper, silver, and silver iodide electrodes, and oxidation and reduction potentials, has been investigated. The reaction between hydrogen and hydroxyl ions appears to be "instantaneous," *i.e.*, it takes place in less than 0·004 sec. This is in general the case for reactions between acids, bases, and salts, provided no secondary reactions occur, such as the hydration of anhydrides, *e.g.*, carbon dioxide, in which the ion or molecule undergoes a fundamental change. These secondary reactions may proceed in measurable time, or they also may be practically instantaneous. For the most part the formation of complexes is immeasurably rapid, but the complex iron and nickel cyanides are an exception. A number of oxidation and reduction reactions are of measurable velocity, but if the difference between the normal potentials of the respective pairs of reactants is large, then the velocity of reaction is generally large also. M. S. BURR.

Rate of hydrolysis and hydrogen-ion concentration. H. COLIN and (MLLE.) A. CHAUDUN (Compt. rend., 1928, **186**, 142—143).—If the power of hydrolysis of an acid in solution is due solely to the hydrogen-ion concentration it produces, then $(p_H-p'_H)=\log k'/k$, where $k'a'/ka$ is the ratio of the rates of initial hydrolysis of two solutions containing the quantities a' and a of sugar ($a'>a$), and the same amounts of acid. It has been shown for 0·1N-solutions of hydrochloric, sulphuric, oxalic, formic, or acetic acids, containing 5% or 40% of sucrose, that this is not the case, and that in the presence of added sugar or of salts (potassium bromide, chloride, or nitrate) the variations of the hydrolysis coefficient are independent of those of the p_H value. The rate of inversion is always increased by the addition of a salt which does not contain an ion in common with the acid. The p_H value is also modified but no simple quantitative relation exists between these changes. J. GRANT.

Velocity coefficient for bimolecular reactions in solution. R. G. W. NORRISH and F. F. P. SMITH (J.C.S., 1928, 129—138).—Lewis (A., 1918, ii, 263) has given an expression for the velocity coefficient of a bimolecular gaseous reaction, $k_T=m\times114\times10^{21}[(\sigma_1+\sigma_2)/2]^2\sqrt{u_1^2+u_2^2}(e^{-E/RT})$ (1) where σ_1, σ_2 are the molecular diameters, u_1, u_2 are the velocities of the reacting molecules, m is the number of resultant molecules formed at each collision, and E is the energy of activation obtained from the temperature coefficient of the reaction. The authors have examined this equation in relation to non-ionic reactions in solution. The interactions of trimethylamine with *m*- and with *p*-nitrobenzyl chloride in benzene solution were studied at 25°, 30°, and 35°. E_1 and E_2 can be calculated for the reactions from the temperature coefficients. E_1-E_2 was also calculated by using equation (1), making the assumption that no great differences exist in solvation or molecular velocity in the two cases. Thus by division the relation $\log_e k_2/k_1=(E_1-E_2)/RT$ is obtained. The first method gave $E_1-E_2=110$ g.-cal., the second, 200 g.-cal.

An expression is deduced in which corrections for dissolution are introduced. On using this to calculate the velocity coefficient for the reaction between *p*-nitrobenzyl chloride and trimethylamine at 30° a result $1{\cdot}2\times10^5$ is obtained, whereas the experimental value is 0·00219. The various causes which might account for this difference are discussed.

H. INGLESON.

Comparative studies in oxidation. II. W. H. HATCHER and C. R. WEST (Trans. Roy. Soc. Canada, 1927, [iii], **21**, III, 269—276; cf. *ibid.*, 1926, [iii], **20**, III, 327).—In the oxidation of organic substances by potassium permanganate in acid solution, formic acid is frequently an ultimate product. The rate of oxidation of 0·02M-formic acid by 0·08N-permanganate has therefore been studied in solutions of sulphuric acid of different concentrations, and also in phosphoric, acetic, and perchloric acids. The rate of oxidation is inversely proportional to the hydrogen-ion concentration. With no acid other than formic, oxidation was complete in 5 min. The results obtained have been used in the quantitative identification of formic acid as an intermediate oxidation product of the following substances: maleic, malic, oxalacetic, fumaric, malonic, tartaric, lactic, and glycollic acids, and glycol. The curves obtained by plotting time against the amount oxidised indicate two main types of reaction: the first where the oxidation begins with great rapidity and then slows down in accordance with the requirements of the formic acid, and the second where the curve rises more slowly and regularly, following the formic acid curve only after a considerable time. In the latter case there is sometimes a point of inflexion between the first and second parts of the curve. Malic, tartaric, and perhaps lactic acids are members of the first group. The oxidation of lactic acid is not so complete as that of the other acids, and gives rise to acetic acid which is not further attacked. From the form of the curves the number of molecules of formic acid produced can be determined. The following facts relating to the oxidation of these acids are deduced: oxalacetic acid is not an oxidation product of malic acid, nor tartaric of fumaric and maleic acids, pyruvic of lactic acid, oxalic of glycollic acid, nor, finally, oxalic and glyoxylic acids of glycol; malonic acid does not produce mesoxalic acid, but probably passes through tartronic to formic and glyoxylic acids, and thence gives rise to another molecule of formic acid. This method of studying the oxidation of a complex organic compound is claimed to be better than any method depending on the isolation of intermediate compounds.

M. S. BURR.

Effect of constitution of a chloroamine on its hydrolysis constant. F. G. SOPER and G. F. SMITH (J.C.S., 1928, 138—143).—A continuation of previous work (A., 1924, i, 1176; 1925, i, 381). A 20% acetic acid solution was employed as solvent with the object of increasing the range of concentrations within which determinations could be made. The authors conclude as a result of variation of the aryl and acyl radicals R′ and R, respectively, in the chloroamines NR′RCl that when R′ is kept constant whilst R is varied the hydrolysis constants of the series decrease when a similar change in R in a series of fatty acids would lead to an increase in the ionisation constants of the acids. Substitution in the aryl nucleus (with R constant) causes an increase in the hydrolysis constant when a similar substitution in the phenol R'·OH would cause an increase in the ionisation constant of the phenol. It is thought that these facts may be explained by assuming that chloroamines can exist in tautomeric forms.

H. Ingleson.

Esterification in mixed solvents. B. V. Bhide and H. E. Watson (J. Indian Inst. Sci., 1927, **10A**, 71—77).—See A., 1927, 1036.

Thermal and photochemical decomposition of caryophyllene nitrosite. P. Valenzuela and F. Daniels (Philippine J. Sci., 1927, **34**, 187—197).—The thermochemical decomposition of caryophyllene nitrosite has been examined quantitatively in nitrobenzene, paraffin, and limonene solutions at 76°, 100°, and 110°. The reaction appears to be complex. The velocity coefficients differ widely in the different solvents; for nitrobenzene solutions they are abnormal, but in the other two solvents at 100—110° they are normal.

E. Holmes.

Reduction of methylene-blue in hexose–phosphate mixtures. G. Blix (Skand. Arch. Physiol., 1927, **50**, 8; Chem. Zentr., 1927, ii, 1352).—With $0·5M$-phosphate and p_H 7·5 at 37·5° the decolorisation time falls with increasing hexose concentration; lævulose is oxidised 6—11 times as rapidly as mannose and galactose 15—20 times as rapidly as dextrose. The reaction velocity increases uniformly with increasing phosphate concentration and diminishing hydrogen-ion concentration; it is reduced or unchanged by neutral salts. Apparently, in phosphate solution the hexoses form a readily oxidisable compound (hexose-X) which attains equilibrium at 37° in 2—3 hrs. The velocity of decolorisation is increased by small (max. $10^{-4}M$) and decreased by larger concentrations of ferric or cupric salts. The favourable influence of metallic salts, but not the total oxidation, can be arrested by hydrogen cyanide. The oxidation is not affected by insulin, but is arrested by $5\times10^{-5}M$-adrenaline (in alkaline solution) or by $10^{-4}M$-pyrocatechol. The significance of the results is discussed in connexion with the oxidation–reduction system of the cell.

A. A. Eldridge.

Reactions depending on vapour at interface of two immiscible liquids. G. Harker and R. K. Newman (J. Proc. Roy. Soc. New South Wales, 1926, **60**, 45—54).—The rate of the hydrolysis over a given area of an *iso*amyl acetate–dilute hydrochloric acid interface at 100° is practically equal to that of the hydrolysis which occurs over an equal area of a solution of hydrochloric acid of the same concentration when the mixed saturated vapour of water and the ester is passed over it. As in the previous experiments with benzyl chloride (A., 1924, ii, 307), it is therefore clear that at the liquid–liquid interface the saturated vapours of both liquids are present. The rate of reaction at this interface is scarcely altered by increase in pressure.

R. Cuthill.

Heterogeneous reactions with a continuously changing solid phase. I. S. Liepatov [with H. Salgaller] (Ber., 1928, **61**, [*B*], 45—55).—A study of the reaction between barium and copper acetates and nitroalizarin, used in two forms obtained respectively by decomposing the sodium salt by hydrochloric acid and washing the product with water until free from sodium and chlorine and by washing the free acid with alcohol and water. The products are colloidal but differ in degree of dispersivity as shown by their rate of reaction with copper acetate. The chemical nature of the reaction between nitroalizarin and barium acetate is established by observations on the effect of the successive treatment of the acid with barium acetate and barium hydroxide. The change cannot, however, be expressed on the basis of the usual assumption of a constant active mass of the solid phase. It is therefore assumed that the latter is appreciably, although slightly, soluble in water and that the reaction occurs mainly within it; the whole mass of the solid phase therefore participates in the change and its concentration is consequently a variable quantity. Possibly a slow reaction takes place in the liquid phase. The kinetics of the change are expressed by the equation $dx/dt=K(A-yx)$, in which y is a constant dependent on the velocity of the secondary process (cf. Liepatov, A., 1926, 674, 789). Since this equation is also applicable not only to adsorption but also to swelling and diffusion it is regarded as having its origin in Fick's law of diffusion. It is probable that the rate of chemical change is great in comparison with that of diffusion which is experimentally determined.

The influence of electrolytes (acids and salts) on the course of the change has been examined.

H. Wren.

Rate of decomposition of commercial calcium cyanide. M. S. Benjamin (J. Proc. Roy. Soc. New South Wales, 1926, **60**, 38—44).—Treatment of a commercial calcium cyanide with sulphuric acid (1 : 4) under the ordinary pressure gave less than the theoretical amount of hydrogen cyanide, but the yield was much improved by reducing the pressure, and cooling the reactants in a freezing mixture, a fact which is probably a consequence of the readiness with which hydrogen cyanide forms secondary and polymerisation products. The rate of evolution of hydrogen cyanide at 20° in air saturated with water vapour was very low, but was somewhat greater when a growing plant was present, and very much greater in an atmosphere of carbon dioxide saturated with water vapour. Field experiments showed that, weight for weight, calcium cyanide is a more efficient fumigant than the potassium salt and sulphuric acid, presumably because calcium cyanide evolves hydrogen cyanide actually in contact with the living parts of the plant, a higher local concentration thus being attained than is possible when the potassium salt is used.

R. Cuthill.

Metallic corrosion in the light of quantitative measurements. G. D. Bengough, J. M. Stuart, and A. R. Lee (Proc. Roy. Soc., 1927, **A**, **116**, 425—467).—The present position of the theory of corrosion as chemical or electrochemical oxidation of a metal is reviewed and discussed. The factors, independent of the corroded metal, which influence the process are the temperature, the pressure of the oxygen gas, the hydrogen-ion concentration, the amount and distribution of the oxygen supply, the nature and distribution of the corrosion products, the conductivity of the liquid, and the metal-ion concentration. The factors relating to the metal include the electrical properties of the metal, the state of aggregation, the presence of internal stresses, the overvoltage, and, for impure metals, the nature and concentration of impurities in solid solution. Previous quantitative methods of investigation are criticised and a new oxygen absorption method of measuring corrosion is described. Most of the external factors mentioned above are known and controllable. The oxygen absorption–time curves of zinc undergoing corrosion under various conditions have been obtained with the new apparatus and their interpretation is discussed.

W. E. Downey.

Velocity of dissolution of aluminium. W. Kuczyński (Rocz. Chem., 1927, 7, 397—401).—The velocity of dissolution of aluminium plates in 1·5N-hydrochloric acid diminishes if nitrates or chlorates be added to the acid. Aluminium anodes passivated in potassium chromate dissolve unevenly in the acid, giving a pitted surface. R. Truszkowski.

Chemical properties [corrosion] of pure aluminium. C. Matignon and J. Calvet (Compt. rend., 1927, **185**, 909—912; cf. A., 1927, 657).—The rate of corrosion of pure aluminium (99·3%) prepared by the method of Hoopes (B., 1926, 63) has been measured in terms of the hydrogen liberated. With a 1·67N-solution of sodium hydroxide at 23° the initial rate for pure aluminium is less than for ordinary aluminium, but the final rates are nearly the same. Pure, clean aluminium is only slightly attacked by pure hydrochloric acid (2·65N) at 24°. The rate of attack is greater for an uncleaned sample, and is increased by the addition of impurities such as salts of copper (1·9 mg. copper per litre) or mercury, but not by salts of iron, zinc, or tin. J. Grant.

Intensive drying. A. Smits (Chem. Weekblad, 1928, 25, 82—90).—The methods, apparatus, and conclusions of the author and his co-workers are summarised. The effect of drying is to shift the equilibria which result in fluids from the existence of a very small proportion of the total molecules in an active state; this proportion is of the order of 10^{-10}, which is of the magnitude of the proportion of water molecules necessary for the activation of an inactive, completely dried system. S. I. Levy.

Mechanism of the oxidative action of hydrogen peroxide in the presence of ferrous iron. Oxidation of glycollic acid. S. Goldschmidt, P. Askenasy, and S. Pierros (Ber., 1928, **61**, [B], 223—233).—Hydrogen peroxide, when mixed with ferrous sulphate and glycollic or glyoxylic acid, causes oxidation within a few seconds. The extent of the reaction depends on the molecular ratio of ferrous sulphate to substrate. The change can only be caused by the ferrous salt and comes to an end when ferrous is completely converted into ferric iron. A similar change is not induced by ferric iron or by a previously-prepared mixture of ferrous salt and hydrogen peroxide. The presence of ferric iron causes a very slow consumption of hydrogen peroxide which invariably occurs when the quantity of the latter, in presence of ferrous iron and substrate, is greater than that required in the primary reaction. The greatest proportion of hydrogen peroxide per mol. of glycollic acid which can be used for exclusive production of glyoxylic acid depends on the concentration of ferrous iron and substrate and becomes more nearly equal to that used in the primary reaction as the concentration of iron diminishes. Glyoxylic acid is further oxidised to oxalic acid when its proportion has become considerable. Glycollic acid is not appreciably attacked by hydrogen peroxide alone, whereas in presence of ferric iron it is very slowly oxidised through glyoxylic to formic and carbonic acids.

Since the consumption of peroxide depends on the quantity of ferrous iron, it is highly improbable that the change is truly catalytic. It appears rather to be an induced reaction. It is unlikely, however, that *ferrous glycollate* is an intermediate product (cf. Wieland and Franke, A., 1927, 944) since the maximum consumption of hydrogen peroxide is observed with conditions ($p_{\rm H}$ 3·6) under which this salt is almost completely converted into glycollic acid. More probably the primary product is a ferrous peroxide (cf. Manchot, A., 1903, ii, 151), formed without change of valency of the metal and in part reacting with glycollic acid to give glyoxylic acid and re-form the ferrous iron, whereas a second part is converted by ferrous into ferric ions. H. Wren.

Catalysis of ethyl formate [hydrolysis] by monochloroacetic acid and of ethyl acetate [hydrolysis] by dichloroacetic acid in neutral salt solutions. H. S. Harned and J. E. Hawkins (J. Amer. Chem. Soc., 1928, **50**, 85—93).—On addition of halides of sodium or potassium or of sodium nitrate the velocity of hydrolysis increases rapidly and passes through a maximum; no initial increase occurs in presence of potassium nitrate and with barium chloride salt saturation occurs before the maximum is reached. Addition of sulphates produces a rapid decrease in velocity which passes through a minimum; this is due to the removal of hydrogen ions to form hydrogen sulphate ions. Methods of calculating the activity coefficients of the acids are worked out.

S. K. Tweedy.

Acceleration of the reduction of indigo by pyridine. A. Binz and G. Prange.—See B., 1928, 83.

Theory of autoxidation and anti-oxygenic action. C. Moureu and C. Dufraisse (Compt. rend., 1927, **185**, 1545—1548).—A comment on the criticism by Perrin (A., 1927, 609) of the authors' theory. J. Grant.

Autoxidation and antioxygenic action. Theory of the mechanism of the catalysis of autoxidation. C. Moureu and C. Dufraisse (Compt. rend., 1928, **186**, 196—199; cf. this vol., 180).—The authors' discussion of Perrin's theory of the mechanism of oxygenic action, and of his criticism of their own theory, is continued and summarised.

The behaviour of certain catalysts both as antioxygens and as antiluminants is probably the result of independent influences, and a theory which attributes the two effects to the same cause cannot be reconciled with phenomena such as the inversion of catalysis during an auto-oxidation reaction, or the relationship of inverse catalysts. The work of Gaffron (A., 1927, 1225) is explainable by the authors' theory in which the formation of a primary peroxide, containing active oxygen only, is followed by its catalytic destruction with the liberation of all the oxygen. J. GRANT.

Reichinstein's displacement principle. F. H. CONSTABLE (Proc. Camb. Phil. Soc., 1928, **14**, 56—64).—An attempt has been made to deduce a new displacement principle for the velocity of a bimolecular reaction at a catalyst surface. Reichinstein ("Die Eigenschaften des Adsorptionsvolumens," 1916) assumed that the total number of molecules of all substances adsorbed by a given surface is constant, and independent of their concentrations in the space around the surface layer. The new work takes into account the lack of heterogeneity of the surface, and the Langmuir–Frankel theory of inelastic collisions of gaseous molecules with a solid surface. R. A. MORTON.

Catalytic decomposition of nitric oxide. S. UCHIDA (J. Soc. Chem. Ind. Japan, 1927, **30**, 171—180).—The author has previously found that the lowering of the yield of the product of the catalytic oxidation of ammonia by too long contact of the gas mixture on the catalyst was largely due to the catalytic decomposition of nitric oxide into nitrogen and oxygen, and concluded that the reaction is of the first order at 600°, the velocity coefficient being 1/170 of that of oxidation of ammonia for the same catalyst. This conclusion is now confirmed experimentally. The catalytic decomposition of pure nitric oxide was effected by a transpiration method by using platinum gauze and ferric oxide (with or without bismuth oxide) as catalyst at various temperatures in the range of 600—1000°. A part of the effluent gas was passed through 90% sulphuric acid, and the amount of nitric oxide decomposed was calculated from the quantity of the higher nitrogen oxide absorbed in the acid. The reaction is of the first order when the temperature is comparatively low (600—700°). At higher temperatures, however, the velocity coefficient as calculated under the assumption of the first-order reaction varies, and, indeed, it decreases gradually with the time of contact. This may be due to the oxygen set free during the reaction (cf. Green and Hinshelwood, A., 1926, 915). The velocity coefficient (as first-order reaction) at 600° is 0·39 for platinum gauze and 0·013 for ferric oxide. These two values are only 1/80 of those obtained by calculation, but the ratio of platinum and ferric oxide values is fairly concordant with the previous calculated value, *i.e.*, 28 : 1. From the temperature–velocity coefficient diagram, the temperature at which nitric oxide begins to dissociate at a platinum surface was found to be 500°, which was in good agreement with the results of various authors. S. OKA.

Reduction of potassium nitrate by water-gas. J. MILBAUER and V. JUDENIČ (Chem. Obzor, 1926, **1**, 16—22; Chem. Zentr., 1927, ii, 1338).—The action of hydrogen on a mixture of potassium nitrate and potassium or sodium hydroxide at 440—480° affords, in the presence of cupric oxide as catalyst, 96% of the calculated yield of nitrite. The action of carbon dioxide at 200—400° gave 65—70%, and of water-gas 70—75% of the calculated yield. The addition of calcium chloride effects no improvement. A. A. ELDRIDGE.

Decomposition of calcium cyanamide. II. Action of Japanese acid earth on calcium cyanamide solution. E. TOMITA (J. Soc. Chem. Ind. Japan, 1927, **30**, 194—198).—The freshly-prepared calcium cyanamide was extracted with water, the solution was added with various amounts of Japanese acid earth, and the whole kept stirred for 1 hr. at various temperatures between 0° and 90°, the amounts of cyanamide in the filtered solution being compared. Addition of the acid earth diminished the alkalinity of the extracted solution and lessened the decomposition in the solution. The effect is more marked if the acid earth is previously dried at 105°. The higher the temperature, the greater was the amount of decomposition, the difference being more marked in the case of the undried earth. N. KAMEYAMA.

Catalytic activity of metallised silica gels. III. Synthesis of water. L. E. SWEARINGEN and L. H. REYERSON (J. Physical Chem., 1928, **32**, 113—120; cf. A., 1927, 839, 1038).—The catalytic activity of the gels previously used (A., 1927, 198) in synthesising water from mixtures of oxygen (6—9%), hydrogen (50%), and nitrogen has been determined over the temperature range −17° to 290° at various rates of flow. The silverised gel initiates the reaction below 100° and its efficiency increases with rise of temperature, the most rapid increase occurring between 140° and 180°. Above 200°, the whole of the oxygen present is removed. The copperised gel shows a measurable reaction at 80°, and the efficiency increases steadily to 165°, when a rapid rise occurs, and at 200° complete conversion of the oxygen into water takes place. The platinum and palladium gels are 100% efficient at all temperatures studied provided the rate of flow of the gas mixture is sufficiently slow, and the platinum gel is the more efficient of the two with the faster rates of flow. The copper catalyst compares favourably with that prepared by Pease and Taylor (A., 1922, ii, 701). L. S. THEOBALD.

Catalysis and the dissolution of aluminium. M. CENTNERSZWER (Z. physikal. Chem., 1928, **131**, 214—225).—Metals which reduce the overvoltage of hydrogen greatly accelerate the dissolution of aluminium in acids when the two metals are placed in contact, on account of the activation of the surface due to removal of the passive layer. In sulphuric acid aluminium is so strongly passive that even platinum is incapable of producing activation, which is, however, gradually brought about by addition of chlorine ions to the solution. Amalgamated aluminium dissolves in *N*-hydrogen chloride solutions 25 times as rapidly as does the pure metal, there being an induction period of 2 hrs. The maximum velocity of evolution of hydrogen from water by the amalgamated metal is 0·12 cm.^{3}/min./cm.^{2}; the surface of the metal rapidly becomes covered with a grey film of aluminium hydroxide, and the dissolution velocity diminishes. H. F. Gillbe.

Copper sulphate as the Deacon chlorine catalyst? R. A. Beebe and D. B. Summers (J. Amer. Chem. Soc., 1928, **50**, 20—24; cf. Taylor, A., 1926, 365).—Hydrogen chloride converts anhydrous copper sulphate quantitatively into copper chloride (or oxychloride) at 450° within 6 hrs. The latter compound, therefore, is the true catalyst when copper sulphate is used in the Deacon process.

S. K. Tweedy.

[Catalytic] conversion of alcohols into petroleum spirit. A. Mailhe and Renaudie.—See B., 1928, 117.

Catalytic preparation of formaldehyde. B. Neumann and P. Biljcevic.—See B., 1928, 82.

Catalytic decomposition of formic acid vapour. C. H. D. Clark and B. Topley (J. Physical Chem., 1928, **32**, 121—126).—The catalytic decomposition of formic acid vapour has been studied by the methods previously used (Hinshelwood and Topley, J.C.S., 1923, **123**, 1014) at 210° for osmium, nickel, tungsten, molybdenum, and tantalum. The values of the unimolecular velocity coefficient, k_{CO_2}, calculated for 200° and a surface of catalyst 1 cm.^{2} in a reaction bulb of 20 c.c. are for osmium $9{\cdot}2\times10^{-2}$, and for nickel 1×10^{-4}. The values of k_{CO}, calculated on the same basis, for silica, pyrex and soda glasses, and tungsten are 1×10^{-6}, $1{\cdot}5\times10^{-6}$, 4×10^{-6}, and $2{\cdot}5\times10^{-5}$, respectively. With molybdenum and tantalum, the decomposition does not follow the usual course, a marked excess of hydrogen being produced, and with nickel, under the conditions employed, no methane was formed (cf. Wescott and Engelder, A., 1926, 693). L. S. Theobald.

Improved activated magnesium for the preparation of the Grignard reagent and a comparative study of various catalysts. H. Gilman, J. M. Peterson, and F. Schulze (Rec. trav. chim., 1928, **47**, 19—27).—By heating with iodine in a vacuum an alloy of magnesium containing 12·75% of copper, a product is obtained which is much more active in Grignard reactions than Baeyer's activated magnesium. It is only necessary to use this compound to start the reaction, which may be continued with the ordinary magnesium catalyst. The copper–magnesium compound loses its activity by exposure to the air for a short time but becomes still more highly active when re-heated. Comparative tests have also been made with a number of catalysts other than activated magnesium. M. S. Burr.

Negative catalysts for the hydrogenation of fatty oils. IV. Influence of impurities in the catalyst-carriers. S. Ueno and T. Saida (J. Soc. Chem. Ind. Japan, 1927, **30**, 374—377).—A sample of the kieselguhr was recovered from a spent nickel catalyst by treatment with dilute sulphuric acid and alkali. Nickel catalysts were prepared by using the original and the recovered kieselguhr, and the results were compared. The recovered kieselguhr was as effective as the original material, in spite of the fact that the former contained much impurity, especially calcium sulphate, which would have had a retarding influence on the catalytic reaction. It is concluded that the inhibiting influence of these impurities depends on their existence in the system in a peculiar form. Y. Tomoda.

Electrolytic formation of magnesium amalgam and its decomposition by the air. N. W. Kondyrev (Ber., 1928, **61**, [*B*], 208—212).—Magnesium amalgam is obtained by electrolysis of an ethereal solution of magnesium ethyl bromide using a mercury cathode and a magnesium anode. The product usually contains less than 1% of magnesium but richer alloys are prepared by squeezing the warmed amalgam and collecting the crystalline portion. The amalgam reacts readily with moist air at temperatures below 40—50° with production of magnesium hydroxide and hydrogen. Above this temperature interval reaction does not occur to any great extent in ordinary air although decomposition takes place in air saturated with aqueous vapour at all temperatures between 15° and 100°. Examination of the electrical resistance, cooling curve, and change in *E.M.F.* with varying temperature does not disclose any discontinuity. The increasing apathy of magnesium amalgam towards air with rise of temperature is attributed therefore to the increasing "humidity deficit." H. Wren.

Electrochemical oxidation of β-phenylpropionic acid. F. Fichter and R. Senti (Festschr. A. Tschirch, 1926, 410—414; Chem. Zentr., 1927, ii, 54—55).—Electrolytic oxidation of β-phenylpropionic acid partly dissolved, partly suspended, in 2*N*-sulphuric acid, with a current density of 0·004 amp./cm.^{2} (the anode being a lead vessel coated with lead dioxide and the cathode a lead stirrer) yields *p*-hydrocoumaric acid (phlorotic acid), together with quinone, quinol, propionic acid, succinic acid, and phenolic condensation products. β-Phenylpropionyl peroxide, m. p. 37°, explodes at 130°, was obtained from β-phenylpropionyl chloride, b. p. 117—119°/13 mm., acetone, and sodium peroxide solution at 0°; when exploded by heating it yielded αδ-diphenylbutane, m. p. 52°. A. A. Eldridge.

Photochemistry of chlorine. F. Weigert and M. Nicolia (Z. physikal. Chem., 1928, **131**, 267—277).—The occurrence of isochromatic fluorescence in pure dry chlorine has been investigated by means of the Bunsen–Roscoe actinometer employed in conjunction with a mercury-vapour lamp. Contrary to expectation, decrease of the distance between the vessel containing chlorine and the actinometer causes the quantity of hydrogen chloride produced to diminish by about 60%. Lambert's law is held to be invalid for chlorine, and the occurrence of fluorescence could not be substantiated. H. F. Gillbe.

Photochemical union of chlorine and hydrogen. I. S. Horiba and T. Ichikawa (Sexagint [Osaka celebration], Kyoto, 1927, 73—94).—The primary changes during the photochemical reaction between chlorine and hydrogen have been studied by recording the minute pressure changes of the reacting system on a photographic film with the aid of an optical lever and oscillograph. The photochemical induction period, in the sense of a period immediately after exposure to light during which the reaction does not proceed, does not exist. For an initial period of 1·5—2 sec., however, the velocity of the reaction changes with time, finally attaining a steady value, and it is this phase of the reaction which is more correctly termed the induction period. The existence of a chain mechanism is confirmed by the results.

H. F. Gillbe.

Photochemical formation of carbonyl chloride. III. M. Bodenstein and T. Onoda (Z. physikal. Chem., 1928, **131**, 153—174).—The principal reaction between chlorine, carbon monoxide, and oxygen at the ordinary temperature results in the formation of carbon dioxide, whilst as the temperature is raised the quantity of carbonyl chloride produced increases, until at 300° formation of carbon dioxide ceases. The course of the reaction at high temperatures is governed by the equation $d[COCl_2]/dt = kI[Cl_2]/[CO]$, where I is the intensity of light absorbed. The reaction is unaffected by oxygen. From 270° to 300° the velocity coefficient of the carbonyl chloride formation is considerably influenced by hydrolysis of the reaction product by water vapour; at the higher temperatures all the water present is removed in the early stages of the reaction. At 400° simultaneous chemical and photochemical formation of carbonyl chloride may be observed by employing low pressures and intense irradiation. The equilibrium of the reaction in the dark is unaltered by illumination. H. F. Gillbe.

Photochemical synthesis of carbonyl chloride. J. Cathala (J. Chim. phys., 1927, **24**, 663—711).—An apparatus is described for measuring the rate of combination of carbon monoxide and chlorine under the influence of rays from a gas-filled quartz mercury lamp. The gaseous mixture was prepared by decomposing purified carbonyl chloride at a temperature above 800°. A method for the purification of carbonyl chloride by distillation in a vacuum is described. The progress of the reaction was examined by determining the proportion of combined and uncombined chlorine in the gaseous mixture after definite periods of illumination. The rate of the reaction is best expressed by the equation $d[COCl_2]/dt = k[CO] \times [Cl_2]^{\frac{3}{2}}$, which is the same as that found by Bodenstein (Rec. trav. chim., 1922, **41**, 585) for the thermal synthesis of carbonyl chloride. Oxygen and carbon dioxide have a strong inhibiting effect on the photochemical reaction, but not on the thermal reaction. The retarding effect of carbon dioxide is due to the oxygen produced by the decomposition of the carbon dioxide by ultra-violet light. If the active rays are screened off, carbon dioxide has no longer any influence on the photochemical reaction. If the photochemical synthesis is carried out at 357° the carbon dioxide is again without effect, probably because the retarding effect of the oxygen is destroyed at this temperature. The course suggested for the photochemical synthesis is the same as that adopted by Bodenstein (*loc. cit.*) for the thermal synthesis.

M. S. Burr.

Photolysis of sodium hypochlorite solutions. A. J. Allmand and W. W. Webb (Z. physikal. Chem., 1928, **131**, 189—204).—The quantity of sodium chlorate produced by the photochemical decomposition of sodium hypochlorite solutions is independent of the chloride, sulphate, and free alkali concentrations, the intensity of illumination, and the hypochlorite concentration from $0·08M$ to $0·01M$; at higher dilutions the chlorate yield diminishes. Increase of the average frequency of the absorbed light results in increased yield. Measurements of the quantum efficiency of the reaction show that at constant frequency decrease of hypochlorite concentration causes the ratio λ (molecules decomposed/quanta absorbed) to decrease markedly, whilst increase of frequency causes a great increase of λ as the 254 $\mu\mu$ group of mercury arc lines is approached. Extinction coefficient measurements show the Lambert–Beer law to be valid for sodium hypochlorite solutions, and that the extinction coefficient is independent of the reaction products. The extinction coefficients for the mercury lines of wave-length 436 and 405 $\mu\mu$ are 0·08 and 0·40, respectively. The mechanism of the decomposition at wave-length 254 $\mu\mu$ cannot be identical with that of the photolysis of aqueous solutions of hypochlorous acid and of chlorine, and a modified scheme is suggested for the reaction. H. F. Gillbe.

Photochemical decomposition of nitrous and nitric oxides. J. Y. Macdonald (J.C.S., 1928, 1—14).—The decomposition of the gases has been studied using light of wave-length 1860—1990 Å. with the object of calculating the quantum efficiency of the processes and of determining the mechanism of the decompositions. These efficiencies were found to be 3·9±0·2 for nitrous oxide and 0·73±0·05 for nitric oxide. The value for nitrous oxide is constant over the range of temperatures employed (0—40°). The absorption coefficient increases 1·47±0·05 times for a rise of 10°. In the experiments, pressures of about 20—650 mm. and exposures varying from 2 to 66·5 min. were employed. With nitrous oxide there is no induction period. It is shown that nitrous oxide absorbs much more strongly than does nitric oxide. Beer's law holds strictly for both gases.

The gases decompose according to the following general equations: $4N_2O=2NO+O_2+3N_2$, $2NO=N_2+O_2$, and $3NO=N_2O+NO_2$ the former reaction predominating for nitric oxide. Possible mechanisms of these changes are discussed. H. Ingleson.

Photochemical decomposition of azomethane. H. C. Ramsperger (J. Amer. Chem. Soc., 1928, **50**, 123—132; cf. A., 1927, 425, 737).—The ultra-violet absorption curve of azomethane is maximal at about 3390 Å. and minimal at 2700 Å. The photochemical decomposition of this substance in the mercury lines at 3660 Å. was followed by pressure measurements; in each of four experiments at different pressures two molecules of gas were decomposed for each light quantum absorbed, which may be due to the activation of an azomethane molecule by transference of energy from a newly-formed ethane molecule. The temperature coefficient does not exceed 1·02 per 10°. The results are discussed in light of the second theory suggested by Rice and the author. S. K. Tweedy.

Thermal and photochemical decomposition of azo-compounds, and the problem of reaction rates. H. C. Ramsperger (Proc. Nat. Acad. Sci., 1927, **13**, 849—853).—A preliminary account is given of experiments which have established that the rate of thermal decomposition of azo*iso*propane is constant in the pressure range 0·025—4·60 cm., and in the temperature range 250—290°. The observed rate corresponds with a heat of activation of 40,900±500 g.-cal. The results are discussed with reference to theory of unimolecular reactions and with the photochemical decomposition of azo*iso*propane.
R. W. Lunt.

Reduction of carbon dioxide by light. E. Baur (Z. physikal. Chem., 1928, **131**, 143—152).—A discussion of the mechanism. H. F. Gillbe.

Photochemical changes of hydrocarbons. S. Tołłoczko (Przemysl Chem., 1927, **11**, 245—253; Chem. Zentr., 1927, ii, 546).—On exposure of ethane to light from a mercury lamp (λ 2300—4000 Å.), hydrogen and methane were produced; the contraction was determined. The composition of the condensate was not determined; the reactions $(x+1)C_2H_6=C_{2(x+1)}H_{4(x+1)+2}+xH_2$ and $(x+1)C_2H_6=C_{(x+2)}H_{2(x+2)+2}+xCH_4$ are postulated. Methane is not affected by the radiation. A. A. Eldridge.

Formation of formaldehyde and of sugars by the action of ultra-violet rays on alkali and alkaline-earth hydrogen carbonates. G. Mezzadroli and G. Gardano (Atti R. Accad. Lincei, 1927, [vi], **6**, 160—165).—The hydrogen carbonates investigated were those of barium, calcium, strontium, magnesium, sodium, potassium, lithium, and ammonium. Of these, the calcium salt is decomposed the most, and the sodium salt the least, rapidly by ultra-violet rays. Ammonium hydrogen carbonate gives a greater proportion of aldehyde than the alkali hydrogen carbonates, but the greatest yield of formaldehyde is obtained from calcium hydrogen carbonate. The amount of formaldehyde formed rises to a maximum and then gradually diminishes, owing to oxidation and polymerisation. The presence of sugar in small amounts is observable immediately formaldehyde appears. T. H. Pope.

Photochemical reactions. Influence of polarised rays on the reaction between sodium and potassium amalgams and water. H. L. Anand and S. S. Bhatnagar (Z. physikal. Chem., 1928, **131**, 134—142).—The influence of polarised light on the reaction between water and amalgams of the alkali metals is selective as regards the polarisation; the greatest influence is exerted when the plane of the electric vector is parallel to the plane of incidence, and the least when the two are at right angles. The conception that the first stage in a photochemical reaction consists in the emission of electrons has been confirmed. H. F. Gillbe.

Becquerel effect. N. Sasaki and K. Nakamura (Sexagint [Osaka celebration], Kyoto, 1927, 249—254).—The Becquerel effect exhibited by the light-sensitive solutions of an iron salt and iodide is due to the change of concentration of the iodide ion.
H. F. Gillbe.

Non-activity of infra-red radiation in thermal acceleration of reduction of ceric ions by acetaldehyde in acid solution. C. Fromageot (Bull. Soc. chim., 1927, [iv], **41**, 1585—1588).—When ceric ions are reduced by acetaldehyde in acid solution at the ordinary temperature, only activated aldehyde molecules are oxidised, and the rate of reaction is ultimately determined by the rate of activation. Infra-red radiation does not influence the rate of reaction, nor does the frequency of the absorbed radiation calculated from the temperature coefficient of the reaction velocity appear to correspond with any of the absorption bands of the aldehyde. This reaction, therefore, does not agree with Perrin's view that the thermal acceleration of a reaction is brought about by certain infra-red frequencies occurring at the higher temperature, unless it is assumed that the radiation is absorbed by the water before it reaches the aldehyde molecules. R. Cuthill.

Characteristic surface of photographic films. H. Arens and J. Eggert (Z. physikal. Chem., 1928, **131**, 297—309).—A three-dimensional method of representation has been developed for the relationships between the degree of blackening of a photographic emulsion and the logarithms of the intensity of illumination and time of exposure. H. F. Gillbe.

Tentative hypothesis of the latent image. A. P. H. Trivelli.—See B., 1928, 107.

Intensification of the latent image. II. Decomposition of hydrogen peroxide and the mechanism of latent image intensification. E. P. Wightman and R. F. Quirk.—See B., 1928, 141.

Intramolecular rearrangement by photochemical action. (Mme.) Ramart-Lucas and F. Salmon-Legagneur (Compt. rend., 1928, **186**, 39—41).—The action of ultra-violet light alone is capable of converting *iso*butyl bromide into *tert.*-butyl bromide and propyl bromide into *iso*propyl bromide without any trace of dissociation. This supports the authors' theory that such changes involve the movement of single electron linkings only, with an intermediate stage in which some of the atoms are linked by semi-valency (cf. Perrin, A., 1927, 1009).
B. W. Anderson.

Changes in carbohydrate solutions due to sunlight in presence of uranium salts and to ultra-violet rays. Abelous, Aloy, and Valdiguié (Compt. rend. Soc. Biol., 1927, **96**, 1385—1386; Compt. rend., 1927, ii, 674).—Lævulose and such sugars as are formed by hydrolysis of other carbohydrates readily suffer change in sunlight in presence of uranium salts and in ultra-violet light with formation of aldehydic substances, particularly formaldehyde.
A. A. Eldridge.

Photolytic action on pure sucrose of the total or filtered radiations of the mercury arc. A. Andant and E. Rousseau (Compt. rend., 1928, **186**, 365—366).—The formation of dextrose in a fresh 5% solution of sucrose containing magnesium sulphate and 1% of sulphuric acid has been determined by Grimbert's method at hourly intervals during irradiation at 15° by the mercury arc. By the use of suitable screens the separate effects of the infra-red, visible, and ultra-violet radiations could be determined, comparison being made with the absorption coefficients determined by a thermopile. The photolytic effect of the infra-red radiation was of the same order as that of the total naked arc, whilst that of the pure radiation λ 3650 Å. (passed by Wood's filter) was much greater. This is an example of the antagonistic effect of rays of different wave-lengths (cf. A., 1927, 738). J. GRANT.

Photobromination of cinnamic acid and stilbene. III. R. M. PURAKAYASTHA and J. C. GHOSH (J. Indian Chem. Soc., 1927, 4, 553—559).—From theoretical considerations the authors deduce that the velocity coefficient for this reaction in yellow light should be given by the equation $k=(1/t)\{[1/(a-x)^{\frac{1}{2}}]-1/a^{\frac{1}{2}}\}+(1/3Bt)\{[1/(a-x)^{\frac{3}{2}}]-1/a^{\frac{3}{2}}\}$, where a is the initial concentration of the bromine, B is a constant, and k, t, and x have their usual meanings. Berthoud had previously given a similar equation but without the second term. Experiments show that the authors' equation is correct and this supports their view of the mechanism of the reaction. An induction period and an after-effect were observed, and Berthoud's rotating-sector method of varying the intensity of the light is criticised. C. D. LANGFORD.

Photo-activation of cod-liver oil. F. HAFFNER and P. PULEWKA (Klin. Wochschr., 1926, 5, 2113—2130; Chem. Zentr., 1927, i, 3204—3205).—Activation of cod-liver oil by light takes place only in presence of oxygen. Boiling inactivates the oil, but it again affects a photographic plate after renewed illumination. Blood or tissue could not be photo-activated by sunlight, but photoactive substances were obtained by the extraction of animal tissue with alcohol and chloroform. A peroxidic substance, to which the photoactivity is due, can be removed from active cod-liver oil by a current of air or carbon dioxide. Experiments suggest that the peroxidic lipin substance may exercise a catalytic effect similar to that of oxidase in biological systems.

A. A. ELDRIDGE.

Reactions in the solid state. W. JANDER (Z. angew. Chem., 1928, 41, 73—79).—A *résumé* and discussion of recent work, from which it is concluded that reactions may occur between solids, depending on the possibility of changes of position of atoms within the crystals; an apparatus for the examination of heterogeneous equilibria at high temperatures and pressures is described. S. I. LEVY.

Structure of hydrogen peroxide, and mechanism of its reactions. P. N. RAIKOV (Z. anorg. Chem., 1928, 168, 297—304).—It is suggested that hydrogen peroxide is an equilibrium mixture of two tautomeric forms, a true peroxide, $H_2O\cdots\cdots O<$, and a pseudo-form, H·O·O·H. In the true form, which is the source of the oxidising properties of hydrogen peroxide, the reactive oxygen atom is held loosely by the secondary valencies of the other oxygen atom, thus causing the hydrogen atoms also to be held less firmly, so that one of them migrates without difficulty to form the symmetrical pseudo-form. It is presumably owing to the readiness with which this change occurs, and to the presence of only a small proportion of the true form in the equilibrium mixture, that the reducing action of hydrogen peroxide, which must be ascribed to the pseudo-form, takes place so rapidly. The change of the pseudo-form into the true form, on the other hand, apparently occurs relatively slowly, which would account for the comparative slowness with which hydrogen peroxide effects oxidation at the ordinary temperature. The spontaneous decomposition of the peroxide may be ascribed to the interaction of the tautomerides, so that foreign substances will promote or hinder the decomposition according as they accelerate or retard the tautomeric change.

R. CUTHILL.

Hydrogen peroxide as an oxidising agent in acid solution. VIII. W. H. HATCHER and G. W. HOLDEN (Trans. Roy. Soc. Canada, 1927, [iii], 21, III, 237—243; cf. A., 1925, ii, 684, *et seq.*).—A method of Clover and Houghton (A., 1904, i, 707) has been adapted to the determination of peracid in mixtures containing relatively large quantities of organic acid and hydrogen peroxide. Iodine is liberated from potassium iodide solution and titrated with 0·0143*N*-thiosulphate solution. With acetic, glycollic, lactic, and formic acids, but not with oxalic acid, hydrogen peroxide forms a peracid. Contrary to the statement of Clover and Richmond (A., 1903, i, 396), the reaction is reversible and a catalyst is not essential. The time required for the attainment of equilibrium at 0°, in the different acids, and for different values of the concentration ratio hydrogen peroxide/acid, has been determined, and the values of the equilibrium constants have been calculated. In addition, the equilibria in acetic and glycollic acids have been studied at the ordinary temperature. M. S. BURR.

Union of helium with mercury. J. J. MANLEY (Phil. Mag., 1927, [vii], 4, 699—720).—Preliminary experiments with certain pure common gases at a pressure of a few mm. are described and the results summarised. For each experiment the gas was contained over mercury within an oscillating barometric tube, and in every instance a solid mercury compound was formed. Similar experiments made with helium resulted in a lessened pressure, from which the synthesis of a helide was inferred. Experiments show that the helide is incondensible at the temperature of liquid air. Various synthesisers were next used, the most efficacious being a form of Siemens ozone generator containing platinised asbestos. For an analysis, the compound was decomposed by a heated platinum spiral and the resultant mercury determined with a special micro-balance. The first quantitative experiment led to the formula $HgHe_{10}$. In all subsequent experiments conducted with the utmost care, pressure changes were almost negligible. In one of these experiments, the density of the gaseous mixture was measured with an Aston micro-balance and from this and the weight of the mercury obtained, the formula found was HgHe or $HgHe_2$. Experiments with a quartz spectrograph led to the conclusion that the helide is rapidly resolved into its constituents when traversed by an intense beam of ultra-violet light; difficulty was therefore experienced in photographing an expected absorption line. The line, a very weak one, was obtained on two occasions only; its wave-length was 2624; the value found by Messrs. Hilger was 2638 Å. Confirmatory evidence for the synthesis and continued existence of mercury helide was obtained with the aid of interferometers. The pressure most favourable for the synthesis appears to be 6 mm. Similar experiments made with argon in the same apparatus led to results entirely negative.

J. J. Manley.

Refractive indices of alkali fluoborates. J. H. de Boer (Physica, 1927, 7, 99—101; Chem. Zentr., 1927, ii, 205).—Directions, for instructional purposes, are given for the preparation of potassium fluoborate and for the study of its optical properties.

A. A. Eldridge.

Complex copper silicates. A. Duboin (Compt. rend., 1928, **186**, 234—235).—The compound $K_2O,CuO,4SiO_2$ has been produced in the form of blue crystals (d^0 2·87), readily decomposed by hydrochloric acid, by the addition of silica and copper oxide to a bath of fused potassium fluoride. The mass is allowed to cool and then reheated in the presence of an excess of potassium chloride. Compounds of the type $Al_2O_3,2CuO,3K_2O,6SiO_2$ (small, blue, prismatic needles, d^0 2·8) are produced by the addition of silica and the oxides concerned to molten potassium fluoride.

J. Grant.

Recent attempts at the transmutation of the elements. F. Wolfers (J. Chim. phys., 1927, **24**, 727—735).—An attempt has been made to obtain gold from mercury by passing a current of a few milliamp., at 3000—4000 volts, through powdered mercuric chloride for about 100 hrs. Tests with stannous chloride indicated the presence of a trace of gold corresponding with the limits of sensitiveness of the method. By spectroscopic tests, which were less sensitive, the results were negative. The different methods employed in attempts to transmute the elements are critically examined, and the conclusion is reached that, apart from the work of Rutherford and his colleagues, none of these has given results which may be regarded as undoubtedly positive.

M. S. Burr.

Gold purple. II. C. G. Fontana (Atti R. Accad. Lincei, 1927, [vi], **6**, 231—235; cf. Levi and Fontana, A., 1927, 1128).—Substances analogous to purple of Cassius may be prepared from an alkaline, red gold sol without the use of a reducing agent such as a stannous salt, the hydroxide of aluminium, zirconium, or thorium serving as supporting material. The aluminium-gold purple obtained in this way contains 10·80% Au, 66·60% Al_2O_3, and 21·61% H_2O. *X*-Ray analysis shows its structure to be identical with that of purple of Cassius, the gold being present in the elementary form and the aluminium hydroxide being practically amorphous; the side of the granule (Λ), supposed cubic, is 32·8 Å., that of purple of Cassius being 36 Å. The zirconium-gold purple contains 10·21% Au, 63·56% ZrO_2, and 25·37% H_2O; Λ=36·8 Å. Thorium-gold purple contained 11·80% Au, 63·53% ThO_2, and 24·87% H_2O, but its structure was not rendered evident by *X*-ray analysis.

T. H. Pope.

Formation of crystallised silicates in aqueous media. V. N. Ipatiev and B. Mouromtsev (Bull. Soc. chim., 1927, [iv], **41**, 1588—1593).—See A., 1927, 1044.

Relation between resistance of glass to acids and alkalis, and hydrogen-ion concentration. O. K. Botwinkin and A. M. Tanchilevitsch (Z. anorg. Chem., 1928, **168**, 356—360).—The loss in weight of powdered samples of a window glass and a bottle glass after being subjected to the action of solutions of potassium hydroxide and hydrochloric acid at concentrations of 0·01—10*N* for 4 hrs. at the ordinary temperature has been determined. With the window glass, the solvent action of the alkali increased with the concentration up to about 0·25*N*, beyond which no further change occurred, whereas the action of the acid, which was throughout the smaller, did not vary greatly with the concentration. In no case, however, did the p_H of the solutions show a change as a result of contact with the glass. The relatively high solvent power of the alkali compared with the acid is ascribed to the greater readiness with which it attacks the free silica.

R. Cuthill.

Separation of metals and their oxides from solutions of salts by hydrogen under pressure. V. N. Ipatiev and V. Niklaev (Bull. Soc. chim., 1927, [iv], **41**, 1591—1598).—The effect of hydrogen under pressure on solutions of stannic chloride and sulphate, and suspensions of the hydroxide at 300—400°, has been studied. With the hydroxide, stannous hydroxide and tin result. The sulphate gives mixtures, the composition of which depends on the conditions, but they may contain stannous sulphate and sulphide, a polysulphide, α-metastannic acid, and the metal. Sulphuric acid and copper sulphate hinder the reaction, reduction going no further than stannous sulphate and stannic sulphite, respectively. The chloride yields stannous chloride, and stannous hydroxide or stannic oxide, the separation of tin starting at about 280°, but in relatively small amount. In presence of silver chloride, a compound which is probably a basic stannous chloride appears.

R. Cuthill.

Physico-chemical properties of stannous oxide. C. G. Fink and C. L. Mantell (J. Physical Chem., 1928, **32**, 103—112).—The effect of heating pure stannous oxide in various atmospheres in an electric furnace has been followed by microscopic examination of the products formed. Above 385°, in an atmosphere of nitrogen, stannous oxide decomposes into tin and the dioxide, and above 240° moist or dry air readily oxidises it. At higher temperatures, it becomes pyrophoric. Sulphur dioxide in acid solution oxidises, and in alkaline solution reduces this oxide. Ditte's method (Ann. Physik, 1882, **27**, 145) for the preparation of stannous oxide readily gives a product of high purity provided that the final value of the p_H of the solution lies between 5 and 6·5. The reduction of stannous oxide by hydrogen takes place in a single stage above 385°, but below this temperature the two stages represented by the equations $SnO_2+H_2=SnO+H_2O$ and $SnO+H_2=Sn+H_2O$ occur.

L. S. Theobald.

Lead tree. V. Kohlschütter (Festschr. A. Tschirch, 1926, 425—430; Chem. Zentr., 1927, i, 3178).—A discussion of the processes controlling the formation of a " lead tree " from zinc and lead salt solution. In addition to ionic reaction and to the influence of crystal form, subsidiary reactions between the deposited metal and dissolved salt influence the development of the tree.

A. A. Eldridge.

Nature of active nitrogen. Synthesis of ammonia from the elements. B. Lewis (J. Amer. Chem. Soc., 1928, **50**, 27—35).—Experiments are described showing that ammonia is formed only when active nitrogen is mixed with atomic hydrogen, indicating that the former contains nitrogen atoms. No ammonia is produced when the nitrogen or hydrogen alone is activated, and hydrazine is never formed. The current interpretations of the spectroscopic data of nitrogen are supported. Glowing active nitrogen is probably a heterogeneous mixture of nitrogen atoms and excited nitrogen molecules.

S. K. Tweedy.

Compounds of hydrazine with metallic sulphites and nitrites. P. Rây and B. K. Goswami (Z. anorg. Chem., 1928, **168**, 329—338).—Neutralisation of a solution of manganous sulphite in an excess of sulphurous acid with hydrazine hydrate yields a white, crystalline *compound*, $MnSO_3,N_2H_4,H_2SO_3$. A solution of cobalt hydrogen sulphite treated in the same way gives a red *compound*, $5CoSO_3,9N_2H_4,6H_2O$, but if it is added to an excess of a concentrated hydrazine hydrate solution the product is $CoSO_3,2N_2H_4,H_2O$ (buff). By the action of sulphur dioxide on a suspension of the latter salt, the *compounds* $CoSO_3,2N_2H_4,H_2SO_3,2H_2O$ (red) and $CoSO_3,N_2H_4,H_2SO_3,0{\cdot}5H_2O$ (red) are formed, whilst under the same conditions the other salt gives $2CoSO_3,N_2H_4,3H_2O$ (brown). A solution of nickel hydrogen sulphite added to an excess of a concentrated hydrazine hydrate solution yields a red *compound*, $NiSO_3,3N_2H_4,H_2O$, but with an amount of dilute hydrazine solution sufficient only to produce neutrality, there results the blue *salt*, $NiSO_3,2N_2H_4,H_2O$, which yields green *crystals* of $4NiSO_3,3N_2H_4,7H_2O$ when treated with sulphur dioxide. Addition of a solution of zinc hydrogen sulphite to an excess of concentrated hydrazine solution gives rise to the *compound* $ZnSO_3,2N_2H_4,1{\cdot}5H_2O$ (white), which reacts with sulphur dioxide to give $ZnSO_3,N_2H_4,H_2SO_3$ (white). By neutralising a solution of cadmium hydrogen sulphite with dilute hydrazine hydrate solution, a white *solid*, $CdSO_3,N_2H_4$, is obtained, and from this by the action of sulphur dioxide the *salt* $CdSO_3,N_2H_4,H_2SO_3$ (white). *Compounds* of hydrazine with the nitrites of cobalt, nickel, and cadmium, $2Co(NO_2)_2,3N_2H_4$ (red), $Ni(NO_2)_2,2N_2H_4$ (blue), and $Cd(NO_2)_2,2N_2H_4$ (white), respectively, are formed by the addition of a hydrazine hydrate solution to a mixed solution of the corresponding acetate and an excess of sodium nitrite at 0°.

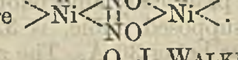
R. Cuthill.

Radical-like alkali salts of a new acid containing nitrogen and oxygen. E. Zintl and O. Kohn (Ber., 1928, **61**, [*B*], 189—199).—A solution of sodium nitrite in liquid ammonia is immediately converted by a similar solution of sodium into the intensely yellow *sodium hydronitrite*, Na_2NO_2; with excess of the metal reduction slowly proceeds further. The salt may also be prepared by cathodic reduction of sodium nitrite in liquid ammonia in a divided cell. Sodium nitrite behaves similarly towards lithium or potassium, but reacts only slowly with calcium. When pure, the alkali hydronitrites appear stable even when gently heated in a vacuum or in nitrogen; at 100—130° violent decomposition ensues with evolution of nitrogen and formation of a lemon-yellow residue containing alkali hydroxide, nitrite, and nitrate. The change appears similar to that observed by Divers (J.C.S., 1899, 75, 102) with sodium hyponitrite, thus suggesting that the primary change is disproportionation to nitrite and hyponitrite. Slow addition of oxygen under conditions which preclude thermal decomposition results in the absorption of 1 atom of oxygen per mol. of hydronitrite with formation of an unstable, brown *peroxide*, (?) $(Na_2NO_2)_2{:}O_2$, decomposed by water into oxygen, sodium nitrite and hydroxide, and hydrogen peroxide. Sodium hydronitrite (1 mol.) absorbs 1 atom of iodine from its ethereal solution giving a black, additive *product*, which rapidly decomposes into sodium nitrite and iodide; with nitric oxide and carbon dioxide it reacts so violently that the products cannot be investigated. Water vapour decolorises sodium hydronitrite with production of nitrous and nitric oxides, sodium hydroxide, nitrite, hyponitrite, and a little nitrate; the course of the change depends somewhat on the conditions, suggesting an initial disproportionation into nitrous acid and dihydroxyammonia. Determinations of the mol. wt. of alkali hydronitrites are precluded by absence of a suitable solvent. It appears probable that addition of sodium to sodium nitrite occurs at the oxygen rather than the nitrogen atom and the hydronitrites $-N(ONa)_2$ are thus analogous to Schlenk's metallic ketyls.

Reduction of alkali nitrates by alkali metals in the presence of liquid ammonia yields alkali oxide and nitrite; the latter is subsequently transformed into hydronitrite.

H. Wren.

Action of nitric oxide on the thiosulphates of the metals of the eighth group. I. L. Cambi and A. Clerici (Atti R. Accad. Lincei, 1927, [vi], **6**, 448—453).—The structure of complex salts of the Roussin's salt type is discussed, and the view that these compounds contain univalent iron, cobalt, or nickel, with the nitrosyl group as a neutral added group, is rejected (cf. Manchot, A., 1927, 33). Investigations of the nitrosothiosulphates of cobalt and of nickel confirm the hyponitrite structure for these compounds. The action of nitric oxide on nickel thiosulphate is discussed and the chemical behaviour of the compound $K_3[NO{\cdot}Ni(S_2O_3)_2],2H_2O$ is described. It is considered that this salt contains hyponitrous residues with the probable structure



$>\overset{\text{II}}{\mathrm{Ni}}<\begin{matrix}\mathrm{NO}\\ \|\\ \mathrm{NO}\end{matrix}>\overset{\text{II}}{\mathrm{Ni}}<$.

O. J. Walker.

Arsine from fused glass. H. M. Elsey (Science, 1927, **66**, 300).—A garlic-like odour was observed when fused borosilicate glass was drawn out so as to expose a fresh surface. The odour is ascribed to arsine, and it is suggested that the odour of arsenic vapour is due to the presence of arsine.

A. A. Eldridge.

Reaction between arsenite and permanganate in sulphuric acid solution. J. Holluta (Z. anorg. Chem., 1928, **168**, 361—368).—The conclusions of Oryng (A., 1927, 742) respecting the mechanism of the above reaction are critically examined in the light of the results previously obtained by the author (A., 1925, ii, 422). R. Cuthill.

Bismuth nitrates. E. Moles and E. Sellés (Anal. Fís. Quím., 1927, **25**, 453—483; cf. Picon, A., 1926, 36; Hepner, *ibid.*, 487, 488).—On dissolution of bismuth in nitric acid and subsequent treatment of the resulting product (keeping in a vacuum or in a current of dry air or carbon dioxide at various temperatures) the compounds $Bi(NO_3)_3,5H_2O,BiONO_3$ (anhydrous, or $+2$, 1, or $0{\cdot}5H_2O$) and $BiONO_3,BiO{\cdot}OH$, respectively. These compounds are regarded as salts of orthonitric acid and are ascribed the formulæ: $[Bi(H_3NO_4)_2(H_2O)_2]NO_4]$, $BiNO_4$, and $BiNO_4,BiO{\cdot}OH$. The co-ordination number 4 is that obtaining in the complex compounds of bismuth. The advantages of the classification indicated are pointed out.

When bismuth is dissolved in nitric acid, precautions being taken to keep the temperature as low as possible, and the resulting solution kept at 60—70°, nacreous, tabular crystals of the monohydrated orthonitrate are deposited. On further heating, prismatic crystals of the complex salt are obtained. When heated in a current of dry carbon dioxide the complex salt is converted into the anhydrous orthonitrate. When kept over sulphuric acid the complex salt loses water and nitric acid. J. S. Carter.

Preparation of iodobismuthites. (Miss) E. M. Bartholomew and G. J. Burrows (J. Proc. Roy. Soc. New South Wales, 1926, **60**, 208—210).—By interaction between bismuth iodide and an organic base in hydriodic acid solution, crystalline *hexaiodobismuthites* having the following formulæ have been prepared: with aniline, $(NH_3Ph)_3BiI_6$ (yellow); with pyridine, $(C_5H_5NH)_3BiI_6$ (scarlet); with dimethylaniline, $(NPhMe_2H)_3BiI_6$ (red); and with *p*-toluidine, $(C_6H_4Me{\cdot}NH_3)_3BiI_6$ (yellow). By taking phenyldimethylarsine and bismuth iodide in the proportions required to give the hexaiodo-compound and treating with excess of hydriodic acid, a *tetraiodobismuthite*, $(AsPhMe_2H)BiI_4$ (scarlet), was obtained.

R. Cuthill.

Element 91; its properties and preparation. A. von Grosse (Ber., 1928, **61**, [*B*], 233—245; cf. Hahn and Meitner, A., 1918, ii, 345; Soddy and Cranston, *ibid.*, ii, 211).—The crude material consisted of residues from Joachimsthal pitchblende in which, after initial purification, protoactinium was present in concentration about 7×10^{-6}. It contained other radioactive substances from which it was freed by treatment with hydrofluoric acid (cf. Hahn and Meitner, A., 1920, ii, 147), after which it contained: $ZrO_2(HfO_2)$ 10—15%, TiO_2 about 60%, Fe_2O_3 2—3%, Ta_2O_5,Nb_2O_5 about 3·5%, P_2O_5 13%, together with sulphate, water, and silica. Fusion of the material with potassium carbonate and dissolution of the residue in water removed almost all the oxides of tantalum and niobium as tantalate and niobate with the phosphoric acid, whereas more than 99% of the protoactinium remained with the insoluble basic oxides, thus demonstrating the great difference in basicity between the pentoxides of tantalum and protoactinium. The oxides were evaporated with sulphuric acid or fused with sodium hydrogen sulphate and the solution of the residue, after addition of so much hydrochloric acid that the concentration attained 10—25%, was treated with concentrated phosphoric acid (or phosphate) whereby 80—90% of the protoactinium was precipitated as phosphate together with zirconium and hafnium phosphates, whereas the other metals remained in solution (under ordinary analytical conditions the precipitation of protoactinium by phosphoric acid is quantitative). Fusion of the mixed phosphates with potassium carbonate (1 : 4) removed phosphoric acid, whilst protoactinium oxide remained quantitatively with the oxides of zirconium and hafnium. Further concentration of protoactinium oxide was effected by a "spiral" process involving the three operations (1) precipitation with phosphoric acid, (2) fusion with alkali carbonate, and (3) fractional crystallisation of the oxychlorides from concentrated hydrochloric acid. In this manner, 27·40 mg. of zirconium oxide were obtained containing at least 6% of protoactinium oxide. Isolation of the latter was effected (1) by addition of thorium oxide and precipitation of the latter as thorium oxalate accompanied by 70—90% of the protoactinium; thorium was subsequently removed as the fluoride and protoactinium precipitated from the filtrate by ammonia; (2) by dissolving the oxides in warm, dilute hydrochloric acid and precipitation of protoactinium by oxalic acid. In this manner, about 2 mg. of *protoactinium oxide* (probably pentoxide) were obtained, the activity of which could not be increased by repetition of the separation process, the product being a colourless, difficultly fusible powder which scarcely emitted light. Its mg.-activity was 622,000 α units. The half-life period of protoactinium, deduced from the α-activities of the pure oxides of protoactinium and uranium, is about 20,000 years, thus agreeing within the limits of experimental error with the datum of Hahn and Walling (Naturwiss., 1927, **39**, 803). On the basis of this value the quantities of protoactinium in radioactive equilibrium with a definite amount of uranium are greater than previously supposed. H. Wren.

Composition of ozone and the time-energy factor in ozone formation. P. C. Saunders and A. Silverman.—See B., 1928, 89.

Thio-salts. IV. Derivatives of a hypothetical thio-aquic acid. L. Fernandes (Atti R. Accad. Lincei, 1927, [vi], **6**, 165—170; cf. this vol., 34).—Parathiomolybdates, $[H_2(MoS_4)_6]H_5R'_5$, completely analogous to the paramolybdates, are described. The ammonium salt, $[H_2(MoS_4)_6](NH_4)_5H_5$, may be obtained in three ways: (1) by leaving solid ammonium thiomolybdate, $(NH_4)_2MoS_4$, under a bell-jar in presence of an open vessel containing ammonia solution; (2) from an aqueous solution of the same salt, slowly in the cold, more rapidly on heating; if the latter is too violent the *trithiomolybdate*, $[H_2(MoS_4)_6](NH_4)_4H_6,16H_2O$, may be formed; (3) by saturating a cold concentrated solution of the normal salt with hydrogen sulphide. The last method is general and is the only known way of obtaining the alkali parathiomolybdates.

These compounds are highly stable and are only slightly soluble in water, by which they are decomposed at the b. p. The action on them of dilute acid precipitates molybdenum sulphide and liberates hydrogen sulphide, the liquid becoming blue owing to the formation of molybdenum-blue. The parathiomolybdates contain 3·5 mols. of hydrogen sulphide of constitution, which, unlike water of constitution, may be determined by ordinary methods. They are derived from a hypothetical thioaquo-acid, $[H_2S_6]H_{10}$ (cf. A., 1927, 636), in which the sulphur atoms may be replaced by the groups MoS_4, co-ordinated by two atoms of hydrogen.

Ammonium parathiomolybdate ($+15H_2O$) forms a deep red, crystalline powder, and the *guanidine* salt ($+8H_2O$) deep red, radiating crystals with green reflexion; the *potassium* salt ($+16H_2O$) is more stable than the two preceding compounds. T. H. Pope.

Detection of intermediate products in oxidations with chromic acid. C. Wagner (Z. anorg. Chem., 1928, **168**, 279—291; cf. following abstract).—If a solution of chromic acid is added to a mixed solution of potassium iodide and sodium hydrogen carbonate, no free iodine is formed, but a reacting mixture of oxalic and chromic acids will liberate appreciable amounts of iodine from the iodide. It is therefore to be concluded that some active intermediate product is formed in the reaction between chromic acid and oxalic acid, and the same is true for the reaction between chromic acid and tartaric acid. This substance is so unstable that it can scarcely be hydrogen peroxide, or a compound of the nature of percarbonic acid, and attempts to detect the formation of these substances have, in fact, been futile, nor is there any evidence in favour of the existence of chromic acid–oxalic acid complexes. In the reaction between chromic acid and lactic acid, however, the intermediate product is more stable, probably owing to the formation of a complex compound with the lactic acid, and proves to resemble pyridinium oxytetrachlorochromanate so closely in behaviour that it is presumably a compound of quinquevalent chromium. This would be in accordance with Jabłczyński's suggested explanation of the apparently autocatalytic nature of the initial stages of the reaction between oxalic acid and chromic acid (A., 1908, ii, 935). In the oxidation of thiocyanic acid, the active substance can be extracted with ether, although it is accompanied by thiocyanogen. The retarding action of manganous salts on the oxidation of formic acid or lactic acid by chromic acid (Dhar, J.C.S., 1917, **111**, 707; Dey and Dhar, A., 1927, 116) is probably to be ascribed to their promoting the transformation of quinquevalent chromium into sexa- and ter-valent compounds. R. Cuthill.

Induction of the reaction between chromic acid and iodide by ferrous salts. C. Wagner and W. Preiss (Z. anorg. Chem., 1928, **168**, 265—278).—Luther's theory (A., 1904, ii, 244; 1907, ii, 555) that the induction of the reaction between chromic acid and iodides by ferrous salts is due to the formation of quinquevalent chromium ions by reaction between ferrous ions and sexavalent chromium ions, these then oxidising other ferrous ions and also iodide ions, has been examined experimentally. Since the equilibrium $Cr^{VI}+Fe^{II} \rightleftharpoons Cr^{V}+Fe^{III}$ is apparently established very rapidly, and the rate of oxidation of ferrous salts by chromic acid is proportional to the square of the concentration of ferrous salt (Benson, A., 1904, ii, 316), the reaction between the Cr^{V} and ferrous ions can primarily involve only one of the latter, the mechanism being somewhat as follows: (*a*) $Cr^{V}+Fe^{II} \longrightarrow ?$; (*b*) $?+Fe^{II} \longrightarrow Cr^{III}+2Fe^{III}$. The reaction with the iodide ion also probably occurs in two stages, with hypoiodous acid as an intermediate product, thus: (*c*) $Cr^{V}+I' \longrightarrow Cr^{III}+HIO$; (*d*) $HIO+H^{\cdot}+I' \longrightarrow I_2+H_2O$. The ratio, *K*, of k_1 to k_2, the velocity coefficients of reactions (*a*) and (*c*) respectively, has been calculated from the amount of iodine liberated when a solution of potassium dichromate is added to a mixed solution of potassium iodide and ferrous chloride acidified with hydrochloric acid, and containing a considerable concentration of potassium chloride, this last being present in order to eliminate disturbances due to variations in the neutral salt effect and degrees of dissociation. Even if the variation of the hydrogen-ion concentration is taken into account, the values of *K* obtained in this way show systematic deviations, which are not, however, such as would result if the orders of equations (*a*)—(*d*) were incorrect. The cause of this anomaly seems rather to lie in a splitting up by a side reaction of the Cr^{V} ions, perhaps into sexa- and ter-valent compounds, for the constancy of *K* is much improved if the reaction mixture contains ferric ions at the outset, and these would, according to the above equilibrium equation, reduce the concentration of Cr^{V} ions. Under these conditions, the value of *K* does not vary greatly with change in the hydrogen-ion concentration, so that k_1 and k_2 must vary in the same way. Experiments on the addition of solutions of pyridinium oxytetrachlorochromanate in glacial acetic acid (Weinland and Fridrich, A., 1906, i, 37) to aqueous iodide solutions shows that in aqueous solution the Cr^{V} ions are very rapidly transformed into sexa- and ter-valent ions, and also that compounds of this type do actually contain quinquevalent chromium. R. Cuthill.

Hydroxylaminomolybdates and complex molybdomolybdates. Action of hydroxylamine on paramolybdates. G. Canneri (Gazzetta, 1927, **57**, 872—880).—Following a discussion of their structure the preparation of the following complex *molybdates* is described: $4MoO_3.4NH_2OH,(NH_4)_2O$; $4MoO_3,4NH_2OH,K_2O$; $4MoO_3,4NH_2OH,Na_2O$;

$4MoO_3,4NH_2OH,(CH_6N_3)_2O$;

$Mo_2O_5,4MoO_3,2(NH_4)_2O,8H_2O$,

$Mo_2O_5,4MoO_3,Na_2O,10H_2O$, and

$Mo_2O_5,4MoO_3,2K_2O,5H_2O$.

R. W. Lunt.

Reaction of several metallic ions in the presence of tartaric acid. S. Hakomori (Sci. Rep. Tôhoku, 1927, **16**, 841—859).—The behaviour of solutions of uranium, lead, titanium, tin, zirconium, antimony, copper, zinc, nickel, cobalt, manganese, and beryllium salts in the presence of tartaric acid has been examined by electrical conductivity, refractometric, ultramicroscopic, and spectroscopic methods. Sexavalent uranium in neutral solution appears to form a complex salt containing one atom of metal to one molecule of tartaric acid, which on exposure to bright sunlight undergoes photochemical reduction to the quadrivalent state; alkalis precipitate a greenish-brown hydroxide from the reduced solution. Lead forms a 1 : 1 complex with tartaric acid only in alkaline solution. Nickel and cobalt in neutral solution give a 1 : 1 complex salt and quinquevalent antimony in acid solution yield similarly a 1 : 2 salt. No satisfactory evidence of the existence of complex salts of the other metals in solution could be obtained. The cobalt complex is completely converted into an ammine by treatment with ammonia; the nickel complex is partly so converted and the copper complex remains unchanged. A. R. Powell.

Action of hydrogen peroxide on ferrous salts. W. Manchot and G. Lehmann (Annalen, 1928, **460**, 179—201).—It is concluded, from the results of four different sets of experiments, that the interaction of hydrogen peroxide and ferrous salts at very low concentrations proceeds in accordance with the equations: (1) $2FeSO_4+3H_2O_2=Fe_2O_5+2H_2SO_4+H_2O$ and (2) $Fe_2O_5=Fe_2O_3+2O$. In presence of potassium iodide, the following equations apply: (1) $2FeI_2+3H_2O_2+6KI=2FeI_5+6KOH$, (2) $2FeI_5=2FeI_3+2I_2$, and (3) $2FeI_3+6KOH=2Fe(OH)_3+6KI$. Manchot's previous assumption of the necessary intermediate formation of the peroxide, Fe_2O_5, is fully substantiated. In concentrated solutions, more hydrogen peroxide is decomposed than is required by the above equations, owing to its interaction with the iron peroxide. This second decomposition cannot be catalytic in action.

In very dilute solutions, a little acid decelerates oxidation of ferrous salts by hydrogen peroxide; addition of more acid after a certain concentration is reached causes, however, an increased velocity of oxidation. The total effect of addition of acid is to cause the initial reaction and the reaction following it to proceed at more equal rates than is the case in absence of acid. In concentrated solutions, the presence of acid diminishes the total decomposition of hydrogen peroxide. The course of the action of hydrogen peroxide on ferrous salts in presence of either potassium iodide or formic acid as acceptor is complicated and difficult to interpret. The peroxide, Fe_2O_5, however, is in all cases formed intermediately. E. E. Turner.

Transformations of iron in nature. II. Importance of micro-organisms in the dissolution and precipitation of iron. R. L. Starkey and H. O. Halvorson (Soil Sci., 1927, **24**, 381—402; cf. Halvorson and Starkey, A., 1927, 425).—The activities of mixed cultures of soil micro-organisms in causing oxidation, reduction, and precipitation of iron in various media and under different conditions have been studied. Under aërobic conditions, in solutions containing dextrose, iron may be dissolved as a result of production of acid. Under anaërobic conditions, in dextrose or peptone media, iron as ferric hydroxide may be dissolved and reduced as a result of decreased oxygen pressure and formation of acid; on exposure to air of solutions in which this has taken place, the iron may be reprecipitated. The latter change may occur in absence of bacterial activity. Precipitation of iron from organic compounds depends on the action of organisms which decompose the organic radicals and not on direct action on the iron. The authors consider that, although ferric hydroxide is precipitated by the action of various groups of micro-organisms, such precipitation under natural conditions is much less frequently due to "iron" bacteria than is generally assumed, and that it is not proved that precipitation of ferric hydroxide by these organisms can take place under conditions where it could not proceed independently of them. C. T. Gimingham.

[Bivalent ruthenium.] H. Remy and T. Wagner (Ber., 1928, **61**, [*B*], 151—153).—The discrepancies between the observations of the authors (A., 1927, 328) and of Gall and Lehmann (this vol., 142) are probably due to differences in the nature of the ruthenium compounds used. H. Wren.

Acid-forming properties of osmium tetroxide. D. M. Yost and R. J. White (J. Amer. Chem. Soc., 1928, **50**, 81—84).—The distribution ratio of osmium tetroxide between carbon tetrachloride and water is greatly diminished when the water contains sodium hydroxide and slightly diminished when it contains potassium chlorate. The acid H_2OsO_5 (which it is proposed to call perperosmic acid) is presumably produced; from the results, $[H^{\cdot}][HOsO_5{}'] / [H_2OsO_5] = K_a = 8 \times 10^{-13}$ at 25°. The acid is thus weaker than carbonic acid. S. K. Tweedy.

Precipitation of iridium from solution by hydrogen under pressure. V. Ipatiev and I. Andreevski (Bull. Soc. chim., 1927, [iv], **41**, 1466—1467).—See A., 1927, 844.

Platinum group metals. VIII. Liberation of chloroiridic acid. S. Nagami (J. Chem. Soc. Japan, 1927, **48**, 501—503).—Chloroiridic acid ($H_2IrCl_6,6H_2O$) was isolated as blackish-red triclinic crystals by dissolving iridium oxide prepared from potassium chloroiridate in concentrated hydrochloric acid and concentrating the solution in a current of chlorine. The compound is very deliquescent in air, and is a strong acid of the order of hydrochloric acid and chloroplatinic acid. Its dissociation is: $H_2IrCl_6 \rightleftharpoons 2H^{+}+IrCl_6{}^{--}$. K. Kashima.

Preparation of oxygen-free nitrogen or hydrogen. A. V. Hill (J. Sci. Instr., 1928, **5**, 22—24).—The purification of a gas from oxygen by passing through a porcelain filter into alkaline sodium hyposulphite (A., 1926, 699) is rendered more effective by using a negatively-charged filter, which produces much smaller bubbles. C. W. Gibby.

Isolation of florentium (element 61). L. Rolla and L. Fernandes (Gazzetta, 1927, **57**, 704—712).—Details are given of the recrystallisation technique adopted in order to obtain a solid solution containing approximately 5% of the double nitrate of thallium and element 61, $Fr(NO_3)_3,2TlNO_3,4H_2O$. R. W. Lunt.

Magnitude of observation errors in chemical analysis. F. Goudriaan (Chem. Weekblad, 1928, 25, 52—57).—The extent to which results may be influenced by inaccuracies in measurement and observation is considered for typical methods of analysis. In ordinary gravimetric work in which atomic weights approximated to the first decimal place are used, only the first three significant figures can be accurate. Similar degrees of accuracy are obtained with direct titrations and in standardisation of solutions. Indirect titrations and determinations are subject to considerably greater possibility of error.

S. I. Levy.

Titrations by optical methods with the aid of Löwe's interferometer for liquids. E. Berl and L. Ranis (Ber., 1928, 61, [*B*], 92—99).—Löwe's interferometer, with distilled water as comparison liquid, is well adapted to various types of volumetric analysis. For the titration of acid with alkali hydroxide the apparatus is readily adapted for concentrations of solutions from $2N$ to $N/2000$, the error with the latter being only about 1·6%. The process may be used with strong or weak acids and weak or strong bases and gives accurate results for the titration of weak acids with weak bases. In precipitation analyses (*e.g.*, magnesium chloride and silver nitrate) the solution under investigation is treated with varied quantities of the precipitant, the mixtures are centrifuged, and observations are made with the supernatant liquid. When a combined neutralisation and precipitation analysis is concerned both determinations may be effected in a single solution, as established by the titration of nitrating acid by barium hydroxide. The total alkali in mixtures of sodium hydroxide and carbonate is determined by titration with silver nitrate, only one inflexion in the graph being observed, since the solubilities of silver oxide and carbonate are approximately equal; carbonate is determined by titration with barium hydroxide. With mixtures of magnesium chloride and sulphate the total base is determined with sodium hydroxide, the chloride with silver nitrate in very dilute solution to avoid co-precipitation of silver sulphate. The interferometric method is well adapted to the preparation and control of standard solutions provided they are prepared from pure materials. H. Wren.

Amalgam method. M. Kobayashi (Sexagint [Osaka celebration], Kyoto, 1927, 95—102).—A survey of the employment of liquid amalgams for volumetric analysis and other purposes.

H. F. Gillbe.

Theory of end-point in electrometric titration. P. S. Roller (J. Amer. Chem. Soc., 1928, 50, 1—8).—A general expression deduced for the hydrogen-ion concentration at the inflexion point of an electrometric neutralisation curve shows that such a point appears during the titration of a weak acid by a strong base only when $cK_a > 27K_w$, where K_a is the ionisation constant of the acid, K_w the ionic product of water, and $1/c = 1/a + 1/b$, a being the initial concentration of the acid solution and b that of the alkali solution. This is not in agreement with the calculations of Eastman (A., 1925, ii, 594). The p_H values at the end-point, p_e, and the inflexion point, p_i, differ: $p_e - p_i = 0{\cdot}65\sqrt{K_w/cK_a}$; the latter point always precedes the former, except when the acid is strong. Decrease in either K_a or c is accompanied by an increase in the error of locating the inflexion point.

S. K. Tweedy.

Use of A.C. galvanometers for conductometric titrations, and the determination of fixed ammonia. M. Matsui and M. Asai (J. Soc. Chem. Ind. Japan, 1927, 30, 550—552).—A recommendation of use of A.C. galvanometers for the conductometric titration. A rapid method for determining fixed ammonia is described in illustration. S. Oka.

Comparison of different methods of electrometric acidimetry and alkalimetry. M. Matsui and M. Asai (J. Soc. Chem. Ind. Japan, 1927, 30, 544—549).—The four methods examined were: (1) titration with an air electrode, a calomel half-electrode, and a potentiometer, (2) differential titration with platinum electrodes and a potentiometer, (3) titration without a potentiometer with a hydrogen electrode and a neutralisation electrode, (4) titration without a a potentiometer with air electrodes. S. Oka.

Determination of the concentration of active hydrogen ions in oligometallic mineral waters. G. Banchi (Giorn. Chim. Ind. Appl., 1927, 9, 518—519).—The values of p_H and of the corresponding hydrogen-ion concentration are given for a number of well waters of the Fiuggi district. Certain of these waters give low values for p_H (5·67 and 5·65); this is partly due to the presence of dissolved carbon dioxide, since agitation of the waters causes increase in these values to about 6, which agrees well with the value found by Kling and Lassieur (A., 1926, 355) for distilled water saturated with carbon dioxide. Moreover, if the water is left exposed, the indicator present indicates a gradual change to alkalinity, this change occurring first in the upper part of the liquid. The alkalinity acquired by the water reaches its maximum value if the water is either shaken and then left in an open vessel or boiled for 5 min. Determination of the p_H of a water appears to be one of the best means of ascertaining the age of the water. T. H. Pope.

Adipic acid as a standard in alkalimetry F. T. van Voorst (Chem. Weekblad, 1928, 25, 22—23).—Adipic acid, which has an equivalent weight (corrected for weighing in air) of 72·99, is readily prepared pure by recrystallisation from distilled water and drying at 130°. The m. p. is 152·0°±0·1°, and the purity is readily determined by the m. p. of the sample. It is a more convenient standard than oxalic acid, the purification of which is extremely troublesome. S. I. Levy.

Oxalic and adipic acids as standards. N. Schoorl (Chem. Weekblad, 1928, 25, 73; cf. preceding abstract).—Oxalic acid is readily obtained as the pure dihydrate by recrystallisation, powdering, drying at 60°, and keeping the dried powder in a moist atmosphere; it has the advantage that normal solutions may be made up, whereas the solubility of adipic acid allows only $0{\cdot}2N$-solutions in water.

S. I. Levy.

Oxalic acid as a standard. W. P. Jorissen (Chem. Weekblad, 1928, 25, 90—91; cf. preceding

abstracts).—Dilute solutions of oxalic acid, which do not remain constant when kept even in the dark, may be kept satisfactorily, if required for titration of permanganate solutions, by addition of sulphuric acid.
S. I. Levy.

Determination of hydrogen in complex gaseous mixtures by absorption in colloidal palladium solution. A. E. Beet.—See B., 1928, 113.

Modified apparatus for moisture determination. A. van der Werth (Chem.-Ztg., 1928, 52, 23—24).—An apparatus is described for the determination by means of tetrachloroethane. Distillation is continuous, the water driven off being automatically separated in a capillary measuring tube integral with the still-head. S. I. Levy.

Volumetric determination of perchlorate ion and of potassium in the presence of sulphates and phosphates. E. S. Tomula (Annal. Acad. Sci. Fennicæ, 1927, A, 29, No. 21).—Perchlorates are reduced by boiling in a reflux apparatus with titanic sulphate and cadmium sulphate solutions in the presence of zinc and iron powders; the chlorides thus formed are determined volumetrically. Potassium is determined by conversion into the perchlorate, which is freed from absorbed perchloric acid by washing with alcohol and reduced as above. If sulphates are present they are removed as barium sulphate; phosphates do not interfere. G. A. C. Gough.

Determination of iodine in minerals. E. Wilke-Dörfurt.—See B., 1928, 95.

Reaction between atmospheric oxygen and strongly acid iodide solutions as a possible source of error in iodometric analyses. H. Ditz (Z. anal. Chem., 1927, 72, 360—367; cf. Böttger and Böttger, A., 1927, 222, 330).—Polemical. A review of recent work on the subject indicates that the errors caused by oxidation of acid iodide solutions by atmospheric oxygen are relatively small and under certain conditions negligible.
A. R. Powell.

Reaction between atmospheric oxygen and strongly acid iodide solutions. W. Böttger (Z. anal Chem., 1927, 72, 367—369).—A reply to Ditz (preceding abstract); the author maintains that removal of dissolved oxygen is advisable, although he admits that some of the high results obtained by him may have been due to presence of chlorine in the hydrochloric acid used. A. R. Powell.

Deposition of ammonium sulphide precipitates. J. Röll (Z. anal. Chem., 1927, 72, 298—301).—Ordinary, prepared ammonium sulphide solution is liable to cause the precipitation of the alkaline-earth metals owing to the presence of thiosulphate, sulphite, and sulphate. If it is freshly prepared it usually contains sufficient free ammonia to precipitate nickel sulphide as a colloidal sol. By passing a current of hydrogen sulphide through the filtrate containing 10% of 5% ammonia solution, these errors are avoided. F. S. Hawkins.

Determination of nitrogen in soils. C. Olsen. —See B., 1928, 101.

Rapid micro-determination of the phosphoric ion by ceruleo-molybdimetry. G. Denigès (Compt. rend., 1928, **186**, 318—319).—The author's method (A., 1927, 433, 1156) is applied to the colorimetric analysis of blood, saliva, urine, fermented liquors, etc. containing 2—12 mg. P_2O_5 per litre. The diluted liquid (5 c.c.) is boiled for 12 sec. with 6 drops of reagent and the blue colour matched against that of a suitable standard less than a month old. Coloured liquids are compensated with blanks in the usual way, and milk is precipitated with acetic acid and Tanret's reagent, and filtered. J. Grant.

Titration of ammonium phosphomolybdate. G. Hammarsten (Compt. rend. Lab. Carlsberg, 1928, 17, No. 5, 1—8).—Ammonium phosphomolybdate can be titrated directly in ammoniacal solution in the presence of acetone. The ammonium phosphomolybdate precipitate is dissolved from the filter with ammonia, the filter is washed with water, acetone is added to the combined solution and washings, which are then titrated with 0·1*N*-alcoholic potassium hydroxide with thymolphthalein as indicator. The method is compared with Scheffer's formaldehyde titration procedure (A., 1927, 953). L. M. Clark.

Use of strips of mercuric chloride paper in the Gutzeit test. A. F. Lerrigo (Analyst, 1928, 53, 90—91).—The Gutzeit tube is packed with plumbised cotton wool up to such a height that the mercuric chloride paper strip (4×70 mm.), when placed in the tube and just projecting from it, is supported. All the arsenic in normal quantities (up to 0·05 mg. As_2O_3) is found to be retained at the lower end of the paper, forming a stain proportionate in length and intensity to the amount present. Mercuric bromide paper in use over an extended period was not found very superior to mercuric chloride paper. D. G. Hewer.

Method of applying the Gutzeit test for arsenic. C. H. Cribb.—See B., 1928, 89.

Production of uniform stains in the Gutzeit test for arsenic. J. R. Stubbs.—See B., 1928, 89.

Spring clip for Gutzeit tube. J. White.—See B., 1928, 89.

Hypophosphite reaction for arsenic. W. P. H. van den Driessen Mareeuw (Pharm. Weekblad, 1928, 65, 70—75).—The hypophosphite test for arsenic recommended by the Dutch and German pharmacopœias does not give satisfactory results with the medicinal iron preparations, particularly where ferric iron is present. It is recommended to reduce the solutions with iron powder, filter, and carry out the test for arsenic with the filtrate; if blank tests are carried out at the same time, the alteration in colour due to the presence of arsenic is readily detected. Limits for the sensitiveness under various conditions are given (cf. Wallrabe, B., 1928, 172). S. I. Levy.

Titrimetric determination of tervalent arsenic by oxidation. F. G. Germuth (Amer. J. Pharm., 1927, 99, 751—754).—Arsenious acid is oxidised rapidly and quantitatively by means of 0·1*N*-potassium permanganate solution in the presence of a trace of potassium iodide, which acts catalytically. The reaction takes place in the presence of mineral acids and the use of an indicator or sodium hydrogen carbonate solution is unnecessary. The titration can be carried out at any temperature up to 95°. A slight correction is necessary for the oxidation of the small amount of potassium iodide added. Other iodides are not as effective as the potassium salt.

S. Coffey.

Determination of permanganic and arsenious acids. N. Kanô (Sci. Rep. Tôhoku, 1927, **16**, 873—879).—To avoid the irregularities usually observed in the direct titration of arsenious acid with permanganate, an excess of the latter should be added, a measured volume of standard hydrogen peroxide solution run in until the solution is colourless, and the titration finished with permanganate; with this procedure sharp end-points and regular results are obtained. The oxidation of the arsenite solution may be carried out in alkaline solution, the liquid being acidified after adding an excess of permanganate and the above procedure followed. For the determination of permanganic acid with arsenious acid the solution of the former is added to an alkaline solution of the latter, the mixture acidified with hydrochloric acid, potassium iodide added to reduce manganic compounds, the solution neutralised with sodium hydrogen carbonate, and the excess of arsenious acid determined iodometrically. A. R. Powell.

Determination of boric acid in glass. A. A. Matschigin and T. Korzuchina.—See B., 1928, 91.

Potentiometric titration of boric acid in the presence of certain inorganic salts. M. G. Mellon and F. R. Swim.—See B., 1928, 86.

Determination of sodium diborate. M. François and L. Seguin.—See B., 1928, 87.

Volumetric determination of small amounts of carbonic acid and free ammonia present in distilled water. N. Bjerrum (Annal. Acad. Sci. Fennicæ, 1927, **A**, **29**, No. 1).—Carbonic acid and free ammonia (or ammonium carbonate) may be determined in distilled water, containing about $0{\cdot}5\times10^{-5}$ g.-mol. of either substance per litre, by titration with $0{\cdot}01N$-sodium hydroxide in an atmosphere of air free from carbon dioxide, using 0·4 c.c. of a special mixed indicator per litre of water. The indicator is composed of 5 g. of phenolphthalein and 1 g. of methyl-red dissolved in a litre of alcohol. The alkali is added until the tint of the solution is similar to that of a sodium phosphate solution, p_H 8·5—9, containing the same amount of indicator; at this stage the carbonic acid is present as hydrogen carbonate. The p_H value is then adjusted to 5·5—5 with $0{\cdot}01N$-hydrochloric acid in a similar manner, when the carbonic acid is present as such. From these values the ammonia and carbon dioxide contents are calculated. The following corrections are applied: (*a*) for the acid and alkali values of the indicator, (*b*) for absorption of the reagents by the walls of the flask, (*c*) for the amount of carbonic acid present in a form other than that assumed at each stage, (*d*) for the amount of hydroxyl and hydrogen ions present at each end-point. The method is tested by analysis of very dilute solutions of sodium carbonate and hydrogen carbonate.

G. A. C. Gough.

Substitution of sodium for potassium compounds [as reagents]. A. R. Smith and F. C. Vilbrandt.—See B., 1928, 122.

Tartrate modification of the cobaltinitrite method for the gravimetric determination of potassium. M. Wikul (Z. anal. Chem., 1927, **72**, 345—359; cf. A., 1926, 491).—The empirical method previously described has been modified to obtain stoicheiometric results. The potassium chloride solution, which should be at least $0{\cdot}05N$, is treated with 1·5—2 times its volume of the reagent described below, the mixture is treated with 3 g. of sodium chloride for every 10 c.c., heated to incipient boiling, allowed to cool, and filtered, and the precipitate of $NaCoOC_4H_4O_6,7K_2NaCo(NO_2)_6,H_2O$ is washed with dilute acetic acid, then with alcohol, dried at 110—120° for 20 min., and weighed; it contains 15·98% of potassium. The reagent, which is prepared immediately before use, is made by mixing 2 vols. of sodium nitrite solution (50 g./100 c.c.) with 1 vol. of cobalt nitrate solution (50 g. of crystals/100 c.c.), and 3 g. of tartaric acid in fine powder are stirred in to every 27 c.c. of the mixture; after evolution of nitrous fumes has ceased, the solution is cooled to 10° and filtered, and the filtrate heated to 75°, treated with hydrogen peroxide, heated to 85°, and cooled for use.

A. R. Powell.

Origin of the error in the precipitation of barium sulphate. D. Balarev (Z anal. Chem., 1927, 72, 303—306).—Determinations of the loss of water and change in specific gravity of specimens of barium sulphate which were precipitated at the ordinary temperature, dried at 120°, and then heated to redness show that the precipitate has a porous structure, and contains many fine capillaries and internal surfaces. Microscopical examination of a specimen which was left in contact with potassium permanganate solution for several days confirmed this view. Hence the error is due to the adsorption of ions and molecules from the solution, and not to the formation of complexes of the type $BaClSO_4,BaCl$.

F. S. Hawkins.

Volumetric determination of barium as chromate. A. Mazzucchelli and B. Romani (Gazzetta, 1927, 57, 900—913).—It has been shown by a number of control experiments that it is impossible to precipitate quantitatively silver and barium chromates successively since they form solid solutions with each other; approximate results are obtained by successive precipitation in 45% alcohol.

R. W. Lunt.

Volumetric determination of magnesium. J. Vondrek.—See B., 1928, 94.

Rapid determination of lead. G. Spacu and J. Dick (Z. anal. Chem., 1927, 72, 289—293).—When a solution of ammonium thiocyanate (2 g.) and pyridine (1 c.c.) is stirred with not more than 0·3 g. of lead as an aqueous solution (50 c.c.) of a salt, the compound Pb(OH)SCN is quantitatively precipitated; it is collected on a Gooch crucible, washed with dilute pyridine and ammonium thiocyanate solution, 95% alcohol, and ether, dried for 60 min. in a vacuum, and weighed. The result is accurate to 0·1%, but with larger quantities of lead an appreciable error is introduced owing to the solubility of the precipitate in the ammonium salts present. An acetate, if present, must be removed by evaporating with nitric acid. F. S. Hawkins.

Gravimetric determination of copper as cuprous thiocyanate. I. M. Kolthoff and G. H. P. v. d. Meene (Z. anal. Chem., 1927, 72, 337—345).—The gravimetric determination of copper by the thiocyanate method gives results which are correct to within 0·15% of the copper present if the precipitation is carried out in warm solutions the acidity of which does not exceed 0·5*N*, and if the amount of thiocyanate added does not exceed that necessary to give a 0·05*N*-solution when all the copper has been precipitated. In more concentrated thiocyanate solutions the precipitate redissolves with the formation of a complex salt. The presence of cobalt, nickel, zinc, manganese, arsenic, and large amounts of iron has no effect on the results, but tartaric acid must be added if the solution contains antimony, bismuth, or tin. After precipitation the solution should be set aside for 24 hrs., then filtered through a glass or porcelain crucible with porous bottom, and the precipitate dried at 110—120° for at least 3 hrs. The method is suitable for the determination of copper in pyrites. A. R. Powell.

Titrations by Fajans' method. II. Determination of mercurous and bromide ions. R. Burstein (Z. anorg. Chem., 1928, 168, 325—326; cf. A., 1927, 847).—If mercurous nitrate solution is added to a solution of potassium bromide to which sodium alizarinsulphonate has been added as indicator, the point of equivalence is shown by the yellow colour of the solution changing to reddish-violet. Mercury may therefore be determined by adding to the solution an excess of potassium bromide, and titrating the excess with standard mercurous nitrate solution.

R. Cuthill.

Dissolution of sulphides in mixtures of acid and hydrogen peroxide. A. S. Komarovsky (Z. anal. Chem., 1927, 72, 293—295).—Mercuric sulphide dissolves in warm 4*N*-hydrochloric acid, to which 6% hydrogen peroxide solution is added drop by drop. Calomel dissolves in 2*N*-hydrochloric acid containing hydrogen peroxide. Nickel and cobalt sulphides are soluble in a mixture of dilute acetic acid and 3% hydrogen peroxide solution. The presence of mercury can be confirmed by adding alkali hydroxide, when mercury is precipitated in the presence of hydrogen peroxide, and yellow mercuric oxide in its absence. Nickel is confirmed by means of dimethylglyoxime, and cobalt by Vogel's method. F. S. Hawkins.

Gallium. I. Arc spectrographic detection and determination of gallium. II. Extraction of gallium from lepidolite. J. Papish and D. A. Holt (J. Physical Chem., 1928, 32, 142—147).—These methods are described together with the results of a spectrographic examination of 55 minerals for the presence of gallium. A 0·007% yield of this element was obtained from lepidolite.

L. S. Theobald.

Determination of manganese in steel by the Proctor Smith reaction in presence of phosphoric acid. B. C. Mukerjee.—See B., 1928, 94.

Detection and determination of small quantities of manganese in water. R. Schmidt.—See B., 1928, 110.

Colorimetric determination of [traces of] manganese. A. C. Janzig.—See B., 1928, 142.

Detection of cobalt by Tananaev's spot method. A. Komarovski and B. Ovetschkin (Chimiko-farm. Vestnik, 1926, Nos. 5—6, 9—10; Chem. Zentr., 1927, i, 3021).—Tananaev's method for the detection of cobalt with potassium thiocyanate, stannous chloride, and aniline has no advantage over Vogel's method using potassium thiocyanate alone.

A. A. Eldridge.

Digallic acid as a reagent for earth-acids. W. R. Schoeller.—See B., 1928, 87.

Volumetric determination of antimony and arsenic. P. E. Winkler (Helv. Chim. Acta, 1927, 10, 837—842).—See A., 1927, 1160.

Determination of antimony as tetroxide with membrane filters and porcelain filtering crucibles. A. Simon and W. Neth (Z. anal. Chem., 1927, 72, 307—316).—The antimony is precipitated as sulphide by passing hydrogen sulphide for 1 hr. through a boiling solution containing 10% of concentrated hydrochloric acid. An equal volume of saturated aqueous hydrogen sulphide is added, the mixture cooled (30 min.), the precipitate collected and washed with 0·5*N*-hydrochloric acid saturated with hydrogen sulphide. In this way the formation of a colloidal sol is avoided. If a membrane filter is used, the sulphide is transferred to a weighed crucible, and oxidised gradually with nitric acid of increasing concentration. The sulphuric acid formed is removed by evaporation on a water-bath, followed by gentle heating, and the crucible is gradually heated to 820—900° in an electric oven, and dried at this temperature for 30 min. When a filtering crucible is used, the oxidation is effected by placing the sulphide over bromine and fuming nitric acid in a desiccator. By using these filters no filter-paper contaminates the precipitate and no reduction to the trioxide occurs on heating. Results accurate to 0·1% are obtained by both methods.

F. S. Hawkins.

Determination of gold and silver in sea-water. M. Yasuda (Bull. Chem. Soc. Japan, 1927, 2, 321—323).—Mercuric chloride is added to the sea-water and reduction effected by magnesium and hydrochloric acid. The mercury deposit containing the gold and silver originally present in the water is separated and ignited. A bead of metal is then obtained by the usual assay methods. If white, the bead is treated at once with nitric acid. If yellow, it is first dissolved in a drop of mercury. Quantities of gold and silver of the order 3—20 and 20—70 mg./m.^{3}, respectively, were found in Japanese sea-water. J. S. Carter.

Hand spectroscope with new reagent tube condenser. F. Löwe (Chem. Fabr., 1928, 3—4).—Two tubes for the solution to be examined are mounted in the prism, which is fixed relatively to the lamp and condenser. The spectra corresponding with the two tubes appear in the eye-piece as vertical bands side by side and having a common boundary; a wave-length scale is projected so as to appear at one side of the double band. S. I. Levy.

Apparatus for observing fluorescence by ultra-violet illumination. G. Kögel (Chem. Fabr., 1928, 55—56).—The light from a " spot-light " tungsten arc lamp is filtered through a water-cooled quartz filter silvered on the outside to remove visible rays, and the remaining ultra-violet rays are reflected on to the illuminating mirror of a microscope if transparent objects are to be examined, or on to the surface of opaque objects by means of a spherical dark-field illuminator. In order to photograph the fluorescence the ultra-violet rays must be absorbed by passing the emergent light from the eye-piece of the micro-scope through a 5 mm. layer of a solution containing 0·5 g. of triphenylmethane in 70 c.c. of alcohol. The luminescence rays pass unabsorbed through this solution and are photographed on panchromatic ultra-rapid plates. A. R. Powell.

Immersion fluid. S. H. Bertram (Chem. Week-blad, 1928, 25, 24).—A very cheap fluid, having almost the same refractive index and dispersion as cedar oil, is prepared by dissolving 35 parts of pale colophony and 15 parts of naphthalene in 50 parts of sesame oil by gentle warming, treating with a little fuller's earth, and filtering. S. I. Levy.

Comparison of attack and utility of modern filtering apparatus. A. Simon and W. Neth (Chem. Fabr., 1928, 41—49).—The resistance of Jena, Berlin, Haldenwanger, and quartz filtering crucibles to attack by various reagents has been compared by observing losses in weight suffered under comparable conditions. A study has also been made of the rapidity and efficiency with which the various types of filter can deal with the different kinds of precipitate commonly obtained in analysis, *e.g.*, aluminium hydroxide, barium sulphate, silver chloride, etc. There is little difference between the types of crucible examined as regards resistance to attack by reagents other than hot alkali. For hot alkalis quartz and Jena glass are considered best. The authors do not recommend the use of Jena blue frit crucibles. H. Ingleson.

Rotary filter stand. W. M. Shaw (Ind. Eng. Chem., 1928, 20, 100—101).—A circular filter stand possesses three shelves fastened by set screws to a tube slipped over the central upright. They accom-modate respectively wash-bottles, funnels, and beakers and can be rotated as a unit for easy access, enabling 12 filtrations to be performed simultaneously in very limited space. C. Irwin.

Hydraulic lift for gas-analysis apparatus. E. J. Tauch.—See B., 1928, 71.

Improved lighting source for m.-p. apparatus. E. V. Fasce (J. Amer. Chem. Soc., 1928, 50, 252—253).—The light from an enclosed 100-watt lamp is directed on to the substance in the m.-p. tube by means of a rod of glass or quartz, 4 cm. × 8 mm. F. G. Willson.

B.-p. apparatus for calibrating thermocouples. T. De Vries.—See B., 1928, 71.

Electrical heating equipment for chemical work. G. Angel.—See B., 1928, 97.

Constant temperature bath. A. V. Hill (J. Sci. Instr., 1928, 5, 24—25).—The temperature of water in a Dewar vessel, a few degrees above that of the room, may be kept constant within 0·0005° by hand adjustment of a rheostat. Incipient changes in temperature are detected by a resistance thermometer actuating a very sensitive galvanometer. C. W. Gibby.

Continuous vacuum distillation apparatus. R. Kummer (Chem. Fabr., 1927, 7).—The apparatus is entirely of glass, with ground joints, all parts being standardised. Two receivers are provided, so arranged that the distillate may be passed from the first to the second, and thence withdrawn, without interrupting the distillation. By means of a dropping funnel with joint ground in to the distilling flask, continuous addition of fresh liquid to the latter may be made. S. I. Levy.

Isothermal calorimetry at high temperatures. A. Magnus and F. Oppenheimer (Z. anorg. Chem., 1928, 168, 305—308).—An isothermal calorimeter suitable for determining the latent heat of fusion of substances with high m. p. is described. The sub-stance is placed in a crucible with a double jacket between the walls of which is a heating coil; the crucible is contained in a tube surrounded by an evacuated jacket containing a second heating coil. By means of the latter coil, the substance is heated almost to its m. p., and when the temperature has become steady a current of known strength and voltage is passed through the coil round the crucible until a sharp rise in temperature of a thermocouple in the melting mass indicates that fusion is complete. From the total quantity of electricity passing through the coil nearer the crucible and the voltage, the latent heat of fusion may be calculated. R. Cuthill.

Dispersion electricity. I. H. G. Bos (Chem. Weekblad, 1928, 25, 66—72).—The name is suggested for the static charges resulting from the dispersion of a substance throughout a medium or milieu. An apparatus consisting of a spray jet and insulated chamber is employed to examine the electrification resulting from the spraying of liquids by compressed air; the potential is measured by means of an electro-meter and condensers. Tables are given of the potentials obtained with water, aqueous solutions, petroleum, and alcohol, using pressures up to 4 atm. The maximum potential obtained in any series of readings is termed the " Dispersel." Both brass and iron sprays gave potentials of the same sign with the liquids treated. S. I. Levy.

Explosion of liquid-air-cooled charcoal tubes. J. Taylor (J. Sci. Instr., 1928, 5, 24).—An explosion may be caused by liquid air coming into contact with highly activated charcoal through cracking of the charcoal tube. It is suggested that the latter should be surrounded by a thin metal tube. C. W. Gibby.

Apparatus for preparing [active] aluminium chloride. G. A. Dawson (J. Amer. Chem. Soc., 1928, 50, 133—134).—A simple pyrex apparatus consists of a wide tube, heated in a combustion furnace, bent at one end (the portion near the bend being wound with nichrome wire) and opened out to a funnel which fits on to a vessel having an outlet. Hydrogen chloride is passed over aluminium kept at dull red heat in the horizontal tube, the wound portion near the bend being heated to the necessary temperature before the furnace is lit. S. K. Tweedy.

Florentium. L. Rolla and L. Fernandes (Gazzetta, 1927, **57**, 924, and Z. anorg. Chem., 1927, **169**, 319—320).—Polemical; a claim for priority. R. W. Lunt.

Geochemistry.

Relation between the variations of pressure and density of the air. D. Espurz (Anal. Fís. Quím., 1927, **25**, 490—493).—A theoretical paper in which arguments are advanced in support of the Loomis–Morley–Guye hypothesis (cf. Moles, A., 1927, 194). J. S. Carter.

Dust storms and salt storms. F. Bordas and A. Desfemmes (Compt. rend., 1928, **186**, 159—161; cf. A., 1927, 1049).—As the result of a dust storm in November, 1927, a sample of rain-water from Montpellier was found to contain the chlorine equivalent of 3·3 $g./m.^2$ of sodium chloride. It is calculated that during the dust and rain storm of November, 1926 (*loc. cit.*), the dust particles were suspended in the atmosphere for 57 days, and 24 $g./m.^2$ of sodium chloride were deposited during this period. J. Grant.

Composition of the thermal waters from Barèges (Hautes-Pyrénées). R. Robine and M. Dejussieu (J. Pharm. Chim., 1928, [viii], 7, 9—13).—Detailed analyses of these waters, originating from 15 springs, are given, together with those of previous investigators. The main constituents appear to be sodium, calcium, aluminium, chlorides, sulphides, sulphates, and silicates, with traces of lithium, iron, and phosphates. One water contains a measurable quantity of manganese, another iodine, and a third magnesium. All contain a fairly large proportion of arsenic. S. Coffey.

Rare gases from some Bulgarian thermal springs. N. P. Péntchev (Compt. rend., 1928, **186**, 249—251; cf. A., 1927, 955).—Further determination of the gases from three Bulgarian thermal springs have shown them to contain nitrogen (96·7—98·7%), with traces of oxygen (0·1%), carbon dioxide (0·2%), argon (1·3—1·7%), and helium (0·014—0·254%). The radium emanations were 1·1—$110·0\times10^{-10}$ curie per litre. The results confirm the astrophysical theory of Moureu and Lepape and are an indication of the geological origin of the rocks. J. Grant.

Mutual relation of carbon dioxide and p_H in sea-water of varying salt content. E. M. Kreps (Int. Rev. ges. Hydiobrol. H., 1926, **15**, 240—257; Chem. Zentr., 1927, i, 3182).—Tables are given. With increasing carbon dioxide concentration the buffer action of sea water is more marked, and by diminution of the alkali reserve it is smaller. A. A. Eldridge.

Salinity of water of Gulf of Carpentaria. G. J. Burrows (J. Proc. Roy. Soc. New South Wales, 1926, **60**, 211—212).—The chlorine content of water taken in 1911 from various parts of the Gulf of Carpentaria was less than that of a sample of sea water collected off the coast of Sydney, indicating that the water of the Gulf is diluted with water containing little or no salt, and probably discharged from the artesian basin. R. Cuthill.

Determinative mineralogy. P. C. Putnam, E. J. Roberts, and D. H. Selchow (Amer. J. Sci., 1928, [v], **15**, 89—102).—Lists of reagents and apparatus for a "field kit," with general remarks on the selection of material and on micro-chemical tests, are given. L. J. Spencer.

Atomic number and terrestrial distribution. P. Vinassa (Atti R. Accad. Lincei, 1927, [vi], 5, 940—945).—The large proportion of iron, nickel, and cobalt, and of elements of atomic number less than 26, in the earth's crust is discussed with reference to atomic stability and the periodic classification. R. W. Lunt.

Silicic acid as a protective colloid in the origin of Mediterranean red soils. A. Reifenberg (Z. Pflanz. Dung., 1927, **10A**, 159—186).—Silicic acid sol acts as a protective and peptising agent towards ferric and aluminium oxides and hydroxides. In cataphoresis experiments ferric hydroxide hydrosol in the presence of silicic acid sol migrates to the anode or cathode according to whether silica or ferric hydroxide is in excess. When considerable amounts of alkali are present migration is always to the anode irrespective of the relative proportions. The iron sol is protected by silica against the flocculating action of neutral salts. The nature of several typical red soils is described and explained on this basis, as also is the high silica content of ferruginous strata of natural limestones. Ferric hydroxide hydrosol protected with silicic acid acquires the property of remaining deflocculated in the presence of limestone. Further, dialysed silicic acid is shown to be an active peptising agent for naturally occurring iron in veins of limestone. A. G. Pollard.

Isomorphous replacement of silicon by aluminium. W. Wahl (Annal. Acad. Sci. Fennicæ, 1927, A, **29**, No. 22).—It is suggested that the apparent anomaly of the isomorphous replacement of quadrivalent silicon by tervalent aluminium in substances of the pyroxene and mellilite groups is actually a normal phenomenon in which silicon with a co-ordination number of six is replaced by aluminium of the same co-ordination number. G. A. C. Gough.

Manganiferous mineral from Kara-Tschaguir in Fergana. A. Saukov (Compt. rend. Acad. Sci. U.R.S.S. [Russia], 1926, 77—79; Chem. Zentr., 1927, ii, 796—797).—The black mineral has *d* 2·985±

0·09, and contains Fe_2O_3 2·7, Al_2O_3 9·8, ZnO 10·4, NiO 11·8, CoO 1·4, CuO 5·41, CaO 0·08, V_2O_5 4·3, MnO_2 23·6, H_2O (−110°) 4·6, H_2O (+110°) 19·9, insoluble 2·95; molybdenum also is present.

A. A. Eldridge.

Natural hydrated magnesia. N. Kurnakov and V. Černyh (Mem. Soc. Russe Min., 1926, [ii], 55, 74—95; Chem. Zentr., 1927, ii, 797).—Brucite has *d* 2·360—2·396, ω 1·5634, ϵ 1·5840, $2V=2$—8°; nemalithite has *d* 2·310—2·397, $2V=18$—26°. Dehydrated brucite has ω_{Na} 1·6282, ϵ_{Na} 1·6192. The positive double refraction becomes negative on dehydration of brucite, and again positive when the dehydrated mineral remains in the air. The two minerals cannot be differentiated by chemical or thermal investigation. A. A. Eldridge.

Hydrotalcite and pyroaurite. N. Kurnakov and V. Černyh (Mem. Soc. Russe Min., 1926, [ii], 55, 118—128; Chem. Zentr., 1927, ii, 797).—The brucite nucleus is present in both minerals; in hydrotalcite it is associated with alumina and in pyroaurite with ferric oxide. Carbon dioxide (0—10·84%) and water (about 8 mols.) are also present.

A. A. Eldridge.

Helium content of uraninite from Karelia. V. Chlopin (Compt. rend., Acad. Sci. U.R.S.S. [Russia], 1926, 195—197; Chem. Zentr., 1927, ii, 798).—Six samples contained 4—5 c.c. per g., and two 0·3—0·4 c.c. The helium content is thus not proportional to the lead : uranium ratio.

A. A. Eldridge.

System iron–oxygen–sulphur in the formation of stone meteorites, and the mineralogical nature and genesis of the black veins in such meteorites. P. Chirvinsky (Z. Min. Geol. Paläont., 1927, **A**, 199—205; Chem. Zentr., 1927, ii, 800).—The reactions taking place in the formation of the meteorites are: $6Fe+3O+S=6Fe+SO_2+O=2Fe+3FeO+FeS$. Oxidation of iron by oxygen occurs only after complete oxidation of silicon and manganese has taken place, whilst sulphur shows a relatively greater affinity for iron, forming troilite, which on account of its lower f. p. fills the veins and cracks. The black veins in the stone meteorites consist of josite, FeO, and troilite, with scorified silicate material and some iron. The ferrous oxide–ferrous sulphide eutectic, m. p. 1060°, may also be formed. The reaction $3Fe+SO_2=FeS+2FeO$ is exothermic, and proceeds from left to right at fairly low temperatures. A. A. Eldridge.

Formation of radioactive manganiferous deposits from Tanokami, and the source of manganese in the deep-sea nodules. S. Iimori (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1927, 7, 249—252).—See this vol., 42.

Green kaolin from Tanokami. S. Iimori (Sci. Papers Ind. Phys. Chem. Res. Tokyo, 1927, 7, 253—257).—See this vol., 42.

Microscopic zircons as guide minerals. J. Zerndt (Bull. Acad. Polonaise, 1927, **A**, 363—377).—Statistics are given of the crystallographic features of microscopic zircons in granites and porphyries from various localities. Similar data are given for the zircons present in the Carpathian sandstones, and conclusions are reached therefrom as to the probable sources of the materials of these sedimentary rocks.

L. J. Spencer.

Hypersthene-andesite of Blair Duguid, near Allandale, N.S. Wales. W. R. Browne and H. P. White (J. Proc. Roy. Soc. New South Wales, 1926, 60, 372—387).—The hypersthene-andesite of the Blair Duguid hills appears some distance away in an altered form as the pebbles of a conglomerate. This change has apparently been effected by solutions of magmatic origin, and has involved the addition of both sodium and potassium to the rock, and the transformation of the hypersthene into iddingsite in some places and into carbonates in others.

R. Cuthill.

Mineral constitution of the Broken Hill lode. F. L. Stillwell (Austral. Inst. Min. Met., 1926, 64, 97—172).—The argentiferous ore now worked at Broken Hill, New South Wales, consists of a granular mixture of blende and galena, other minerals being quite inconspicuous. Polished sections of the ore were examined under the microscope, and, with the aid of etching and chemical tests, the following minerals were identified: pyrite, pyrrhotine, mispickel, willyamite, enargite, cubanite, chalcopyrite, tetrahedrite, dyscrasite, pyrargyrite, etc. These occur in small amount enclosed in or intimately intergrown with the blende and galena. Gangue minerals present in the granular aggregate are garnet, rhodonite, and calcite. L. J. Spencer.

Zoning of mineral deposits in British Columbia. G. Hanson (Trans. Roy. Soc. Canada, 1927, [iii], 21, IV, 119—126).—The known mineral deposits of British Columbia were plotted on a map to show their relation to the intruded masses of igneous rocks. In the mineralised areas the general succession is tungsten, gold, copper, zinc, lead, and silver, as one proceeds away from the igneous rock.

L. J. Spencer.

Organic Chemistry.

Photochemical changes of hydrocarbons. S. Tołłoczko.—See this vol., 255.

Formation of hydrocarbons from propyl alcohol. A. Mailhe and Renaudie (Compt. rend., 1928, **186**, 238—240).—When propyl alcohol is passed over uranium oxide at 400—420° hydrogen, methane, unsaturated hydrocarbons, and carbon monoxide and dioxide are evolved and a yellow liquid consisting mainly of propaldehyde condenses. The liquid, after removal of the aldehyde with water, can be separated into a hydrocarbon fraction consisting chiefly of hexane and hexene and an aldehyde fraction containing β-methylpentenal and αβ-di-

methyl-$\Delta^{\alpha\beta}$-heptadienal, to the breaking down of which the gases mentioned above owe their origin.
B. W. ANDERSON.

Preparation of higher acetylenes. I. Dehalogenation of αα-dichloroheptane in the vapour phase. A. J. HILL and F. TYSON (J. Amer. Chem. Soc., 1928, **50**, 172—177).—αα-Dichloroheptane is obtained in 70% yield by adding heptaldehyde to a stirred suspension of phosphorus pentachloride (1—1·25 mols.) in benzene at not above 20°. It is dehalogenated when passed over soda-lime at 360—430°, the highest yield, 10%, of Δ^{α}-heptinene being obtained by passing 100 g. of dichloroheptane over 300 g. of soda-lime (50% NaOH) at 420°. Substitution of aluminium silicate for soda-lime results in increased decomposition. The Δ^{α}-heptinene is best determined by adding it to a 5% silver nitrate solution in 95% alcohol, when the double salt, $C_5H_{11}\cdot C{\vdots}CAg,AgNO_3$, is precipitated. The salt may be weighed after drying at 60°, or, preferably, the liberated nitric acid titrated after filtration and removal of excess of silver by addition of sodium chloride (cf. Behal, A., 1888, 930).
F. G. WILLSON.

Intramolecular rearrangement [of alkyl halides] by photochemical action. (MME.) RAMART-LUCAS and F. SALMON-LEGAGNEUR.—See this vol., 255.

Identification of alkyl and aryl halides. E. L. HILL (J. Amer. Chem. Soc., 1928, **50**, 167—168; cf. A., 1926, 144).—Mercuric alkyl halides may be prepared as previously described from secondary alkyl and aryl halides, for identification of these compounds. The following are described: *mercuric* n-*nonyl*, m. p. 109°; n-*lauryl*, m. p. 108°; iso*propyl*, m. p. 93·5°; β-*phenylethyl*, m. p. 169°; o-*tolyl*, m. p. 168°, and *p*-tolyl bromide, m. p. 231° (cf. Pope and Gibson, J.C.S., 1912, **101**, 736).
F. G. WILLSON.

Alcoholysis and hydrolysis of some alkyl halides in neutral solution. B. H. NICOLET and D. R. STEVENS (J. Amer. Chem. Soc., 1928, **50**, 135—139).—The rates of hydrolysis and alcoholysis of propyl and *iso*propyl bromides and iodides in boiling alcohol containing small known amounts of water have been measured in presence of calcium carbonate to remove free halogen acids. The secondary halides react in each case more rapidly than the corresponding primary halides (cf. Conant and Hussey, A., 1925, i, 493), and all the reactions are strongly catalysed by the corresponding mercuric halides (cf. Burke and Donnan, A., 1909, ii, 987).
F. G. WILLSON.

Reaction between aluminium and bromoform. S. GAMBARJAN (Ber., 1928, **61**, [*B*], 177—179).—Aluminium turnings, suspended in chloroform, are converted by bromine into a black, voluminous material insoluble in all media. The same product is formed when aluminium is treated with a deficiency of bromine and subsequently with chloroform and, consequently, directly from well-cleaned aluminium and bromoform. The change probably occurs through production of acetylene and action of aluminium bromide on the latter. A similar behaviour is exhibited by *s*-tetrabromoethane, ethylene dibromide, and methylene dibromide. After being heated in a vacuum at 200°, the product retains much aluminium. Treatment of it with solvents for aluminium bromide (carbon disulphide, pyridine, acetophenone) leaves residues containing aluminium, whereas an almost ash-free material containing 38% of oxygen is obtained by means of acetone. The ratio C : H appears to be 1 : 1.
H. WREN.

Reaction of *iso*propyl iodide with mercuric chloride. B. H. NICOLET and W. M. POTTS (J. Amer. Chem. Soc., 1928, **50**, 212—216).—Mercuric chloride reacts with *iso*propyl iodide in absolute ether at 25°, with practically quantitative formation of *iso*propyl chloride (cf. Conant, Kirner, and Hussey, A., 1925, i, 494). The reaction velocity is proportional to the product of the concentrations of the two reactants and of the mercuric iodide formed. It is suggested that the reaction between the *iso*propyl iodide and the mercuric chloride is extremely slow, but that the complex $Pr^{\beta}I,HgI_2$ is formed, which then reacts more rapidly with either mercuric chloride or chloride ion.
F. G. WILLSON.

Oxidation of certain aliphatic and aromatic carbon compounds by dichromate. H. ARK (J.C.S., 1928, 46—47).—Oxidation by potassium dichromate and sulphuric acid is used to determine lower alcohols and some other compounds, by titrating the residual dichromate ion (cf. Grey, J.C.S., 1914, **105**, 2204; A., 1924, ii, 208). Formic acid is oxidised at concentrations of sulphuric acid at which propionic acid is stable; as acetic acid is not attacked, it is suggested that mixtures of the acids might be analysed by oxidation. The method is unsuitable in presence of aldehydes, or of halogen or imino-compounds; succinamide, acetamide, carbamide, and α-amino*iso*butyric acid are unaffected.
E. W. WIGNALL.

Oxidation of polyhydric alcohols with periodic acid. L. MALAPRADE (Compt. rend., 1928, **186**, 382—384).—Oxidation of ethylene glycol, glycerol, erythritol, adonitol, and mannitol with periodic acid proceeds in the cold and reaction is complete after 12 hrs. The number of molecules of periodic acid reduced to iodic acid is one less than that of the hydroxyl groups in the alcohol. The method can be used to determine small quantities of polyhydric alcohols in aqueous solution, and the composition of a mixture of iodic and periodic acids.

When aqueous solutions of pure periodic acid are treated with at least sufficient alcohol to ensure complete reduction, there are formed acids from all compounds except ethylene glycol. Increase in the quantity of the reacting alcohol causes a diminution in the amount of acids produced. When neither of the reacting substances is in excess the change is $[CH_2\cdot OH]_2[CH\cdot OH]_n+(n+1)HIO_4=2H\cdot CHO+nH\cdot CO_2H+(n+1)HIO_3$.
H. BURTON.

Catalytic action. XIX. Catalytic action of reduced copper on methyl alcohol. S. KOMATSU and S. SUZUKI (Mem. Coll. Sci. Kyoto, 1927, **10A**, 339—341).—Primary alcohols can generally be decomposed by heat either into olefine and water or into hydrogen and aldehyde. Methyl alcohol in presence of reduced copper as catalyst gives a mixture of formaldehyde and ethylene. The yield of ethylene is always small, but rises to a maximum of 3% when the copper is made from copper oxide prepared by igniting the nitrate and the temperature is about 500°. The yield of formaldehyde rises to 34·4% at 600° with the same form of metal. Lower temperatures or copper made by other methods gave lower yields. C. D. LANGFORD.

Reaction between diaryloxy*iso*propyl alcohols and phosphorus oxychloride in presence of pyridine. D. R. BOYD and D. E. LADHAMS (J.C.S., 1928, 215—221).—When di-*p*-tolyloxy*iso*propyl alcohol reacts at 0° with excess of phosphorus oxychloride in presence of pyridine, the product obtained on treating the reaction mixture with ice is mainly *di-*p*-tolyloxy*iso*propyl phosphate*, $(C_7H_7\cdot O\cdot CH_2)_2CH\cdot O\cdot PO(OH)_2$, m. p. 158°, but if the reaction mixture is heated at 100° before decomposition with ice, di-*p*-tolyloxy*iso*propyl chloride is formed, together with a comparatively small amount of the corresponding pyridinium salt, isolated as 1-*αγ-di-*p*-tolyloxy*iso*propylpyridinium nitrate*, $C_5H_5N\cdot CH(CH_2\cdot O\cdot C_7H_7)_2NO_3$, m. p. 165° (decomp.) [*chlorate*, m. p. 153° (violent decomp.); *thiocyanate*]. The pyridinium nitrate is decomposed by cold aqueous alkali, giving *p*-cresol and certain resinous products, one of which condenses with aniline, yielding a deep red *compound*, m. p. 117—119° (decomp.). When a large excess of phosphorus oxychloride is not present and the reaction mixture is heated at 100° before decomposition with ice, an excellent yield of *bis-αγ-di-*p*-tolyloxy*iso*propyl phosphate*, m. p. 160°, is obtained, together with a small quantity of a phosphorus-containing *compound* (tri-ester?), m. p. 205—207°, and of di-*p*-tolyloxy*iso*propyl chloride. The following substances have been prepared by analogous reactions: *αγ-diphenoxy*iso*propyl phosphate*, m. p. 137—137·5° [*sodium* salt (+10H$_2$O), m. p. 54°]; *bis-αγ-diphenoxy*iso*propyl phosphate*, m. p. 105°; *αγ-di-o-tolyloxy*iso*propyl phosphate* (*sodium* salt, +10H$_2$O); 1-*αγ-di-o-tolyloxy*iso*propylpyridinium nitrate*, m. p. 154°; 1-*αγ-di-*p*-nitrophenoxy*iso*propylpyridinium nitrate*, m. p. 182°; *αγ-di-*p*-nitrophenoxy*iso*propyl chloride*, m. p. 186°.

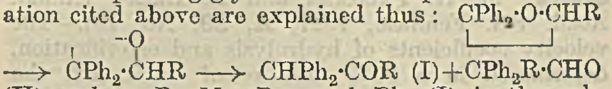
In the absence of pyridine, diaryloxy*iso*propyl alcohols do not yield the corresponding chlorides. Only the mono- and bis-esters are obtained. An explanation of these reactions and of the part played therein by the crystalline additive compound, $(C_5H_5N)_2,POCl_3$, formed from pyridine and phosphorus oxychloride is advanced. M. CLARK.

Preparation of αη-dihydroxyheptane (heptamethylene glycol) and αη-dibromo-*n*-propane. A. MÜLLER and E. RÖLZ (Monatsh., 1927, 48, 733—736).—Reduction of ethyl pimelate by the Bouveault and Blanc method affords *n*-heptane-αη-diol (60% yield), b. p. 148—149°/10 mm. [phenylcarbimide, m. p. 137° (corr.); cf. Dionneau, A., 1915, i, 491]. Treatment of the glycol with hydrobromic acid at 130—140° yields *αη-dibromoheptane*, b. p. 132°/11 mm., in 74% yield. H. BURTON.

Acetone compounds of pentaerythritol. L. ORTHNER (Ber., 1928, **61**, [*B*], 116—118).—*Pentaerythritol* iso*propylidene ether*, $CMe_2{<}\substack{O\cdot CH_2\\ O\cdot CH_2}{>}C(CH_2\cdot OH)_2$, m. p. 128 129°, is prepared by treating pentaerythritol with aqueous acetone containing hydrogen chloride. The *di*iso*propylidene ether*, m. p. 117—117·5°, is obtained from pentaerythritol or its *iso*propylidene ether by the use of anhydrous acetone and copper sulphate. The compound prepared by Bougault by the action of sulphur chloride on pentaerythritol is identified as the disulphite, m. p. 153—154°; its formation is ascribed to the presence of thionyl chloride in the reagent. H. WREN.

Monoacetals of pentaerythritol. A. SKRABAL and S. KALPASANOV (Ber., 1928, **61**, [*B*], 55—57; cf. A., 1927, 27).—The monoacetals are prepared by treatment of 1 mol. of pentaerythritol with 1 mol. of the necessary aldehyde in the presence of concentrated hydrochloric acid. The diacetals simultaneously produced are separated by treatment of the product with cold benzene; the residue is extracted with hot benzene in which the monoacetals dissolve, whereas unchanged pentaerythritol is not appreciably soluble. The following compounds are described: *monoformal*, $CH_2{<}\substack{O\cdot CH_2\\ O\cdot CH_2}{>}C(CH_2\cdot OH)_2$, m. p. 40°; *monoacetal*, m. p. 104°; *monopropal*, m. p. 70°; *mono*iso*butyral*, m. p. 107°. The dipropal has m. p. 25°. H. WREN.

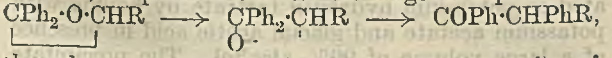
Isomerisation of aromatic trisubstituted ethylene oxides and the re-arrangement phenomena involved. R. LAGRAVE (Ann. Chim., 1927, [x], 8, 363—446).—Treatment of αα-diphenyl-Δ^α-propene, m. p. 51° (*dimeride*, m. p. 130°), with perbenzoic acid in chloroform solution gives *αα-diphenyl-β-methylethylene oxide*, b. p. 178—180°/21 mm., m. p. 34°, d_0^4 1·1038, n^{15} 1·5755 (cf. Stoermer, A., 1906, i, 583), which isomerises on slow distillation into αα-diphenylpropan-β-one. αα-Diphenylpropaldehyde does not isomerise under the same conditions. Dehydration of αα-diphenylbutan-α-ol with sulphuric–acetic acids furnishes *αα-diphenyl-Δ^α-butene*, b. p. 160—163°/10 mm. (*dimeride*, m. p. 110—111°), which yields *αα-diphenyl-β-ethylethylene oxide*, b. p. 175—180°/18 mm., d_0^4 1·1114, n^{15} 1·5790. This oxide isomerises at its b. p. into αα-diphenylbutan-β-one (85%) and αα-diphenylbutaldehyde (15%). Magnesium *iso*butyl bromide and benzophenone or magnesium phenyl bromide and ethyl *iso*valerate form *αα-diphenyl-γ-methylbutene*, b. p. 169—170°/20 mm., d_0^4 0·9946, n^{15} 1·5754, which yields *αα-diphenyl*-β-iso*propylethylene oxide*, b. p. 182—183°/20 mm., d_0^4 1·0507, n^{15} 1·5550, isomerised to αα-diphenyl-γ-methylbutan-β-one (82%) and αα-diphenyl-β-methylbutaldehyde (18%). *αα-Diphenylpentene*, b. p. 170°/13 mm., d_0^4 1·0139, n^{15} 1·5768. yields *αα-diphenyl*-β-n-*propylethylene oxide*, b. p. 175—180°/10 mm., d_0^4 1·052, n^{15} 1·5595, which isomerises into αα-diphenylpentan-β-one. *αα-Diphenyl*-β-iso*butylethylene oxide*, b. p. 196—197°/17 mm., d_0^4 1·035, n^{15} 1·5555, isomerises into αα-diphenyl-δ-methylbutan-β-one (80%) and αα-diphenyl-γ-methylvaleraldehyde (20%), and *αα-diphenyl*-β-n-*butylethylene oxide*, b. p. 195—197°/17 mm., d_0^4 1·037, n^{15} 1·5485, gives αα-diphenylhexan-β-one (80%) together with αα-diphenylhexaldehyde (20%). ααγ-Triphenylpropene, b. p. 228—229°/15 mm. (cf. Paternò and Chieffi, A., 1910, i, 41), furnishes *αα-diphenyl*-β-*benzylethylene* *oxide*, m. p. 69°, which on distillation at 290°/95 mm. isomerises into ααγ-triphenylpropan-β-one (42%) and ααβ-triphenylpropaldehyde (58%), whilst distillation under ordinary pressure gives diphenylmethane and diphenylacetaldehyde. *Triphenylethylene oxide*, m. p. 77°, furnishes phenyl diphenylmethyl ketone, also produced when triphenylethylene glycol is heated at 180°. If this last reaction is carried out in presence of zinc chloride, a small amount of triphenylacetaldehyde is produced in addition to the ketone. Distillation of triphenylacetaldehyde furnishes triphenylmethane. Triphenylethylene when treated with excess of perbenzoic acid yields in addition to the oxide about 20% of phenyl diphenylmethyl ketone, whilst hot 50% oxalic acid converts the oxide into the corresponding glycol. The examples of isomerisation cited above are explained thus:



$$\underbrace{CPh_2\cdot O\cdot CHR}_{} \longrightarrow \overset{|}{C}Ph_2\cdot\overset{-O}{\overset{|}{C}}HR \longrightarrow CHPh_2\cdot COR\ (I)+CPh_2R\cdot CHO\ (II)$$

; where $R=Me$, Pr^{α}, and Ph, (I) is the sole product, but if $R=Et$, Pr^{β}, Bu^{α}, Bu^{β}, or CH_2Ph, (I) and (II) are formed at the same time. The saturation capacity of the two phenyl groups is greater than any combination studied.

Magnesium anisyl bromide reacts with diphenylacetaldehyde to form *αα-diphenyl-β-anisylethan-β-ol*, m. p. 160°, which is oxidised by chromic–acetic acids to *anisyl diphenylmethyl ketone*, m. p. 129—130°, and dehydrated by acetyl chloride to *αα-diphenyl-β-anisylethylene*, m. p. 84—85° (*dibromide*, m. p. 132°). Hydrolysis of the above ketone with alcoholic potassium hydroxide gives anisic acid and diphenylmethane. Treatment of the ethylene with perbenzoic acid in ether yields *αα-diphenyl-β-anisylethylene oxide*, m. p. 104°, which isomerises at its b. p. into anisyldeoxybenzoin, m. p. 85—86°. This change is represented



$$\underbrace{CPh_2\cdot O\cdot CHR}_{} \longrightarrow \underset{O\cdot}{\underset{|}{C}}Ph_2\cdot\underset{\cdot}{C}HR \longrightarrow COPh\cdot CHPhR,$$

thus demonstrating the high saturation capacity of the anisyl group. These results are discussed fully, as are the cases described by Tiffeneau and Lévy (A., 1926, 383, 818).

H. BURTON.

Hydrolysis of *n*-butyl nitrate. H. RYAN and V. J. R. COYLE (Proc. Roy. Irish Acad., 1927, 37, 361—367).—*n*-Butyl nitrate is slowly hydrolysed by 56% aqueous potassium hydroxide at 100°; when refluxed with the reagent some potassium nitrite and tarry substances are formed. Alcoholic potassium hydroxide yields similar products together with traces of an ether. Acetic anhydride and sodium acetate have no action on the ester, whilst the action of alcoholic ammonia is very slow. The addition of an excess of hydrogen sulphide to the latter reagent causes rapid hydrolysis with the deposition of sulphur and the formation of traces of a mercaptan. The ester may also be slowly hydrolysed with iron and acetic acid.

G. A. C. GOUGH.

Natural optically active inositoltetraphosphoric ester. S. POSTERNAK and T. POSTERNAK (Compt. rend., 1928, 186, 261—263).—The picric acid extract of the phosphorus compounds in wheat grain in which the phosphatase had been destroyed was treated with barium acetate and the precipitate thus formed dissolved in just sufficient 10% hydrochloric acid. The crystalline precipitate which then settled corresponded with the formula $(C_6H_{12}O_{21}P_5,2H_2O)_2Ba_5$ (cf. Anderson, A., 1920, i, 801) and consisted of the mixed salts of inositolhexaphosphoric acid and *inositoltetraphosphoric acid*, $\alpha_D^{14\cdot5}$ −3·92° for the free acid, $\alpha_D^{14\cdot5}$ −7·94° after neutralising with sodium hydroxide. The syrupy, uncrystallisable acid last mentioned forms insoluble alkaline-earth and heavy-metal salts and by means of the former it was isolated; it is formed also by the action of phosphatase on sodium inositolhexaphosphate, and this is probably the manner in which it originates in the seed.

B. W. ANDERSON.

Hexaphenylethane alkyl sulphide additive compounds. V. C. ROGERS and G. DOUGHERTY (J. Amer. Chem. Soc., 1928, 50, 149—156).—Additive *compounds*, $(CPh_3)_2,SR_2$, can be obtained by preparing triphenylmethyl from triphenylmethyl chloride and mercury in methyl, ethyl, or propyl sulphide solution. In bromobenzene solution, the rate of oxidation of triphenylmethyl is increased by the presence of either of the above alkyl sulphides. When heated at 150°, the methyl sulphide additive product decomposes, with formation of complex hydrocarbons and, apparently, methyl triphenylmethyl sulphide, from which it is concluded that the additive compounds have a sulphonium structure.

F. G. WILLSON.

Chlorination products of ββ′-dichlorodiethyl sulphide. S. A. MUMFORD and J. W. C. PHILLIPS (J.C.S., 1928, 155—162).—The compounds described by Mann and Pope (J.C.S., 1922, 121, 594) as (I) αββ′-trichloro- and (II) αβββ′-tetrachloro-diethyl sulphides, obtained by the chlorination of ββ′-dichlorodiethyl sulphide, are re-investigated. Analytical figures for (I) and (II) agree better with the formulæ $C_4H_5Cl_3S$ and $C_4H_4Cl_4S$, respectively, than with the formulæ assigned; it is suggested that the compounds are β-chloroethyl-α′β′(or β′β′)-dichlorovinyl and α′β′β′-trichlorovinyl sulphides respectively. This view is supported by their stability towards hydrolysis, by their red colour with sulphuric acid, and by their physical properties (cf. Lawson and Dawson, this vol., 153).

E. W. WIGNALL.

Action of thionyl chloride on organic acids. L. McMASTER and F. F. AHMANN (J. Amer. Chem. Soc., 1928, 50, 145—149).—Thionyl chloride converts chloroacetic acid, but not trichloroacetic acid or glycine, into the acid chloride. Oxalic and tartaric acids are unattacked by thionyl chloride, succinic and glutaric acids yield anhydrides, and malonic, suberic, and sebacic acids form dichlorides; maleic acid yields the anhydride, whilst fumaric acid is unattacked. The nitrobenzoic acids all yield acid chlorides with thionyl chloride, but with difficulty in the case of the *p*-derivative. *m*- and *p*-Aminobenzoyl chlorides can be obtained similarly, but anthranilic acid is unaffected. Salicylic acid yields the acid chloride, but *p*-hydroxybenzoic acid is unaffected, whilst *m*-hydroxybenzoic acid and the hydroxytoluic acids yield vitreous solids of indefinite composition. Phthalic acid is converted by thionyl chloride into the anhydride, *iso*phthalic acid yields the dichloride, but terephthalic acid is unaffected.

F. G. WILLSON.

Preparation of *iso*butyryl chloride. A. Récsei (Chem.-Ztg., 1928, **52**, 22).—*iso*Butyric acid is treated with phosphorus trichloride and the product distilled at ordinary pressure. S. I. Levy.

Purification of palmitic and stearic acids. A. L. Wilkie (J.S.C.I., 1927, **46**, 471—472T).—Reasonably pure palmitic and stearic acids may be obtained by fractional distillation under diminished pressure of a mixture of the ethyl esters through a column of the Dufton type, 150 cm. long, maintained at a uniform constant temperature. The appropriate fractions are hydrolysed. W. J. Powell.

Hydrogenation of methyl oleate, erucate, cetoleate, and clupanodonate. S. Ueno and N. Kuzei (J. Soc. Chem. Ind. Japan, 1927, **30**, 268—275).—The ester (0·5 g.) was hydrogenated in solution in glacial acetic acid or ethyl alcohol in the presence of platinum-black. Methyl oleate and erucate were found to require nearly equal lengths of time for complete hydrogenation; methyl erucate and cetoleate required less time than methyl clupanodonate. It is concluded that the length of time required for the complete hydrogenation is nearly equal for all those members of normal unsaturated acids that belong to the same series and have nearly equal mol. wt., but for acids of different degree of unsaturation the time required depends entirely on the degree of unsaturation, being longer as the acid is more unsaturated. N. Kameyama.

Cork. II. F. Zetzsche, C. Cholatnikov, and K. Scherz (Helv. Chim. Acta, 1928, **11**, 272—276).—When pure cork (A., 1927, 541) is treated with iodine in chloroform solution for 9–13 weeks there is left an inelastic, sandy residue (30—38%), consisting of suberin-free cork cells, and the total cellulose. It does not contain iodine, whereas the portion soluble in chloroform contains about 45% of iodine and gives on hydrolysis traces of fatty acids. Cellulose acetate is not affected by iodine even after 5 months. The results using oxidised and phosphoric acid corks are also given. It is concluded that the cellulose in cork is not in stable combination with the suberin. H. Burton.

Mechanism of the oxidative action of hydrogen peroxide in presence of ferrous iron. Oxidation of glycollic acid. S. Goldschmidt and P. Askenasy.—See this vol., 251.

Biochemical formation of optically active lactic acid. Preparation of zinc *d*(—)-lactate. C. Neuberg and M. Kobel (Annal. Acad. Sci. Fennicæ, 1927, **A**, **29**, No. 8).—In the previous experiments (A., 1927, 592) it is probable that a small amount of lactic acid was formed directly from the yeast. G. A. C. Gough.

Determination of lactic acid in sugar solutions decomposed by alkali. T. E. Friedemann (J. Biol. Chem., 1928, 76, 75—87).—The author's method (A., 1927, 800) for the determination of lactic acid may be applied to the mixture of substances obtained by the action of alkali on a sugar, the error under these conditions being 5—10%. C. R. Harington.

Determination of mercury salicylate and lactate. A. Jonesco-Matin and C. V. Bordleano.—See this vol., 313.

Complete history of Wöhler's first organic synthesis. W. H. Warren (Ber., 1928, **61**, [*A*], 3—7).—Attention is directed to the fact that Wöhler's work on the action of cyanogen on ammonia led him to the isolation and identification of oxalic acid in 1824 and of carbamide, the identification of which was published only in 1828. In one reaction, therefore, Wöhler effected the synthesis of organic compounds of vegetable and animal origin, respectively. H. Wren.

Influence of the substitution sequence CH_2, O, S on reactivity of some aliphatic acids and their esters. M. H. Palomaa and R. Leimu (Annal. Acad. Sci. Fennicæ, 1927, **A**, **29**, No. 10).—The velocity coefficients of hydrolysis and esterification, determined in a 50% mixture of water and the respective alcohol at 25° with hydrogen chloride as catalyst, of the following esters are, respectively: 0·146, 0·424 for methyl glutarate; 0·089, 0·109 for ethyl glutarate; 0·217, 0·357 for methyl diglycollate; 0·152, 0·113 for ethyl diglycollate; 0·115, 0·272 for methyl thiodiglycollate; 0·076, 0·081 for ethyl thiodiglycollate; 0·304, 0·532 for methyl glycollate; 0·221, 0·183 for ethyl glycollate; 0·288, 0·762 for methyl propionate; 0·186, 0·219 for ethyl propionate. It is observed that each substituent has almost the same influence on the velocity coefficients of the ethyl esters as it has on those of the corresponding methyl ester. G. A. C. Gough.

Determination of tartaric acid in presence of other organic acids. E. Bernhauer (Oesterr. Chem. Ztg., 1928, **31**, 4—7).—Tartaric acid is precipitated as potassium hydrogen tartrate by boiling with potassium acetate and glacial acetic acid in presence of a large volume of 96% alcohol. The precipitate is washed with 66% alcohol, dissolved in warm water, and titrated with standard alkali. Details of the procedure and of the limits of accuracy in the presence of other organic acids are given. S. I. Levy.

Bismuth salicylates and citrates. P. Godfrin.—See this vol., 288.

Hydroxy-acids of the sugar group. I. *d*-Saccharic and *d*-gluconic acids. K. Rehorst (Ber., 1928, **61**, [*B*], 163—171).—Crystalline polyhydroxy-acids of the sugar group, free from the corresponding lactones, are prepared by treating solutions of suitable salts with slightly less than the calculated quantity of mineral acid and pouring the products into ethyl alcohol mixed with *iso*butyl or amyl alcohol. Evaporation of the solutions leaves a residual solvent consisting mainly of the higher alcohol, from which the crystalline acid usually separates after further concentration. If ethyl alcohol alone is used, water is the main residual solvent, and from it the acid separates as the lactone. Thus, potassium hydrogen saccharate is converted by use of *iso*butyl alcohol into d-*saccharic acid*, m. p. 125—126°, $[\alpha]_D^{19}$ +6·86° to +20·60°; mutarotation is due to the formation of the lactone and occurs simultaneously with a decrease in the acidity of the solution. From calcium *d*-gluconate and oxalic acid, d-*gluconic acid*, $[\alpha]_D^{20}$ $-6{\cdot}7°$ to $+12°$, is obtained by use of amyl alcohol; *iso*butyl alcohol causes extensive esterification. The acid passes at 78°/12 mm. into a mixture, $[\alpha]_D$ $+61°$ to $+20°$, containing much δ- and little γ-lactone with possibly some unchanged acid. H. Wren.

Allenetetracarboxylic acid. II. J. Pirsch (Ber., 1928, **61**, [*B*], 33—38; cf. A., 1927, 856).—The action of sodium hydrogen carbonate on ethyl γ-bromo-αγ-dicarbethoxyglutaconate proceeds analogously to that of potassium ethoxide (*loc. cit.*), leading very slowly to the formation of ethyl sodio-αγ-dicarbethoxyglutaconate. This compound is also produced when sodium carbonate in boiling absolute alcohol is used, but ethyl allenetetracarboxylate is also formed in minor quantity. The latter compound is the main product of the action of anhydrous normal sodium phosphate (prepared by heating the crystalline material slowly to 240°, powdering the product, and heating it for 8 hrs. at 260° in absence of air) under similar conditions. Ethyl carbonate and minimal quantities of ethyl sodio-αγ-dicarbethoxyglutaconate are also formed. The phosphate apparently behaves merely as acceptor for the liberated hydrogen bromide. Simultaneous oxidation and reduction are observed during the action of potassium acetate on ethyl γ-bromo-αγ-dicarbethoxyglutaconate, the products being ethyl dicarbethoxyglutaconate (identified as ethyl 6-ethoxy-2-pyrone-3 : 5-dicarboxylate, m. p. 94°), ethyl carbonate, and ethyl ethanetetracarboxylate; oxidation thus appears to result in the removal of the central carbon atom of the glutaconic acid skeleton. Pyridine and ethyl γ-bromo-αγ-dicarbethoxyglutaconate afford the *pyridine* salt of ethyl 6-hydroxy-2-pyrone-3 : 5-dicarboxylate, decomp. 181°, converted by boiling concentrated hydrochloric acid into carbon dioxide and glutaconic acid, but unchanged by boiling ethyl alcohol. H. Wren.

Nature of the hydrocarbon group of thymonucleic acid. P. Thomas and E. Maftei (XII Int. Cong. Physiol., 1926, 159; Chem. Zentr., 1927, i, 2435).—The six-carbon sugar of thymonucleic acid is considered to be related to glycuronic acid. A. A. Eldridge.

Sulphopyrotartaric acids. II. H. J. Backer and J. Buining (Rec. trav. chim., 1928, **47**, 111—122; cf. this vol., 46).—Methylsuccinic acid is sulphonated by excess of sulphur trioxide, forming mainly *α-sulpho-α-methylsuccinic acid* ($+H_2O$), m. p. 131° (decomp.) [*thallium*, *barium* ($+2H_2O$), *calcium* ($+7H_2O$), *potassium* ($+H_2O$), *copper* ($+6H_2O$), *nickel* ($+7H_2O$), and *cobalt* ($+7H_2O$) salts]. This acid is produced by the interaction of ammonium sulphite and ammonium citraconate, mesaconate, or α-bromo-α-methylsuccinate, although in the last case some α-hydroxy-α-methylsuccinic acid is formed at the same time. Treatment of the sulphonic acid with brucine gives the *brucine hydrogen* salt ($+4H_2O$), which on decomposition with ammonia yields *ammonium* d-*α-sulpho-α-methylsuccinate*, $[M]_D$ $+31°$ in water. The d-*acid* has $[M]_D$ $+33°$ in water, whilst the *sodium* salt has $[M]_D$ $+31°$. *Ammonium*-l-*α-sulpho-α-methylsuccinate*, $[M]_D$ $-31°$, is obtained by decomposition of the normal *strychnine* salt ($+2H_2O$). Racemisation of the acids or their salts is not effected by heating at 100°. H. Burton.

Constitution of the hydrogen sulphite compounds of aldehydes and ketones. F. Raschig and W. Prahl (Ber., 1928, **61**, [*B*], 179—189; cf. A., 1926, 598).—Schroeter's observation (A., 1926, 1226) that the production of β-hydroxypropyl-β-sulphonic acid by hydrolysis of phenyl propane-ββ-disulphonate and its non-identity with "acetone bisulphite" has been overlooked by the authors (*loc. cit.*) and has led to a repetition of Schroeter's work in this direction (A., 1919, i, 517). Phenyl methanedisulphonate (methionol) is conveniently prepared by the action of methanedisulphonyl chloride on phenol in the presence of benzene and pyridine at 0° and is converted by $2N$-sodium hydroxide at 80° into the sodium derivative; this, with methyl sulphate in boiling toluene, affords phenyl ethane-αα-disulphonate, converted by the successive action of sodium and methyl sulphate into phenyl propane-ββ-disulphonate, identical with Schroeter's compound. Treatment of the compound with barium hydroxide leads to the formation of barium sulphite (mixed with a little barium carbonate) in amount corresponding closely with the loss of one sulphonic acid residue. The solution contains a mixture of barium salts which are converted for purposes of separation into the corresponding copper salts, one of which (*A*), characterised by very sparing solubility in hot acetic acid, approximates in composition to copper β-hydroxypropane-β-sulphonate. A second salt, which separates when the solution of the mixture in hot acetic acid is cooled, resembles closely *copper propane-β-sulphonate* (prepared for comparison from *iso*propyl chloride through *iso*propyl mercaptan), but identity cannot be assumed. Attempts to prepare further quantities of the salt *A* by the same method were unsuccessful and the copper salt which separated in these cases from the acetic acid is not identical with that described above, since it yields a barium salt, $C_6H_{12}O_7S_2Ba$, transformed into a non-homogeneous sulphonamide and oxidised by permanganate to oxalic and sulphuric acids, with, possibly, methanesulphonic acid. The non-identity of salt *A* with *copper β-hydroxypropane-α-sulphonate*, *γ-hydroxypropane-α-sulphonate*, and *α-hydroxypropane-β-sulphonate* is established by direct comparison. The first two are prepared by sulphonation of *iso*propyl and propyl alcohols. To obtain the last, glycerol is converted by sodium hydroxide into propylene glycol and thence into the corresponding chlorohydrin, which yields the monoacetate. This substance with thionyl chloride affords *β-chloropropyl acetate*, b. p. 152°, transformed by saturated potassium sulphite solution at 120° into *potassium α-hydroxypropane-β-sulphonate*; the copper salt derived from it differs entirely from salt *A*.

Further criticisms of the authors' views have been made by Binz (A., 1926, 1123); these are regarded as answered by Bazlen (A., 1927, 842). Further confirmation of the view that the hydrogen sulphite compounds of aldehydes and ketones are hydroxysulphonic acids is found in the Röntgen-spectrographic observations of Stelling ("Zusammenhang zwischen chemischer Konstitution und *K*-Röntgen-Absorptionsspektra," Lund, 1927, p. 168). H. Wren.

Formation of formaldehyde and of sugars by the action of ultra-violet rays on alkali and alkaline-earth hydrogen carbonates. G. Mezzadroli and G. Gardano.—See this vol., 255.

Nonaldehyde from the tetradecenoic acid from sperm oil. A. Wagner (Allg. Öl- Fett-Ztg., 1927, 24, 340—341; Chem. Zentr., 1927, ii, 708).—Tetradecenoic acid, d_4^{20} 0·9018, n_D^{20} 1·4549, iodine value 107, was isolated from sperm-whale oil, and converted into the ozonide which on decomposition with water yielded nonaldehyde (semicarbazone, m. p. 80—84°; after purification with hydrogen sulphite, semicarbazone, m. p. 100°; oxime, m. p. 64°). A. A. Eldridge.

Oxidative synthesis of a dialdehydic carbohydrate, $C_{15}H_{28}O_{15}$, from dextrose. J. A. Mandel and J. B. Niederl (XII Int. Cong. Physiol., 1926, 104—105; Chem. Zentr., 1927, ii, 242).—Oxidation of dextrose with barium hypochlorite solution yields an amorphous *compound* of the composition $C_{15}H_{28}O_{15}$, $[\alpha]_D$ +64°. Reduction affords a *compound*, $C_{15}H_{32}O_{15}$, $[\alpha]_D$ +98° (*acetyl* derivative, m. p. 112—114°). The bisosazone, $C_{39}H_{48}O_{11}N_8$, has m. p. 194°. Oxidation yields monocarboxylic and dicarboxylic *acids*, $C_{14}H_{27}O_{14}\cdot CO_2H$ and $C_{13}H_{26}O_{13}(CO_2H)_2$, respectively. A. A. Eldridge.

Effect of certain β-substituents in the alcohol on affinity and reactivity in acetal formation. J. N. Street and H. Adkins (J. Amer. Chem. Soc., 1928, 50, 162—167; cf. A., 1927, 1172).—Under the conditions previously laid down, the percentage conversions, at equilibrium, of the following β-substituted ethyl alcohols into acetals are in the following decreasing order: β-amino-, β-phenyl-, β-iodo-, β-ethoxy-, β-methoxy- (allyl alcohol), β-bromo-, β-chloro-, β-carbethoxy-, and β-nitro-ethyl alcohol. Generally, the affinity of ethyl alcohol for acetal formation is little affected by β-substitution, as compared with α-substitution. The following acetals are described: *acetal* of *ethylene chlorohydrin*, b. p. 109—110°/30 mm.; *ethylene bromohydrin*, b. p. 129—130°/20 mm.; β-*methoxyethyl alcohol*, b. p. 100°/20—30 mm.; β-*ethoxyethyl alcohol*, b. p. 83—85°/10—15 mm.; β-phenylethyl alcohol, b. p. 201°/15 mm. F. G. Willson.

Rate of synthesis and hydrolysis of certain acetals. H. Adkins and A. E. Broderick (J. Amer. Chem. Soc., 1928, 50, 178—185; cf. preceding abstract).—The rates of reaction of acetaldehyde with methyl, ethyl, *iso*propyl, and *n*-butyl alcohols have been determined with specially purified reagents, in presence of hydrogen chloride (0·000465 g. per mol. of alcohol; cf. Adkins and Adams, A., 1925, i, 785). Only slight differences in the reactivities of the alcohols for acetal formation were observed. Assuming the immediate formation of a semiacetal, with subsequent bimolecular reaction between the latter and the alcohol, the values of the bimolecular reaction constant diminish steadily in the period between 2 and 100 min. from commencement of reaction. Consistent values of the constants are, however, obtained on the assumption that the water eliminated in the acetal formation is largely consumed in hydrolysis of the semiacetal. With the same concentration of catalyst, the rate of hydrolysis of *iso*propyl acetal is much less than that of the synthesis, whilst the hydrolytic reaction constant increases somewhat as the reaction proceeds, both these phenomena being ascribed to the poisoning effect of water. F. G. Willson.

Relation of structure of ketones to their reactivity and affinity in acetal formation. H. E. Carswell and H. Adkins (J. Amer. Chem. Soc., 1928, 50, 235—241; cf. preceding abstract).—Ethyl formate may be determined in presence of alcohol, ethyl orthoformate, a ketone and its acetal by treatment of the mixture with sufficient sodium to react with the alcohol and with sodium ethoxide, and measuring the carbon monoxide evolved (cf. Geuther, Chem. Zentr., 1868, 39, 632). Approximately 2 mols. of carbon monoxide are obtained from 3 mols. of ethyl formate, but the actual amount varies slightly with the amount and kind of ketone present, probably owing to Claisen condensation of the ethyl formate. Applying this method, the extent of acetal formation from ethyl orthoformate and the following ketones has been determined: acetone, methyl ethyl, diethyl, methyl *n*-hexyl, and methyl *tert.*-butyl ketones, acetophenone, propiophenone, and benzophenone. Ethyl orthoformate does not condense with ketones in toluene or xylene solution in presence of hydrogen chloride, this reaction taking place only in presence of hydrogen chloride and a considerable proportion of alcohol. The greatest extent of acetal formation (about 90%) was observed with acetone, and the least (12·5%) with methyl *tert.*-butyl ketone. Substitution of higher *n*-alkyl radicals for the methyl group or groups in acetone reduces slightly the extent of acetal formation, still greater reductions being observed progressively through acetophenone, propiophenone, and benzophenone. The *diethylacetals* of *methyl* n-*hexyl ketone*, b. p. 101—103°/16 mm., d_{25}^{25} 0·8798, and *propiophenone*, b. p. 118—120°/15 mm., d_{25}^{25} 0·9406, are described. F. G. Willson.

Nitrosyl chloride and ketones. H. Rheinboldt and O. Schmitz-Dumont (Ber., 1928, 61, [*B*], 32—33; cf. A., 1925, i, 1131).—Contrary to the observations of Lynn and Lee (A., 1927, 544), "nitrosochlorination" occurs by the action of nitrosyl chloride on ketones in the absence of solvent. Thus pinacolin affords chloro-oximinopinacolin, m. p. 133—134°. The differing results are due to the different relative quantities of nitrosyl chloride and ketone employed. Lynn and Lee's supposed conversion of methyl ethyl ketone into its oximino-derivative could not be confirmed, diacetylmonoxime, m. p. 76°, being obtained by this reaction. H. Wren.

Changes in carbohydrate solutions due to sunlight in presence of uranium salts and to ultraviolet rays. Abelous, Aloy, and Valdiguié.—See this vol., 255.

Comparative reduction values of carbohydrates by the Hagedorn–Jensen, Benedict–Myers, and Folin–Wu methods. G. W. Pucher and M. W. Finch (J. Biol. Chem., 1928, 76, 331—

335).—Comparative results of the determination of known solutions of various sugars by the above-mentioned methods are given. The most consistent results were obtained with the method of Hagedorn and Jensen (A., 1920, ii, 641); in general, the figures agree with those determined by previous workers, except that lævulose is found to have a reducing value 10—20% higher than that of dextrose.

C. R. Harington.

Applications of thallium compounds in organic chemistry. IV. Thallium compounds of polyhydroxy-compounds. R. C. Menzies and (Miss) M. E. Kieser (J.C.S., 1928, 186—190).—The purity of the yellow compounds formed on mixing concentrated aqueous solutions of thallous hydroxide with those of the sugars etc. (Menzies and Wilkins, A., 1924, i, 704) may be judged by comparing the total precipitated thallium content with the amount of hydrolysable thallium (replacing non-acidic hydroxyl groups) indicated by titration (Christie and Menzies, A., 1926, 55). Dextrose, galactose, and especially lævulose compounds give indefinite analytical figures, showing decomposition to acid products; thallium methylglucoside (Fear and Menzies, A., 1926, 604) when rapidly prepared gives titration values very little less than the total thallium content.

Trithallium methylarabinoside, m. p. 215—220° (decomp.) after darkening at 160—210°, which is unaffected by daylight, gives titration values in close agreement with the total thallium.

Thallous gluconate, $C_5H_{11}O_5\cdot CO_2Tl$, prepared from barium gluconate and thallous sulphate, has m. p. 134—144° (darkening), $[\alpha]_D$ +3·3° (c=4·24) in aqueous solution; when prepared from gluconic acid and thallous hydroxide it has m. p. 133—138° (darkening), and $[\alpha]_D$ +4·4° (c=3·9); crystal nuclei are, however, obtained only in preparations from mercury gluconate and metallic thallium. When this compound is treated with thallous hydroxide, *hexathallium gluconate*, $C_5H_6(OTl)_5\cdot CO_2Tl$, lævorotatory in aqueous solution, is obtained; this when freshly prepared gives theoretical titration values for $(OTl)_5$, which diminish on keeping the substance. *Hexathallium sorbitol*, $C_6H_8(OTl)_6$, gives, when freshly prepared, theoretical titration values, which similarly diminish.

Tetrathallium sucrose has been prepared.

E. W. Wignall.

Electron-sharing ability of organic radicals; dextrose and other poly-alcohols. J. B. Allison and R. M. Hixon (J. Amer. Chem. Soc., 1928, 50, 168—172; cf. A., 1927, 814).—The conductance of aqueous solutions of glucosamine has been measured, and Vellinger's value (A., 1926, 778) for the basic dissociation constant confirmed. The dissociation constant of glucosamine, the corresponding constant of dextrose, and the heat of replacement of hydrogen in dextrose by sodium all lie midway between the corresponding constants for methyl- and phenylamines and hydroxides, indicating that the electron-sharing ability of the radical of dextrose (and of those of other polyalcohols) is intermediate between that of the methyl and phenyl group.

F. G. Willson.

Action of superheated water on sugars. I. S. Komatsu and C. Tanaka (Sexagint [Osaka celebration], Kyoto, 1927, 1—12).—2% Solutions of *l*-xylose, *l*-arabinose, rhamnose, dextrose, *d*-galactose, α-methylglucoside, sucrose, maltose, and lactose were heated at 120° and 150° for 2—20 hrs. and the resulting acidity, reducing power, rotation, colour, and percentage of furfuraldehyde were found. All the monosaccharides examined yield pyrone compounds first and subsequently acidic and humic substances. The authors favour the scheme given by Nef:

$$\cdot CH(OH)\cdot CH(OH)\cdot CHO \longrightarrow \cdot CH(OH)\cdot CH(OH)\cdot CH(OH)_2 \longrightarrow \cdot CH(OH)\cdot C(OH){:}CH\cdot OH,$$

and in support show that mannitol, having no carbonyl group, is not appreciably changed by water at 150° in 6 hrs. With disaccharides hydrolysis to monosaccharides occurs first, the rate being related to the rate of hydrolysis by acids. The rate of the subsequent action is found to be related to the ease of attack of *Penicillium glaucum*, but different from the ease of oxidation in alkaline solution. Humic and acidic substances are formed under the same conditions from furfuraldehyde and the humic substances resemble those in the soil.

C. D. Langford.

Action of superheated water on sugars. II. C. Tanaka (Sexagint [Osaka celebration], Kyoto, 1927, 13—26).—A more detailed study of the action of superheated water on lævulose, dextrose, sucrose, rhamnose, and xylose is given and, in support of the view that the reaction takes place in two steps, it is shown that hydroxymethylfurfuraldehyde, methylfurfuraldehyde, and furfuraldehyde yield products apparently identical with those obtained from the sugars from which they would be expected. It is suggested that coal may have been formed by a related series of changes.

C. D. Langford.

Transformation of β-glucosides and β-acetyl-sugars into their α-varieties. E. Pacsu (Ber., 1928, 61, [*B*], 137—144).—Addition of 3 mols. of anhydrous stannic chloride to a solution of 1 mol. of a β-acetyl-sugar in anhydrous chloroform causes quantitative production of the corresponding α-variety; the change is complete within 6—7 days at the ordinary temperature, in 4—5 hrs. in warm solution. Isomerisation of β-glucosides proceeds more slowly and, under similar conditions, gives an equilibrium mixture containing about 92% of the α-glucoside; if the proportion of stannic chloride is reduced to 1 mol., equilibrium is established in the presence of 75% of α-glucoside. Stannic chloride does not appear to cause isomerisation of α-acetyl-sugars or α-glucosides. If the reaction with β-penta-acetylglucose is allowed to proceed further, the acetyl group attached to carbon atom 1 is replaced by chlorine with production of the known dextrorotatory acetochloroglucose, identified by conversion into tetra-acetyl-β-methylglucoside. It appears therefore that the acetohalogeno-sugars belong to the α-series and not, as previously supposed, to the β-group. This view is in harmony with their high dextrorotation. Replacement of the chlorine atom is therefore accompanied by a Walden inversion. The method of isomerisation described above appears applicable to all similar derivatives of mono- and di-saccharides. Inversion occurs only with respect to the groups attached to the 1-carbon atom, the remainder of the molecule being unchanged. The following transformations are recorded: β- into α-penta-acetylglucose, $[\alpha]_D^{20}$ +102·70° in chloroform; β-penta-acetylglucose into α-acetochloroglucose; β- into α-penta-acetylmannose, $[\alpha]_D^{20}$ +55·26° in chloroform; tetra-acetyl-β- into tetra-acetyl-α-methylglucoside, hydrolysed to α-methylglucoside, m. p. 166—167°, $[\alpha]_D^{20}$ +156·9° in water. H. Wren.

Properties and preparation of lævulose. H. I. Waterman, A. Rooseboom, and E. L. Oberg (Chem. Weekblad. 1928, 25, 50—52).—Lævulose is decomposed even at low temperatures by lime, whether added as calcium oxide or hydroxide. The lime compound consists of fine white needles, which become yellow and decompose when kept in a vacuum over phosphoric oxide. It may be used for the separation of the pure sugar from invert-sugar and from beet molasses, the precipitated compound being filtered, washed, and immediately decomposed with carbon dioxide. S. I. Levy.

Synthesis of lactose. A. Pictet and H. Vogel (Helv. Chim. Acta, 1928, **11**, 209—215).—Mainly an account of work already published (A., 1927, 960). The following is new. When β-galactose is heated at 150°/14 mm., there is formed β-*galactosan*, m. p. 154—155°, $[\alpha]_D^{20}$ +30·49° to +80·66° in water after 24 hrs. owing to the regeneration of β-galactose. β-Galactosan differs from the α-isomeride (A., 1922, i, 811) in that it is hydrolysed instantaneously with cold, very dilute sulphuric acid forming galactose, and when treated with phenylhydrazine or acetic anhydride gives galactosazone or penta-acetylgalactose. A formula is suggested. When it is heated with β-glucose and a small amount of zinc chloride at 150°/14 mm., and the product is acetylated and hydrolysed, lactose is formed. H. Burton.

Formulæ of *Digitalis* glucosides. I. Digitoxin. A. Windaus (Nachr. Ges. Wiss. Göttingen, 1926, 170—174; Chem. Zentr., 1927, i, 2912—2913).—The formula $C_{41}H_{64}O_{13}$ is ascribed to digitoxin, whence on hydrolysis: $C_{41}H_{64}O_{13}+3H_2O=C_{23}H_{34}O_4$ (digitoxigenin) $+3C_6H_{12}O_4$; tetrahydroanhydrodigitoxigenin is $C_{23}H_{36}O_3$, tetrahydroanhydrodigitoxigenone, $C_{23}H_{34}O_3$, and the derived lactone $C_{23}H_{36}O_2$. Digitoxigenin is a singly unsaturated dihydroxylactone, yielding an unsaturated trihydroxymonocarboxylic acid, dixgenic acid, and when warmed with hydrochloric acid yields, by elimination of the elements of water, a doubly unsaturated monohydroxylactone, anhydrodigitoxigenin, $C_{23}H_{32}O_3$. A. A. Eldridge.

Digitin of Nativelle. P. Bourcet and G. Dugue (Compt. rend., 1928, **186**, 395—397).—Treatment of the digitin, m. p. 281°, of Nativelle (Mon. Sci., 1874, [iii], 4, 827) with chloroform affords digitonin and a soluble product, m. p. 273°, α_D −66·5° (acetyl derivative, m. p. 244—245°), identical with digin (Tambach, A., 1912, i, 375) and gitogenin (Windaus and Schneckenburger, A., 1913, i, 1213). The authors suggest that the names digin and digitin be replaced by gitogenin. H. Burton.

Extraction of the active glucosides of *Adonis vernalis*. G. A. Pevzner (Trans. Sci. Chem.-Pharm. Inst., 1923, No. 3, 78—84).—The whole of the active principle is extracted in a Soxhlet apparatus with absolute ethyl alcohol, by percolation with methyl or ethyl alcohol, or by extraction (20 times) with water. Alcohol increases, whereas heating at 100° diminishes, the activity of the product. Chemical Abstracts.

Alcoholic potassium hydroxide as microchemical reagent for starch and aleurone. F. Netolitzky (Festschr. A. Tschirch, 1926, 362—365; Chem. Zentr., 1927, i, 2933).—Starch grains are affected by warm alcoholic potassium hydroxide at rates differing according to their origin. With aleurone grains the globoid is at first clearly observed; after some time the protein crystalloid is removed. The ash of aleurone grains of *Bertholletia* seeds (13—15%) contains P_2O_5 35—36%, CaO 8·5—9·5%, MgO 17—19%, and K_2O 15%. A. A. Eldridge.

Polysaccharides. XXXVII. Behaviour of various celluloses towards snail cellulase. P. Karrer and P. Schubert (Helv. Chim. Acta, 1928, **11**, 229—230; cf. B., 1926, 44, 945).—Enzymic hydrolysis of seven specimens of cellulose shows that after 7 weeks 22—38·4% is degraded. β-Cellulose is hydrolysed more rapidly than α-cellulose, whilst filter-paper is almost completely decomposed (93%) after about 3 months. H. Burton.

Polysaccharides. XXXVIII. Behaviour of viscose silks towards snail cellulase. O. Faust, P. Karrer, and P. Schubert (Helv. Chim. Acta, 1928, **11**, 231—233).—Hydrolysis of 12 specimens of viscose silks, 6 from one cellulose and 6 from another, shows that least decomposition occurs when the viscose silk is precipitated from an acid bath containing 5·4% of an aromatic sulphonic acid. The hydrolysis is much decreased when the viscose silk is precipitated from an acid bath containing relatively large amounts of sodium sulphate. H. Burton.

Depolymerisation of inulin. H. Vogel and A. Pictet (Helv. Chim. Acta, 1928, **11**, 215—220).—When inulin is heated with glycerol at 120°/15 mm. for 3 hrs. and the reaction mixture diluted with methyl alcohol and ether there is precipitated *trilævulosan*, m. p. 165°, decomp. 173°, $[\alpha]_D$ −29·66° in water (*nona-acetate*, m. p. 91°, $[\alpha]_D$ −35·52° in benzene), which does not reduce Fehling's solution or give an osazone, and is hydrolysed by 5% sulphuric acid to lævulose. When the mixture is heated at 140°/15 mm. for 6 hrs. there are formed a *dilævulosan*, m. p. 96°, $[\alpha]_D$ −24·8° (*hexa-acetate*, m. p. 92°, $[\alpha]_D$ −29·8° in benzene), which is a reducing agent, together with a syrupy *substance*, $[\alpha]_D$ +12·5° in water, probably a compound of lævulosan and glycerol (cf. Pictet and Reilly, A., 1921, i, 544). Hydrolysis of the above acetates by Zemplen's method gives the original lævulosans. The lævulosan of Pictet and Reilly (*loc. cit.*) when heated at 120°/14 mm. with a small amount of zinc chloride furnishes a *dilævulosan*, m. p. 138—140°, $[\alpha]_D$ +21·5° in water (*hexa-acetate*, m. p. 83—84°, $[\alpha]_D$ +6·98° in benzene), which is also a reducing agent. H. Burton.

Metallic complexes of cellulose nitrates. A. Apard (Compt. rend., 1928, **186**, 153—154).—When

1% solutions of cellulose nitrate are electrolysed, using lead, mercury, copper, zinc, cadmium, and iron as electrodes, gelatinous metal–cellulose nitrate complexes are formed at the anode, whilst some of the metal dissolves. Gelatinous residues of a more variable composition are formed by agitating the oxides of silver, calcium, bismuth, barium, aluminium, etc. with 1% solutions of cellulose nitrate in acetone.

B. W. ANDERSON.

Constitution of pine lignin. VI. Identity of α-lignosulphonic acid with coniferaldehydesulphonic acid. P. KLASON (Ber., 1928, 61, [*B*], 171—176; cf. A., 1920, i, 822; 1922, i, 324; 1923, i, 187; 1925, i, 371, 1246).—Vanillin is converted by methyl-alcoholic sodium hydroxide in the presence of toluene into its sodium derivative, which is transformed by the successive action of chloromethyl ether and acetaldehyde in dilute alkaline solution into 3-methoxy-4-methoxymethoxycinnamaldehyde (cf. Pauly and Wäscher, A., 1923, i, 342). Treatment of the latter compound with a saturated aqueous solution of sulphur dioxide eliminates the methoxymethoxy-residue with production of coniferaldehydesulphonic acid, isolated as the β-*naphthylamine* salt. This compound has the same percentage composition and properties as the β-naphthylamine salts of the α-lignosulphonic acids. It appears, therefore, that α-lignin of pine, comprising 75% of the total lignin, is formed by condensation of coniferaldehyde, into which it can be degraded by sulphurous acid; the acid is always firmly united to the ethylenic linking of the aldehyde, so that in the technical boiling process the lignin appears mainly as the sulphonic acid of paraconiferaldehyde. These views on the relationship of lignin to coniferaldehyde are strengthened by the observation of the identity of hadromal and coniferaldehyde (cf. Hoffmeister, A., 1927, 1189).

H. WREN.

Synthesis and purification of hexamethyleneimine. A. MÜLLER and A. SAUERWALD (Monatsh., 1927, **48**, 727—732).—Treatment of αζ-dibromo-*n*-hexane (1 mol.) and *p*-toluenesulphonamide (1 mol.) with aqueous-alcoholic potassium hydroxide solution affords N-p-*toluenesulphonylhexamethyleneimine*, m. p. 72—74°, together with αζ-di-*p*-toluenesulphonamido-*n*-hexane. Treatment of the former compound with concentrated hydrochloric acid at 160° gives hexamethyleneimine hydrochloride, m. p. 236° (corr.) (lit. 222°). Pure hexamethyleneimine has b. p. 138·0—138·2°/749 mm., d_4^{15} 0·8841, d_4^{20} 0·8799, d_4^{25} 0·8770, n_D^{20} 1·4654; the following derivatives are described: chloroplatinate, decomp. 196—197° (corr.) (lit. 149° and 191°); *chloroaurate*, decomp. 206° (corr.); picrate, m. p. 146·5° (corr.) (lit. 85°); *phenylthiocarbimide*, m. p. 143° (corr.); the *benzoyl* derivative, m. p. 36° (corr.), when treated with phosphorus pentachloride yields *αζ-diphenoxy*-n-*hexane*, m. p. 83—83·5° (corr.). *NN*-Dimethylhexamethyleneiminium iodide [*chloroplatinate*, decomp. 233° (corr.)] has m. p. 265° (corr.) with slight decomp. (lit. 214—215°).

H. BURTON.

Alkylamino-ethanols and -propanols. J. S. PIERCE (J. Amer. Chem. Soc., 1928, **50**, 241—244).—Condensation of allylamine with β-chloroethyl chloroformate affords β-*chloroethyl allylcarbamate*, b. p. 103·5—104·5°/1·3 mm., d_4^{20} 1·1811, n_D^{27} 1·4668. When boiled with 1·5 mols. of alcoholic potassium hydroxide, the latter is converted into 3-*allyl*-2-*oxazolidone*, b. p. 123—125°/0·7 mm., d_4^{20} 1·113, n_D^{27} 1·4691, whilst with 4 mols. of alkali, β-*allylaminoethyl alcohol*, b. p. 77—80°/1·5 mm., d_4^{20} 0·9398, n_D^{27} 1·4602, is obtained (cf. Pierce and Adams, A., 1923, i, 484). γ-*Chloropropyl allylcarbamate*, b. p. 110—111°/1 mm., d_4^{20} 1·1390, n_D^{20} 1·1390, *methylcarbamate*, b. p. 104·5—106°/1 mm., d_4^{20} 1·1821, n_D^{27} 1·4548, and n-*amylcarbamate*, b. p. 135—137°/2 mm., d_4^{20} 1·0629, n_D^{21} 1·4560, obtained similarly, yield, when boiled with 4 mols. of alcoholic potassium hydroxide, γ-*allylamino*-, b. p. 88—90°/0·8 mm., d_4^{20} 0·9319, n_D^{27} 1·4629, γ-*methylamino*-, b. p. 74—77°/2·5 mm., d_4^{20} 0·9315, n_D^{27} 1·4418, and γ-n-*amylamino-propyl alcohol*, b. p. 103—105°/1·8 mm., d_4^{20} 0·8858, n_D^{21} 1·4493, respectively.

F. G. WILLSON.

Determination of arginine. A. BONOT and T. CAHN (Bull. Soc. Chim. biol., 1927, 9, 1001—1016).—See A., 1927, 269.

Interaction of sulphur monochloride with organic compounds containing the reactive methylene group. Formation and properties of dithioketones and dithioethers. IV. K. G. NAIK and Y. N. BHAT (J. Indian Chem. Soc., 4, 525—530).—*Dithioketones*, $R_2C{<}\begin{matrix}S\\|\\S\end{matrix}$, are obtained from sulphur monochloride and the following amides: malondiethylamide, m. p. 202° after softening at 186°; malondi-*n*-propylamide, m. p. 180° after softening at 172°; malondi*iso*butylamide, m. p. 202° after softening at 196°; malondiheptylamide, m. p. 125°; malondi-*m*-toluidide, m. p. 180° after softening at 158° [*tetranitro*-derivative, m. p. 166° (decomp.)]. Methylmalondi-*m*-toluidide gives the *dithio-ether*, m. p. 187—188°. *Malondi*-n-*heptylamide*, m. p. 132°, *methylmalondi*-m-*toluidide*, m. p. 157°, and *methylmalondibenzylamide*, m. p. 142°, are incidentally described.

C. D. LANGFORD.

Formation of cyanate in the determination of alkali cyanides with copper sulphate. J. LEBOUCQ (J. Pharm. Chim., 1927, [viii], 6, 20—25).—The percentage of potassium cyanide which combines to form a complex copper cyanide in the volumetric determination of alkali cyanides by means of copper sulphate has been shown never to exceed 85·3% of that present. The remaining 14·7% of the cyanide becomes oxidised during the reaction to cyanate, proved by separating it as hydrazodicarbonamide with semicarbazide. The results are thus in accordance with Treadwell's suggested equations for the reaction: $2CuSO_4+2NH_3+7KCN+H_2O=2K_2Cu(CN)_3+(NH_4)_2SO_4+K_2SO_4+KCNO$, or $2CuSO_4+2NH_3+7KCN+H_2O=K_2(NH_4)Cu_2(CN)_6+2K_2SO_4+NH_4CNO$.

E. A. LUNT.

Coloration of alkali thiocyanates on exposure to light. E. MONTIGNIE (Bull. Soc. chim., 1928, [iv], 43, 106—108; cf. Kahane, this vol., 34).—The pink colour which develops on exposure of solutions of alkali thiocyanates to sunlight is due to the oxidation by dissolved oxygen of the traces of ferrous salts which are usually present. On keeping coloured solutions in the dark for a few hours the colour disappears. Assuming the iron to be present as ferrous sulphate, the observed effects may be represented by the scheme: $2FeSO_4+O+6HCNS \rightleftharpoons H_2O+2H_2SO_4+2Fe(CNS)_3$. The decolorisation effected on boiling is due to hydrolysis of the ferric thiocyanate and subsequent reduction of ferric hydroxide to ferrous hydroxide. Re-oxidation occurs on exposure to the air and the colour returns. Traces of quinol prevent the appearance of the pink colour. Coloration occurs in presence of strong acids and salts which are largely ionised, but not in presence of weak acids. The colour is extracted by ether, amyl alcohol, and ethyl acetate, but not by chloroform or benzene. J. S. CARTER.

Residual affinity and co-ordination. XXX. Complex ethylenethiocarbamido-salts of univalent and bivalent metals. G. T. MORGAN and F. H. BURSTALL (J.C.S., 1928, 143—155).—Additive products of unoxidised sulphur compounds to cupric or auric salts readily yield complexes (cf. Morgan and Ledbury, J.C.S., 1922, **121**, 2883) in which the cuprous or aurous state is stabilised. Thiocarbamide has such an action, but forms polynuclear derivatives (cf. Kohlschütter, A., 1903, i, 468; 1906, i, 812; Contardi and Dansi, this vol., 159); thus on mixing aqueous solutions of potassium cyanate and of copper sulphate, saturated with sulphur dioxide, and treating the resultant *substance*, $Cu_2K(CNO)_3$, with thiocarbamide in aqueous solution, *pentathiocarbamidodicuprous cyanate hydrate*, $[Cu_2,5CH_4N_2S](CNO)_2,H_2O$, is obtained as a colourless substance, of which the aqueous solution decomposes on keeping or on heating, or on treatment with sodium hydroxide. This is attributed to the co-ordinating power of the two amino-groups. When the action of the latter is inhibited by forming a cyclic compound, ethylenethiocarbamide (symbolised " etu " in formulæ), this difficulty is largely avoided. Cuprous, aurous, argentous, palladium, cadmium, mercury, and lead salts containing this substance have been prepared.

On mixing aqueous solutions of ethylenethiocarbamide and cupric nitrate, there is a transitory green coloration, followed by separation of sulphur; the solution on evaporation yields colourless *tetrakisethylenethiocarbamidocuprous nitrate*, $[Cu,4\ etu]NO_3$, m. p. 140—141°. *Monoaquopentaethylenethiocarbamidodicuprous nitrate*, $[Cu_2,5\ etu,\ H_2O](NO_3)_2$, is obtained by using a larger proportion of cupric nitrate, and drying over sulphuric acid; this is easily oxidised, as is its *trihydrate* ($+3H_2O$), m. p. 145—146°. When the latter is treated in solution with aqueous sodium hydroxide, followed by heating, *ethylenethiocarbamidocuprous oxide*, darkening at 180°, decomp. 200°, is obtained. *Trisethylenethiocarbamidocuprous sulphate*, $[Cu,3\ etu]_2SO_4$, decomp. 240—251°, and *acetate*, $[Cu,3\ etu]AcOH$, decomp. 250—255°, are obtained from cupric sulphate and acetate, respectively. *Bisethylenethiocarbamidocuprous chloride*, $[Cu,2\ etu]Cl$, m. p. 166—167°, is obtained from cuprous chloride; the *bromide* has m. p. 162—163°, the *iodide*, m. p. 160—161°.

Tetrakisethylenethiocarbamidoargentous nitrate, $[Ag,4\ etu]NO_3$, m. p. 96—97°, which yields with potassium iodide a white precipitate decomposed on heating, and *trisethylenethiocarbamidodiargentous nitrate*, $[Ag_2,3\ etu](NO_3)_2$, darkening at 200°, exploding at 224°, are similarly obtained. When the former is treated with potassium persulphate solution, *trisethylenethiocarbamidodiargentous persulphate*, darkening at 160°, decomp. 205°; and when with aqueous sodium hydroxide, *ethylenethiocarbamidoargentous oxide*, darkening at 120°, decomp. 170°, or on keeping; and when with potassium iodide, *ethylenethiocarbamidoargentous iodide*, $[Ag,\ etu]I$, m. p. 162°, are obtained. *Trisethylenethiocarbamidoargentous chloride*, $[Ag,3\ etu]Cl$, m. p. 167—168°, is prepared from silver chloride, and is stable and unaffected by light; *bisethylenethiocarbamidoargentous bromide*, m. p. 152°, similarly prepared, resembles the cuprous compound.

Bisethylenethiocarbamidoaurous chloride, $[Au,2\ etu]Cl$, is obtained as a *hydrate* (which becomes anhydrous at 110°, yellow at 210°, and decomp. at 242°), by the interaction of auric chloride solution and ethylenethiocarbamide. When it is treated in solution with dilute nitric acid, the corresponding (anhydrous) *nitrate*, with properties resembling those of tetrakisethylenethiocarbamidocuprous nitrate; and when with potassium iodide, *ethylenethiocarbamidoaurous iodide*, m. p. 225° (decomp.), are obtained. On treating the chloride with sodium hydroxide solution, a precipitate is obtained. If this is treated with hydrobromic acid and ethylenethiocarbamide, *bisethylenethiocarbamidoaurous bromide hydrate*, $[Au,2\ etu]Br,H_2O$, is obtained; this melts in its water of crystallisation at 100°, and resolidifies with m. p. 191°; the *anhydrous* compound is obtained by keeping over sulphuric acid, but reverts in the atmosphere to the hydrate. If, however, the above precipitate is heated by boiling the solution, it forms *ethylenethiocarbamidoaurous oxide*, $[Au,\ etu]_2O$, blackening at 200°. Auric chloride solution and thiocarbamide yield *bisthiocarbamidoaurous nitrate hydrate*, $[Au,2CH_4N_2S]NO_3,H_2O$, decomp. 155°.

Tetrakisethylenethiocarbamidocadmium nitrate, $[Cd,4\ etu](NO_3)_2$, m. p. 178°, and *bisethylenethiocarbamidocadmium chloride*, m. p. 220°, *bromide*, m. p. 208°, and *iodide*, m. p. 165°, $[Cd,2\ etu]X_2$, are similarly prepared, as are *ethylenethiocarbamidoplumbous chloride*, $[Pb,\ etu]Cl_2$, m. p. 183°, *trisethylenethiocarbamidomercuric nitrate*, $[Hg,3\ etu](NO_3)_2$, decomp. 196°, and *tetrakisethylenethiocarbamidopalladous chloride*, $[Pd,4\ etu]Cl_2$, blackening at 210°, m. p. 270°; the latter on treatment with sodium hydroxide gives a precipitate which dissolves in dilute nitric acid and ethylenethiocarbamide to give the corresponding *nitrate*, m. p. 235°, which, like the chloride, is very sparingly soluble in water. The ionic structure of the compounds is discussed and conductivities are tabulated. E. W. WIGNALL.

Reactions between phosphorus pentachloride or trichloride and acetone cyanohydrin. A. CHRZĄSZCZEWSKA and W. SOBIERAŃSKI (Rocz. Chem., 1927, 7, 470—476).—Acetone cyanohydrin reacts with phosphorus pentachloride to yield *α-chloroiso-butyronitrile*, b. p. 51·5—52·5°/6 mm.; with phosphorus trichloride *tri-α-cyanoisopropyl metaphosphate*, b. p. 153—154°/4 mm., is formed. R. TRUSZKOWSKI.

Alkylation of hydromolybdenocyanic acid. F. HÖLZL [with G. I. XENAKIS] (Monatsh., 1927, **48**, 689—709).—When potassium molybdeno-octacyanide is treated with methyl sulphate there is formed the *compound* $[(CN)_4Mo(CNMe)_2(H_2O)_2],4H_2O$ (I). Methylation of silver molybdenocyanide with methyl iodide affords a complex mixture of compounds from which the *substance* $[(CN)_4Mo(CNMe)_4],2MeOH$ (II) is obtained by extraction with absolute methyl alcohol. When (I) is treated with potassium cyanide solution potassium molybdenocyanide is regenerated, whilst the action of water on (II) is to furnish (I). These reactions suggest that the octa(methylcarbylamine)molybdenum ion, $[Mo(CNMe)_8]^{\cdot\cdot\cdot\cdot}$, is unstable, whereas the corresponding ferrous ion is stable (A., 1927, 864). When (II) is treated with alkali the carbylamine odour is developed, and with silver nitrate a light yellow precipitate is formed which also gives the carbylamine odour with alkali. An aqueous solution of (II) when kept for a long time does not give a precipitate with silver nitrate. Extraction of the residue after removal of (II) with water furnishes the *compound* $[(CNMe)_4(CN)_2Mo(O\cdot)\cdot]_2$ (III), which decomposes in air, gives no precipitate with silver nitrate, but reduces ammoniacal silver nitrate. Treatment of the residue after removal of (II) and (III) with dilute hydrochloric acid and subsequent evaporation of the acid-soluble products in a vacuum gives a residue from which by extraction with warm methyl alcohol and water, *substances* (IV) and (V) were obtained together with an insoluble residue (VI). Compound (IV) titrates as a tribasic acid (*ammonium* salt described), develops a carbylamine odour in aqueous solution, and decomposes on keeping into (V). Its constitution is probably $\{(CN)_4Mo(H_2O)[C(OH)NHMe]_3\} \rightleftharpoons [(CN)_4Mo(H_2O)(CO'NHMe)_3]H_3$. The compound (V) is a weak acid in aqueous solution, and loses 1 mol. of water when dried over phosphoric oxide. It is represented $[(CN)_3(OH)Mo(H_2O)(CO'NHMe)]H \rightleftharpoons [(CN)_3Mo(H_2O)_2CNMe]OH$. The insoluble residue (VI) is formulated as $[(CN)_2(H_2O)CNMe\cdot Mo(O\cdot)\cdot]_2$. Ethylation of silver molybdenocyanide gives a corresponding series of complex compounds.

H. BURTON.

Activated magnesium for the preparation of the Grignard reagent and a comparative study of various catalysts. H. GILMAN, J. M. PETERSON, and F. SCHULZE.—See this vol., 253.

Constitution of Grignard's organo-magnesium compounds. I. L. KIERZIK (Rocz. Chem., 1927, **8**, 446—456).—See A., 1927, 1176.

Behaviour of aluminium triethyl with nickel catalyst at high temperatures. A. MÜLLER and A. SAUERWALD (Monatsh., 1927, **48**, 737—739).—Aluminium triethyl is not affected by nickel-black I (Zelinski, A., 1925, i, 1052) in presence of hydrogen.

H. BURTON.

***cyclo*Propane derivatives.** P. BRUYLANTS (Bull. Soc. chim. Belg., 1927, **36**, 519—532).—See A., 1927, 877.

Propyl*cyclo*butane and *cyclo*butyl ethyl ketone. N. D. ZELINSKI and B. A. KASANSKI (J. Russ. Phys. Chem. Soc., 1927, **59**, 659—661).—See A., 1927, 648.

Direct conjugation of benzene rings by means of the diazo reaction. W. BRYDÓWNA (Rocz. Chem., 1927, **7**, 436—445).—Ullmann's reaction with bromo-, chloro-, methoxy-, carboxy-, and methyl-substituted anilines does not lead to the production of diphenyl derivatives, only azo compounds or their corresponding chloro-derivatives being formed. Only phenols are produced by the action of anhydrous acetic acid on nitro-, methyl-, and methoxy-substituted diazobenzenes and on diazofluorene. The corresponding hydrocarbons are obtained in about 20% yield by the reduction of *iso*diazo-derivatives of various substituted anilines, of α- and β-naphthylamine, and of diazotised *m*-aminocinnamic acid and *p*-aminoacetophenone. In the case of diazobenzene and of the diazonitrobenzenes diphenyl derivatives were also obtained, whilst the aminobenzoic acids yielded phenols in addition to hydrocarbons; in all other cases azo compounds were formed. It hence appears that the direct conjugation of two aryl nuclei is favoured by the absence of substituents in the nucleus or by the presence of nitro-groups; other substituents inhibit this reaction.

R. TRUSZKOWSKI.

Catalytic action. XX. Catalytic chlorination. I. S. TEI and S. KOMATSU (Mem. Coll. Sci. Kyoto, 1927, **10**, *A*, 325—330).—When a mixture of benzene and chlorine is passed over reduced copper (made from the oxide prepared by igniting the nitrate) the products are benzene hexachloride (2 forms), chlorobenzene, 1 : 2 : 4-trichlorobenzene, and a little 1 : 2 : 4 : 5-tetrachlorobenzene. Low temperature favours substitution, higher temperature (200—300°) and previous treatment of the catalyst with chlorine favours the formation of the hexachloride; under these conditions 59% may be formed. Chlorobenzene and copper that had been treated with chlorine gave 1 : 2 : 4 : 5-tetrachlorobenzene, β-monochlorobenzene hexachloride, pentachlorobenzene, *p*-dichlorobenzene, and traces of 1 : 2 : 4-trichlorobenzene. This shows that previous substitution favours substitution and not addition. In the second case the additive product was found in only one form, which corresponded with the variety found in smaller amount in the unsubstituted product.

C. D. LANGFORD.

Synthesis of benzene hydrocarbons by organomagnesium compounds. L. BERT (Compt. rend., 1928, **186**, 373—375).—Benzyl chloride and its homologues are produced from the corresponding benzene compounds, trioxymethylene, hydrogen chloride, and fused zinc chloride. ω-Chloroethyl- and ω-chloropropyl-benzenes are prepared from magnesium aryl or aralkyl bromides and β-chloroethyl *p*-toluenesulphonate, or from the requisite alcohol obtained from magnesium aryl or aralkyl bromides and ethylene chlorohydrin. A list of 21 hydrocarbons prepared in 30—80% yield by decomposition of magnesium aralkyl chlorides by water is given. H. BURTON.

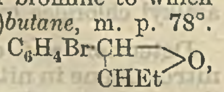
Detection and colorimetric determination of nitrotoluene in nitrobenzene. H. MURAOUR (Bull. Soc. chim., 1928, [iv], **43**, 71—73).—*m*-Dinitrobenzene and 2 : 6-dinitrotoluene give no coloration with alcoholic sodium hydroxide and 2 : 4-dinitrotoluene only a feeble coloration. In presence of *m*-dinitrobenzene, however, 2 : 6-dinitrotoluene affords a red and 2 : 4-dinitrotoluene an intense blue coloration, and the reaction is applied to the determination of nitrotoluenes in nitrobenzene, comparison being made colorimetrically with known mixtures after further nitration. The red coloration given by dinitrothiophen disappears with excess of alcoholic sodium hydroxide. Traces of dinitrotoluene in nitrotoluene may also be determined by the method, but the reaction is less sensitive when applied to the detection of dinitrobenzene in nitrobenzene (2 : 4-dinitrotoluene is used). R. BRIGHTMAN.

Synthetic musks. R. DE CAPELLER (Helv. Chim. Acta, 1928, **11**, 166—170, 170—172).—3-*n*-Butyltoluene, b. p. 84°/19 mm., obtained from *m*-xylyl bromide, *n*-propyl bromide, and sodium, is nitrated by fuming nitric–sulphuric acids yielding 2 : 4 : 6-*trinitro*-3-n-*butyltoluene*, m. p. 78·5°, which is inodorous. When toluene is condensed with excess of *tert*.-butyl chloride in presence of aluminium chloride or ferric chloride, there is formed 3 : 4-*di*-tert.-*butyltoluene*, b. p. 227·5—228°/735 mm., 117—118°/15·5 mm., m. p. 31·5—32°. 2 : 4 : 6-*Trinitro*-3-n-*amyltoluene*, m. p. 65·2—65·6°, obtained from 3-n-*amyltoluene*, b. p. 220·5—222·5° (corr.)/738 mm., is also inodorous. H. BURTON.

Elimination of side-chains during the nitration of aromatic compounds. H. BARBIER (Helv. Chim. Acta, 1928, **11**, 157—161; cf. this vol., 291).—In the nitration of 2-*iso*butyl-*m*-tolyl methyl ether there are formed as by-products a *dinitro*-m-*tolyl methyl ether*, m. p. 101°, and trinitro-*m*-tolyl methyl ether, m. p. 92° (cf. Baur, A., 1894, i, 449; Blanksma, A., 1903, i, 164), thus demonstrating the elimination of the *iso*butyl group. Nitration of 2 : 4-dimethyl-6-*iso*butylacetophenone furnishes, in addition to the 3 : 5-dinitro-derivative, a small amount of 2 : 6-dinitro-5-*iso*butyl-*m*-xylene, m. p. 68° (cf. Baur-Thurgau, A., 1898, i, 523; 1900, i, 639).

If a compound containing several side-chains is nitrated it is usually a group in one of the *m*-positions which is partly eliminated.

A summary of examples of elimination of different groups during the nitration of aromatic compounds is given. H. BURTON.

***d*-Bromo-Δ^a^-butenylbenzene.** R. QUELET (Compt. rend., 1928, **186**, 236—238).—p-*Bromophenylpropylcarbinol*, b. p. 147°/11 mm., d_4^{11} 1·339, n_D^{11} 1·558 (*phenylurethane*, m. p. 83°), may be obtained either by condensation of butaldehyde with the magnesium derivative of *p*-dibromobenzene (48% yield), or by condensation of *p*-bromobenzaldehyde with magnesium *n*-propyl bromide (90% yield). The above alcohol, when dehydrated by heating with potassium hydrogen sulphate, forms p-*bromo*-Δ^α^-*butenylbenzene*, m. p. 30°, b. p. 126—127°/14 mm., d_4^{31} 1·282, n_D^{31} 1·580, the addition of bromine to which gives αβ-*dibromo*-α-(p-*bromophenyl*)*butane*, m. p. 78°. The corresponding *ethylene oxide*,  $C_6H_4Br\cdot CH{-}CHEt{>}O$, has b. p. 138°/12 mm., d_4^{15} 1·362, n_D^{15} 1·557. *p*-Bromo-Δ^α^-butenyl benzene readily forms with magnesium a Grignard compound which yields Δ^α^-butenylbenzene when treated with water. B. W. ANDERSON.

Derivatives of *p*-dichlorobenzene containing sulphur. E. GEBAUER-FULNEGG and H. FIGDOR (Monatsh., 1927, 48, 627—638).—2 : 5-Dichlorobenzenesulphonanilide, m. p. 160°, when suspended in chloroform and treated with sodium hypochlorite, gives the *sulphonphenylchloroamide*, m. p. 101—103°. When the sulphonyl chloride is reduced by zinc and sulphuric acid, 2 : 5-*dichlorothiophenol*, m. p. 27°, b. p. 112—116°/50—52 mm., is obtained (yellow *lead* salt); this can be oxidised to 2 : 5 : 2′ : 5′-tetrachlorodiphenyl sulphide and converted by methyl sulphate into 2 : 5-*dichlorothioanisole*, m. p. 51°, and by chloroacetic acid into 2 : 5-*dichlorophenylthioglycollic acid*, $C_6H_3Cl_2\cdot S\cdot CH_2CO_2H$, m. p. 130° (Kalle and Co., G.P. 241910, 243087), from which 4 : 7 : 4′ : 7′-tetrachlorothioindigotin is obtainable.

The energetic action of chlorosulphonic acid on *p*-dichlorobenzene yields a crude disulphonyl chloride, m. p. 75°, which by slow evaporation of a carbon disulphide solution yields mainly large crystals of p-*dichlorobenzene*-2 : 6-*disulphonyl chloride* (I), m. p. 114° (identified by conversion by phosphorus pentachloride into 1 : 2 : 3 : 5-tetrachlorobenzene), separated by sorting from small crystals of the by-product, p-*dichlorobenzene*-2 : 5-*disulphonyl chloride* (II), m. p. 182° (*disulphonamide*), converted by phosphorus pentachloride into 1 : 2 : 4 : 5-tetrachlorobenzene.

The isomeride (I) is converted into p-*dichlorobenzene*-2 : 6-*disulphonic acid*, into the corresponding *disulphonamide*, and *disulphonanilide*, m. p. 215—217°, and the latter into p-*dichlorobenzene*-2 : 6-*disulphonphenylchloroamide*. (I) is reduced with difficulty to 2 : 5-*dichloro*-1 : 3-*dithiolbenzene*, m. p. 85° (*lead* salt), which easily oxidises; the *dimethyl thioether*, m. p. 179°, and the 2 : 5-*dichloro*-m-*phenylenedithioglycollic acid*, m. p. 189—190°, are prepared, and from the latter a dithioindigoid *dye*.

Whereas the action of sodium chlorosulphonate on *p*-dichlorobenzene at 150—180° yields only the monosulphonyl chloride, that of chlorosulphonic acid and sodium chloride at 210—220° gives a 50% yield of hexachlorobenzene. Attempts to prepare a sulphonyl chloride from 2 : 5-dichloronitrobenzene failed; the action of fuming nitric and sulphuric acids on *p*-dichlorobenzenesulphonyl chloride gave, however, a 2 : 5-*dichloronitrobenzenesulphonyl chloride*, m. p. 65°, characterised by giving an intense orange colour on heating with potassium hydroxide solution. E. W. WIGNALL.

Indene halogenohydrins. C. COURTOT, FAYET, and PARANT (Compt. rend., 1928, **186**, 371—373).—Hydrolysis of 2 : 3-dichlorohydrindene with water yields 2-chloro-3-hydroxyhydrindene, m. p. 126° (Spilker, A., 1893, i, 518; Heusler and Schieffer, A., 1899, i, 365), together with an *isomeride*, m. p. 110—111°. These compounds when oxidised with chromic–sulphuric acids give the same *chlorohydrindone*, m. p. 38—39° [*mononitro*-derivative, m. p. 115°; *amino*-derivative, m. p. 149°; *dinitrophenylhydrazone*, m. p. 205° (decomp.)], and are probably *cis*- and *trans*-isomerides.

2-Bromo-3-hydroxyhydrindene, m. p. 130° (Kramer and Spilker, A., 1891, i, 205; cf. Read and Hurst, J.C.S., 1922, **121**, 2550), when oxidised yields 2-bromo-1-hydrindone, m. p. 38°, and reacts with *p*-toluidine to form a secondary *base* (2-p-*toluidino-3-hydroxyhydrindene*), m. p. 115°, also formed from the chloro-compound, m. p. 126°. The chloro-compound, m. p. 110—111°, and *p*-toluidine yield an isomeric *base*, m. p. 148°.

The iodohydrin, m. p. 120°, of Tiffeneau and Orékhoff (A., 1920, i, 313) is 2-iodo-3-hydroxyhydrindene.

H. Burton.

Conjugated unsaturated hydrocarbons. I. Synthesis of diphenyl derivatives. II. Synthesis of diphenylene derivatives. III. Addition of hydrogen and bromine. IV. Molecular compounds and colour reactions. R. Kuhn and A. Winterstein (Helv. Chim. Acta, 1928, **11**, 87—116, 116—122, 123—144, 144—151).—I. Phenylacetic acid reacts with cinnamaldehyde in presence of boiling acetic anhydride and lead oxide to form αδ-diphenylbutadiene (34% yield, cf. Thiele, A., 1899, i, 612). Reduction of cinnamaldehyde with aluminium amalgam in moist ether affords *s*-distyrylethylene glycol (*dicinnamoyl* derivative, m. p. 159°), which with 99% formic acid at 40° yields s-*tetrastyryldiethylene dioxide*, m. p. 133·5—134°. αζ-Diphenylhexatriene, m. p. 200° (dibromide, m. p. 124—125°) (cf. Farmer and others, this vol., 151), is obtained by reduction of the above glycol with phosphorus di-iodide or titanous chloride, by the action of phosphorus tribromide in chloroform, and from the dibromide by reduction with zinc dust and acetone, hydrogen and platinum-black, by the action of silver carbonate, acetate, and nitrate, and quantitatively by treatment with potassium iodide and acetone. αθ-*Diphenyloctatetraene* (16%), m. p. 232°, is best obtained from succinic acid (1 mol.), cinnamaldehyde (2 mols.), acetic anhydride (3 mols.), and lead oxide (1·5 mol.). Other methods of preparation are given (cf. Fittig and Batt, A., 1904, i, 744). Condensation of cinnamaldehyde and dihydromuconic acid affords ακ-*diphenyldecapentaene* (7%), m. p. 253° (partial decomp.). From benzylidenecrotonaldehyde and succinic and hydromuconic acids there are formed αμ-*diphenyldodecahexaene* (10%), m. p. 267° (decomp.), and αο-*diphenyltetradecaheptaene* (4%), m. p. 279° (decomp.). αρ-*Diphenylhexadecaoctaene* (4%) is obtained from succinic acid and cinnamylidenecrotonaldehyde and has m. p. 285° (decomp.). The solubilities of these hydrocarbons in benzene and chloroform diminish with increase of mol. wt. The action of potassium permanganate in acetone towards some of the compounds has been studied.

II. Fluorenone condenses with succinic acid in presence of boiling acetic anhydride and lead oxide to form αδ-*di(diphenylene)butadiene* (6·5%), sublimes at 360°, and with dihydromuconic acid to give αζ-*di(diphenylene)hexatriene* (2·1%), m. p. 340° (decomp.). Condensation of fluorene with cinnamaldehyde in presence of sodium ethoxide gives α-phenyl-δ-diphenylenebutadiene (63%), m. p. 155° (cf. Thiele and Henle, A., 1906, i, 571) (picrate, m. p. 179°); with benzylidenecrotonaldehyde there is formed α-*phenyl*-ζ-*diphenylenehexatriene* (11%), m. p. 155·5°, and with cinnamylidenecrotonaldehyde α-*phenyl*-θ-*diphenyleneoctatetraene* (5%), m. p. 166°, is produced. α-*Phenyl*-δ-(2 : 7-*dibromodiphenylene*)*butadiene* and α-o-*nitrophenyl*-δ-*diphenylenebutadiene* have m. p. 210° and 186°, respectively.

III. Reduction of αζ-diphenylhexatriene with aluminium amalgam and moist ether or sodium amalgam and alcoholic benzene affords αδ-*dibenzylbutadiene* (50—60%), m. p. 79°, which is hydrogenated in presence of platinum oxide or palladium-black to αζ-*diphenyl*-n-*hexane*, m. p. 137°, and yields on ozonolysis phenylacetic acid. αζ-*Dibenzylhexatriene* (50%), m. p. 68° (ozonolysis product, phenylacetic acid), and αθ-*dibenzyloctatetraene* (50%), m. p. 109—110°, are obtained similarly from αθ-diphenyloctatetraene and ακ-diphenyldecapentaene. In these reductions addition of hydrogen is at the terminal carbon atoms. When α-phenyl-δ-diphenylenebutadiene is reduced with aluminium amalgam there is formed α-benzyl-β-fluorenylethylene (cf. Thiele and Henle, *loc. cit.*) (ozonolysis product, phenylacetic acid), whilst reduction with sodium amalgam and alcoholic benzene affords α-*phenyl*-δ-*diphenylene*-Δ^{γ}-*butene* (60%), m. p. 81° (ozonolysis products, fluorenone and γ-phenylpropionic acid), also obtained from α-benzyl-β-fluorenylethylene by treatment with sodium amalgam and alcoholic benzene. Reduction of α-phenyl-δ-(2 : 7-dibromodiphenylene)butadiene with aluminium amalgam yields a *dihydro*-compound, m. p. 185°.

Hydrogenation of the unsaturated hydrocarbons in presence of platinum oxide or palladium and acetic acid yields αδ-*dicyclohexyl*-n-*butane*, b. p. 294°/725 mm., αζ-*dicyclohexyl*-n-*hexane*, b. p. 212°/14 mm., αθ-*diphenyl*-n-*octane*, αθ-*dicyclohexyl*-n-*octane*, m. p. 26°, and α-*phenyl*-γ-*fluorenylpropane*, m. p. 71°.

Addition of 1 mol. of bromine to αζ-diphenylhexatriene affords a dibromide identical with that obtained from *s*-distyrylethylene glycol, which when treated with lead acetate in acetone yields a αζ-*diphenylhexadienediol* (15% yield), m. p. 158—159°, which differs from the above glycol but regenerates the original bromide. Ozonolysis of the dibromide yields not more than 50% of the theoretical amount of benzoic acid (assuming a γδ-dibromide), together with a small amount of a compound containing bromine, m. p. 270°, thus demonstrating that the addition of bromine is asymmetrical. Diphenylhexatriene *tetrabromide*, m. p. 180—181°, hexabromide, m. p. 279—280° (decomp.) (cf. Smedley, J.C.S., 1908, **93**, 372), *diphenyloctatetraene octabromide*, m. p. 248° (decomp.), *diphenyldecapentaene hexabromide*, m. p. 175° (decomp.), *di(diphenylene)hexatriene octabromide*, m. p. 218°, and α-*phenyl*-ζ-*diphenylenehexatriene tetrabromide*, m. p. 170° (decomp.), are described. αδ-*Diphenyl*-Δ^{α}-*butene* has m. p. 47° and is obtained from magnesium γ-phenylpropyl bromide and benzaldehyde with subsequent elimination of water.

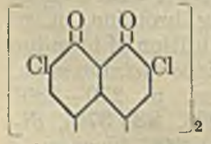
IV. Molecular compounds of the following hydrocarbons and 2 mols. of picric acid, styphnic acid, or 1 : 3 : 5-trinitrobenzene are described: αδ-diphenyl-Δ^{α}-butene (*picrate*, m. p. 102° with previous sintering; *trinitrobenzene*, m. p. 101°); αζ-diphenyl-$\Delta^{\alpha\epsilon}$-hexadiene (*picrate*, m. p. 112° with previous sintering; *trinitrobenzene*, m. p. 145—145·5°); αζ-diphenylhexatriene (*picrate*, m. p. 170°; *styphnate*, m. p. 193—194°; *trinitrobenzene*, m. p. 161—162°); αδ-di(diphenylene)-butadiene [*picrate*, m. p. 262° (decomp.); *trinitrobenzene*, m. p. 240° (decomp.)]. The *picrates* of αζ-di(diphenylene)hexatriene and α-phenyl-ζ-diphenylenehexatriene have m. p. 270° (decomp.) and 179° (decomp.), respectively. The colours of solutions of a large number of the hydrocarbons in concentrated sulphuric acid, chloroform, and concentrated sulphuric acid, and acetic anhydride, chloroform, and concentrated sulphuric acid, and the position of the maximum bands of the absorption spectra are given.

H. BURTON.

Nitration of anthracene to 9 : 9′-dinitro-9 : 9′-dihydroxy-10 : 10′-dihydrodianthracene. J. S. TURSKI and A. BERLANDSTEIN (Rocz. Chem., 1927, 7, 457—466).—Anthracene yields on nitration under certain special conditions 9 : 9′-*dinitro*-9 : 9′-*dihydroxy*-10 : 10′-*dihydrodianthracene*, m. p. 267—268°, soluble in sodium hydroxide and yielding anthraquinone on oxidation.

R. TRUSZKOWSKI.

Perylene and its derivatives. XVI. A. ZINKE, K. FUNKE, and H. IPAVIC (Monatsh., 1927, 48, 741—754; cf. A., 1926, 71; A., 1927, 350).—Chlorination of perylene in ice-cold carbon tetrachloride suspension affords a *compound*, $C_{20}H_{11}Cl_9$, m. p. 235° after previous darkening and sintering. Similar treatment of 3 : 9-dichloro- or 3 : 9-dibromo-perylenes gives the *compounds* $C_{20}H_9Cl_7$ and $C_{20}H_9Cl_5Br_2$, m. p. 260° (decomp.) and m. p. 240° (decomp.), respectively. When perylene is chlorinated in nitrobenzene solution at 130—140° there is formed hexachloroperylene (A., 1925, i, 384), whilst in presence of anhydrous aluminium chloride and nitrobenzene *decachlorotetrahydroperylene*, m. p. above 400°, is produced. This compound is converted by fuming sulphuric acid at 150—160° into *octachloro-octahydroperylene*-3 : 4 : 9 : 10-*diquinone*, m. p. above 400°, which when reduced with alkaline sodium hyposulphite and treated with the appropriate aroyl chloride affords the *tetrabenzoyl*, m. p. 322·5° (decomp.), and *tetra*-p-*bromobenzoyl*, m. p. 375° (decomp.), derivatives of tetrachloroperylene-3 : 4 : 9 : 10-diquinol. The benzoyl derivative is hydrolysed and oxidised at the same time by warm concentrated sulphuric acid into *tetrachloroperylene*-3 : 4 : 9 : 10-*diquinone* (annexed formula), also produced from the above octachloro-quinone by reduction with amalgamated zinc and hydrochloric–acetic acids.



Reduction of the octachloro-quinone with warm alkaline sodium hyposulphite followed by atmospheric oxidation affords a green substance (probably a quinhydrone) which when treated with cold concentrated sulphuric acid yields a dark brown *substance*, $C_{20}H_5O_4Cl_5$. Treatment of the octachloroquinone with boiling aniline furnishes a *compound*, $C_{38}H_{25}O_4N_3Cl_4$, m. p. 305—307° (decomp.), whilst distillation with zinc dust and zinc chloride gives perylene.

H. BURTON.

Hydrogenation of aniline under pressure in the presence of osmium and iridium. W. S. SADIKOV and A. L. KLEBANSKY (Ber., 1928, 61, [*B*], 131—137).—The osmium catalyst is prepared by reducing osmic acid on asbestos with hydrazine. Hydrogenation is effected at 300° under high pressure; the extent of the reaction depends largely on the purity of the aniline and the mass of the catalyst. An equilibrium appears to be established between catalyst, initial substance, and hydrogenated products. In one instance the final material contained benzene 4%, *cyclo*hexylamine 25%, di*cyclo*hexylamine 20%, *cyclo*hexylaniline 5%, and unchanged aniline 29%. The iridium catalyst is formed by reduction of ammonium chloroiridate and activated by treatment with oxygen at 350—400°. The observed products of hydrogenation of aniline are benzene, *cyclo*hexane, *cyclo*hexylamine, di*cyclo*hexylamine, and unchanged aniline. Hydrogenation occurs more readily in the presence of osmium than of iridium and less decomposition is observed.

H. WREN.

Reduction of nitro-derivatives with iron and soluble chlorides. A. BRETNÜTZ and A. PENSA (Notiz. chim.-ind., 1927, 2, 183; Chem. Zentr., 1927, ii, 243—244).—Iron filings, in presence of aqueous ferric chloride (preferably) or sodium chloride solution, stirred at 34 r.p.m. (opt.), was used as a reducing agent for nitrobenzene, *p*-nitrotoluene, *m*-dinitrobenzene to *m*-nitroaniline, *p*-nitrophenol, and picric acid. Nitrobenzene is readily reduced to aniline (1—1·5 hrs. at 100°) when the chlorine concentration (ferric chloride) is 0·0174—0·0319 g./c.c. *p*-Nitrotoluene (100 g.) gives a theoretical yield with 132 g. of iron and 0·0259 g. of chlorine as ferric chloride in 2 hrs.; *m*-dinitrobenzene gives a theoretical yield of *m*-nitroaniline in 2·5 hrs. using 0·035 g. of chlorine per c.c. *p*-Nitrophenol (25 g.) is completely reduced in 1·25 hrs. on a boiling water-bath with 0·009 g. of chlorine per c.c. of solution. Picric acid is vigorously reduced.

A. A. ELDRIDGE.

Anomalous effect of *o*-*p*-orienting groups on the m. p. of dihalogenated benzene derivatives. G. B. HEISIG (J. Amer. Chem. Soc., 1928, 50, 139—145).—2-*Chloro*-4-*bromo*-6-*iodoaniline*, m. p. 97—97·5°, is obtained by treating 2-chloro-4-bromoaniline in aqueous acetic acid with iodine chloride. 4-*Chloro*-2-*bromo*-6-*iodoaniline*, m. p. 109·5—110°, is obtained similarly from 4-chloro-2-bromoaniline. 2-*Chloro*-6-*bromo*-4-*iodoaniline*, m. p. 115·5—116°, is obtained by brominating 2-chloro-4-iodoaniline in glacial acetic acid, or by chlorinating 2-bromo-4-iodoaniline (*acetyl* derivative, m. p. 140—140·5°). s-*Chlorobromoiodobenzene*, m. p. 85·5—86°, is obtained from either of the above trihalogenated anilines by treatment with sodium nitrite and sulphuric acid in boiling alcohol.

The m. p. of an *o*- or *m*-dihalogenobenzene is always raised by the introduction of a third substituent. The m. p. of a *p*-dihalogenobenzene is raised similarly if the entering substituent is one which causes *m*-substitution, but 2 : 5-dibromo- and 2 : 5-di-iodo-nitrobenzene are exceptional, both having a lower m. p. than the corresponding dihalogeno-derivative. The m. p. of a *p*-dihalogenobenzene is generally lowered by the introduction of a third substituent having *o*-*p*-orienting influence, but 2 : 5-dichlorophenol has a higher m. p. than *p*-dichlorobenzene.

F. G. WILLSON.

Acetylene derivatives. VII. Reaction of trichloroethylene with amines. P. Ruggli and I. Marszak (Helv. Chim. Acta, 1928, **11**, 180—196).—Phenylglycinediphenylamidine (Sabanejev's base, A., 1876, i, 55), NHPh·CH$_2$·C(:NPh)·NHPh (I), m. p. 190° (*picrate*, decomp. 135—140°), is prepared from trichloroethylene (1 mol.), aniline (3 mols.), and 15% aqueous sodium hydroxide (3 mols.) by heating for 40 hrs.; from phenylglycineanilide, aniline, and phosphorus trichloride at 150°; from phenylglycine, aniline, and phosphorus trichloride at 160°, and from chloroacetic acid, aniline, and phosphorus trichloride at 160°. Benzoylation of the base yields N-*benzoylphenylglycinediphenylamidine*, m. p. 142°, and bromination in presence of chloroform and anhydrous sodium carbonate gives *p*-bromophenylglycine-*p*-bromoanilide. When the base is treated with boiling alcohol for 60 hrs. or with aniline and aniline hydrochloride in boiling alcohol for 24 hrs. there is formed phenylglycineanilide. From trichloroethylene and *p*-toluidine, *p*-anisidine, *p*-phenetidine, and 4-aminodiphenyl there are formed p-*tolylglycinedi*-p-*tolylamidine*, m. p. 157°; p-*anisylglycinedi*-p-*anisylamidine*, m. p. 158—159°; p-*phenetylglycinedi*-p-*phenetylamidine*, m. p. 112—113°, and 4-*diphenylylglycinedi*-4-*diphenylylamidine*, m. p. 189—190°. p-*Anisylglycine*-p-*anisidide* and *phenylglycine*-p-*bromoanilide* have m. p. 132° and 153—154°, respectively. H. Burton.

Odour and constitution among the aromatic mustard oils [thiocarbimides]. I. G. M. Dyson (Perf. Ess. Oil Rec., 1928, **19**, 3—5; cf. B., 1926, 215).—The effect of alkyl substituents on the odour of aromatic thiocarbimides has been examined. In phenylthiocarbimide the introduction of an *o*-methyl group contributes sweetness, the *m*-group pungency, and the *p*-group an anise-like character. In the six xylyl thiocarbimides, duplication of a methyl group in the same orientation strengthens the effect. When both *o*- and *m*-methyl groups are present together the effect of the *m*-group predominates and the 2 : 3- and 2 : 5-xylylthiocarbimides are pungent. The influence of the *p*-groups overwhelms that of the *o*- or *m*-groups. Similar considerations apply in the 2 : 4 : 6-, 2 : 4 : 5-, and 2 : 3 : 5-trimethylphenylthiocarbimides. Pentamethylphenylthiocarbimide has only a very faint floral odour. *p*-Ethyl- and *n*-propylphenylthiocarbimides have a strong anise-like odour, whereas the corresponding 4-iso*propylphenylthiocarbimide*, b. p. 271°, has a harsher odour. 2-*Cymylthiocarbimide*, b. p. 268°, is distinctly pungent. The following compounds are described: o-3-*xylylthiocarbimide*, b. p. 262°, o-3-*xylylthiocarbamide*, m. p. 182°; p-iso*propylphenylthiocarbamide*, m. p. 167°; s-*di*-p-iso*propylphenylthiocarbamide*, m. p. 198°; 2-*cymylthiocarbamide*, m. p. 174°; s-*di*-2-*cymylthiocarbamide*, m. p. 202°. E. H. Sharples.

Orientation effects in the diphenyl series. V. Independence of the two nuclei in diphenyl compounds. R. J. W. Le Fèvre and E. E. Turner (J.C.S., 1928, 245—255; cf. A., 1926, 946, 1029, 1131).—The compound obtained by hydrolysis of the nitration product of phthalylbenzidine is mainly 2-nitrobenzidine (cf. Koller, A., 1904, i, 778). Nitration of 4-acetamidodiphenyl in acetic acid with subsequent hydrolysis of the dinitro-derivative produced affords 3 : 4′-dinitro-4-aminodiphenyl, which is reduced by aqueous-alcoholic ammonium sulphide to 3-*nitrobenzidine*, m. p. 208—210°. Nitration of the *diacetyl* derivative, m. p. 249—250°, of this compound, followed by hydrolysis, yields 3 : 3′-dinitrobenzidine. 4-*Chloro*-4′-*phthalimidodiphenyl*, m. p. 245°, furnishes after nitration and hydrolysis 4-chloro-2 : 3′dinitro-4′-aminodiphenyl and 4-chloro-3 : 2′-dinitro-4′-aminodiphenyl, which is converted by alcoholic ammonia at 160—180° into 2 : 3′-dinitrobenzidine. Similar results are obtained using 4-*bromo*-4′-*phthalimidodiphenyl*, m. p. 260°.

By boiling benzidine with an excess of the appropriate ester the following derivatives were prepared: NN′-*di*-o-*carbethoxybenzoyl*-, m. p. above 300°; NN′-*dicinnamoyl*-, NN′-*dicarbethoxy-benzidines*, and 4 : 4′-*diethyloxamidodiphenyl*. Dinitration of these last two compounds with subsequent hydrolysis affords 3 : 3′-dinitrobenzidine (Strakosch's dinitrobenzidine, Ber., 1872, **5**, 236). NN′-*Dicarbethoxy*-derivatives were prepared from the following benzidines and ethyl chloroformate: 2-nitrobenzidine, m. p. 187—188°; 2 : 2′-dinitrobenzidine, m. p. 200—201°; 2 : 3′-dinitrobenzidine, m. p. 158°, and 3 : 3′-dinitrobenzidine m. p. 216—217°.

Chlorination of 4-nitrodiphenyl in presence of a small amount of stannic iodide yields 4-chloro-4′-nitrodiphenyl. The condensation product of benzidine with carbamide is *NN′*-dicarbamylbenzidine (cf. Schiff, A., 1878, 669; Michler and Zimmermann, A., 1882, 182; Snape, A., 1896, i, 241). This compound can be used to detect traces of nitrates in concentrated sulphuric acid, a reddish-purple colour being produced at concentrations of 1 g. in 500,000 c.c.

The orientation experiments show that one nucleus in diphenyl, even if substituted (C_6H_4R–), always exerts an *op*-directing influence. If the 4′-position is occupied by an *op*-directing group the radical C_6H_4R– frequently exerts a small *op*-influence. There appears to be no mobile conjugation (electronic tautomerism) between the two nuclei, and it is concluded that they are independent. Bell and Kenyon's modification (A., 1927, 145) of Turner's *para*-bridge formula for diphenyl (A., 1923, i, 1085) is based on unsatisfactory evidence, and a slight modification (electronic) renders the formula satisfactory as a basis for explaining the laws of substitution in the diphenyl series. H. Burton.

Reduction of azobenzene by Grignard reagents. H. Rheinboldt and R. Kirberg (J. pr. Chem., 1928, [ii], **118**, 1—13; cf. Franzen and Deibel, A., 1905, i, 843; Rheinboldt and Roleff, A., 1925, i, 542; Gilman and Pickens, A., 1925, i, 1336; Gilman and Adams, A., 1926, 947).—Azobenzene reacts with 2 mols. of a Grignard reagent according to the equations: (i) NPh:NPh+2RMgX=XMg·NPh·NPhMgX+2R·; (ii) 2R·=(R–H)+(R+H); (iii) 2R·=R·R. If R=Me or Ph, (ii) does not occur, the product being ethane or diphenyl. When R=Et or Pr$^{\alpha}$, (iii) is absent, and the products are ethylene and ethane, or propylene and propane. When R=·CH$_2$·CHMe$_2$, (ii) and (iii) both occur, giving *iso*butylene (dibromide, b. p. 147—149°), *iso*butane, and di*iso*butyl [βε-dimethylhexane], b. p. 108—110°. The formation of butane from azobenzene and magnesium ethyl bromide (Franzen and Deibel, *loc. cit.*) is not observed.

C. HOLLINS.

Colour and constitution. II. Effect of substituents on the colour of azo dyes. H. H. HODGSON and F. W. HANDLEY (J.C.S., 1928, 162—166).—Reduction of 3-chloro-6-nitrothioanisole with tin and acetic–hydrochloric acids furnishes 4-*chloro-2-thioanisidine* (*acetyl*, m. p. 110°, and *benzoyl*, m. p. 106°, derivatives), whilst treatment with sodium disulphide yields 4 : 4′-*dinitro*-5 : 5′-*dimethylthioldiphenyl disulphide*, m. p. 216—217°. Treatment of this compound with hot alkaline sodium sulphide and subsequent addition of methyl sulphate gives 2 : 4-dimethylthiolnitrobenzene, which furnishes 2 : 4-*dimethylthiolaniline* (*hydrochloride*, *acetyl*, m. p. 114°, and *benzoyl*, m. p. 125°, derivatives). 3-Chloro-6-nitroacetanilide and sodium disulphide yield 3 : 3′-*diacetamido*-4 : 4′-*dinitrodiphenyl disulphide*, m. p. 192—193°, which furnishes 6-*nitro-3-thioanisidine*, m. p. 116°. 3-*Chloro-4-nitrothioanisole* has m. p. 61° and yields 2-*chloro-4-thioanisidine* (*hydrochloride*, m. p. 217—218°; *acetyl* derivative, m. p. 129°).

With β-naphthol-6-mono- and -3 : 6-di-sulphonic acids as second components, *azo* dyes have been prepared from the above thioanisidines, and from *o*-, *m*-, and *p*-chloro-, 2 : 4- and 2 : 5-dichloro-, and 2 : 4-dimethoxy-anilines, 5-chloro-2-anisidine, 5-chloro-2-thioanisidine, and aniline. The bathochromic effects of the different groups in different positions are the same as those already described (A., 1926, 515).

H. BURTON.

Preparation of *cyclo*hexanol ethers. Formation of tetrabenzyl*cyclo*hexanones. R. CORNUBERT and H. LE BIHAN (Bull. Soc. chim., 1928, [iv], 43, 74—78).—The sodium compounds of *cyclo*hexanols are readily obtained by the action of sodamide in dilute ethereal solution (cf. A., 1927, 666); with alkyl halides they afford the corresponding ethers. Thus *cyclo*hexanol with sodamide and methyl sulphate gives *cyclo*hexyl methyl ether, b. p. 134·5—135°, $d^{14.5}$ 0·8860, $n_D^{14.5}$ 1·4390. 4-Methy*cyclo*hexanol similarly yields 4-*methyl*cyclo*hexyl methyl ether*, b. p. 151°, $d^{20.5}$ 0·8612, $n_D^{20.5}$ 1·4321. Commercial "pure" *cyclo*hexanol with allyl chloride or bromide affords cyclo*hexyl allyl ether*, b. p. 83—84°/38 mm., and a small quantity of a substance, $C_{15}H_{22}O$, b. p. 155—158°/18 mm., probably a triallyl*cyclo*hexanone. 2-*Methyl*cyclo*hexyl methyl ether* has b. p. 69—70°/15 mm. With benzyl chloride commercial *cyclo*hexanol gives, in addition to cyclo*hexyl benzyl ether*, b. p. 165·5—166·5°, d^{20} 0·9941, n_D^{20} 1·5178, a little *tetrabenzyl*cyclo*hexanone*, m. p. 178°, b. p. above 360°/15 mm. 4-Methyl*cyclo*hexanol similarly affords 4-*methyl*cyclo*hexyl benzyl ether*, b. p. 153·5—154°/17 mm., d^{18} 0·9681, n_D^{18} 1·5090, and a little *tetrabenzyl*-4-*methyl*cyclo*hexanone*, m. p. 184°. R. BRIGHTMAN.

Preparation of 2-bromo-*p*-cresol from *p*-nitrotoluene. H. J. LUCAS and N. F. SCUDDER (J. Amer. Chem. Soc., 1928, 50, 244—249).—2-Bromo-4-nitrotoluene is obtained in 76% yield by adding bromine in slight excess to *p*-nitrotoluene in presence of iron filings, with cooling. After keeping for 24 hrs., the mixture is heated gradually to 150° until evolution of hydrogen bromide ceases (cf. Cohen and Dutt, J.C.S., 1914, 105, 505). Reduction of the bromonitrotoluene with alcoholic ammonium sulphide affords 2-bromo-*p*-toluidine, m. p. 27·3—27·5°, in 84% yield, and from this 2-bromo-*p*-cresol (*benzoate*, m. p. 74·6—75·1°) is obtained in 80·5% yield by adding a solution of the diazotised amine gradually to a solution of sulphuric acid and sodium sulphate at 130—140°, the cresol being distilled off as it is formed by a current of steam at 160—180°.

F. G. WILLSON.

Preparation of iodine-substituted benzonitriles of the phenol ether type. CHEM. FABR. AUF ACTIEN (VORM. E. SCHERING).—See B., 1928, 83.

Bases obtained from *p*-phenetidine and from *p*-toluidine with formaldehyde in acid solution. R. LEPETIT, G. MAFFEI, and C. MAIMERI (Gazzetta, 1927, 57, 862—871).—In addition to the products already described (A., 1917, i, 452), the action of formaldehyde on *p*-phenetidine hydrochloride at 60° yields: (1) the base, m. p. 132°, obtained by Reverdin (A., 1921, i, 564) by treating methylenedi-*p*-phenetidine with nitric acid; the authors consider the formula of this base to be, not $C_{18}H_{24}O_2N_2$ or $C_{18}H_{22}O_2N_2$, but $C_{19}H_{22}O_2N_2$, which is in good agreement with the results of Reverdin's analyses of the base, its nitrate and nitroso-derivative; (2) a *base*, $C_{19}H_{24}O_3N_2$, m. p. 114°, the salts of which have a bitter taste and anæsthetic properties.

The base, m. p. 140° (*loc. cit.*), gives the following derivatives: *diacetyl*, $C_{21}H_{26}O_4N_2$, m. p. 116—117°; two *benzoyl* derivatives, $C_{31}H_{30}O_4N_2$ (m. p. 180—181°) and $C_{26}H_{28}O_4N_2$ (m. p. 132—133°); *methyl* derivative, m. p. 114°, identical with the base (2) (see above); *ethyl* derivative, m. p. 82—83°, and the *hydrochloride* of the *allyl* derivative, $C_{21}H_{27}O_3N_2Cl$, m. p. 202°. When oxidised by means of acid permanganate, the base, m. p. 140°, yields a *compound*, m. p. 210°, of indifferent character; when reduced by zinc dust and acetic acid, it gives *p*-phenetidine, methyl-*p*-phenetidine, and a *base*, $C_{20}H_{18}O_4N_2$, m. p. 91°.

The interaction of *p*-toluidine and formaldehyde in acid solution yields: (1) a base, $C_{17}H_{16}ON_2$, m. p. 140°, probably identical with that of, m. p. 146—147° obtained from *p*-phenetidine (*loc. cit.*); (2) a base, $C_{16}H_{16}N_2$, m. p. 158°; (3) methyl-*p*-toluidine; (4) a *base*, $C_{17}H_{20}ON_2$, m. p. 97—98°, which forms an *oxalate*, $C_{17}H_{18}N_2,H_2C_2O_4$, m. p. 255—259° (decomp.); (5) a *base*, $C_{17}H_{18}N_2$, m. p. 137—138°.

T. H. POPE.

Adjacent substitution. I. Reactions of 3-chloro-2-aminoanisole. H. H. HODGSON and A. KERSHAW (J.C.S., 1928, 191—193).—Reduction of 3-chloro-2-nitroanisole with iron powder and 50% acetic acid gives 3-*chloro-2-aminoanisole*, b. p. 246° (slight decomp.) (*hydrochloride*, m. p. 211°; *hydrobromide*, sublimes at 250°; *nitrate*, m. p. 137°; *acetyl*, m. p. 123°, *diacetyl*, m. p. 145·5°, and *benzoyl*, m. p. 135°, derivatives). The *sulphate* is very soluble in water. By the usual methods 2 : 3-dichloro-, m. p. 33° (cf. Hollemann, A., 1917, i, 556), 3-*chloro*-2-*bromo*-, m. p. 50°, 3-*chloro-2-iodo*-, m. p. 53·5°, and 3-*chloro-2-cyano-anisoles*, m. p. 114·5°, were prepared.

3-*Chloro*-2-*thiocyanoanisole* has m. p. 43°. Diazotisation of the aminoanisole yields stable diazonium salts which are unaffected by dilute acids, but the sulphate when treated with bromine gives 3-*chloroanisole*-2-*diazoperbromide*, m. p. 115—116° (decomp.). This compound when boiled with acetic acid furnishes 3-*chloro*-2 : 6-*dibromoanisole*, m. p. 92°, and with ammonia yields 3-*chloroanisole*-2-*diazoimide*, m. p. 35°. Reduction of 3-*chloroanisole*-2-*diazonium chloride* affords 3-*chloroanisyl*-2-*hydrazine hydrochloride*, and the following 3-*chloroanisyl*-2-*hydrazones* are described: *benzaldehyde*, m. p. 92°; o-*nitrobenzaldehyde*, m. p. 131°; m-*nitrobenzaldehyde*, m. p. 131°, and p-*nitrobenzaldehyde*, m. p. 105°. The *azo dyes* formed from 3-chloro-2-aminoanisole and naphtholsulphonic acids show that the bathochromic effect of the methoxy-group is almost completely inhibited in presence of the *o*-chlorine atom (cf. this vol., 284).
H. BURTON.

Relationship between constitution and taste of some carbamide derivatives. H. F. J. LORANG (Rec. trav. chim., 1928, **47**, 179—190).—The relationship between the constitution and taste of substituted phenylcarbamides described in the literature is reviewed. The following are new: 1-*ethoxy*-2 : 4-*dicarbamidobenzene*, m. p. 215°, obtained from 2 : 4-*diaminophenetole hydrochloride*, decomp. about 180°, and potassium cyanate; 1 : 3-*diethoxy*-4 : 6-*dicarbamidobenzene*, m. p. 233° (decomp.), prepared similarly from 4 : 6-*diamino*-1 : 3-*diethoxybenzene hydrochloride*. 1 : 3-Dicarbamidobenzene and the above carbamides are not sweet.
H. BURTON.

Catalytic action. XVIII. Catalytic reduction of β-naphthol. I. NISHIMATSU and S. KIMURA (Sexagint [Osaka celebration], Kyoto, 1927, 217—228).—The investigation of the hydrogenation of β-naphthol by hot reduced nickel was undertaken to test Mohr's hypothesis of the configuration of hydrogenated naphthalene derivatives. At 135—140° only naphthalene, hydronaphthalenes, and *ar*-hydronaphthols were obtained. The hydrocarbons had presumably been formed from the expected *ac*-compounds by loss of water. Reduction at 120—130° yields a mixture of *ac*- and *ar*-tetrahydro-β-naphthols, hexa-, octa-, and deca-hydro-β-naphthols. Two forms of both *ar*- and *ac*-tetrahydro-β-naphthols were found: *ar*- (1), b. p. 262—264°, m. p. 55—56°, (2) b. p. 272—275°, m. p. 56—58°; *ac*- (1), b. p. 151—154°/21 mm. and 138—143°/15 mm., (2) b. p. 154—157°/23 mm. and 148—149°/18 mm. Of the four possible decahydro-β-naphthols three were isolated, having m. p. 103° and 75°, and a liquid b. p. 122—125°/12 mm. The values of the other physical constants given are in fair agreement with those given by previous workers.
C. D. LANGFORD.

Stability of phenol ethers at an ethylene bridge. H. THOMS and F. A. HEYNEN (Festschr. A. Tschirch, 1926, 211—220).—Eugenol ethylene ether was hydrogenated with palladised barium sulphate, and the product nitrated, yielding *di(nitrohydroeugenol)ethylene ether*, m. p. 167·5°, reduced with stannous chloride and acetic and hydrochloric acids to *di(aminohydroeugenol)ethylene ether*, m. p. 245°; a 2-methoxy-4-propyl-1-phenyl ethylene ether is one of the fission products on hydrogenation of dieugenol ethylene ether.
A. A. ELDRIDGE.

3 : 3′ : 5 : 5′-Tetranitro-2 : 2′-dimethoxydiphenyl. H. RAUDNITZ (Ber., 1928, **61**, [*B*], 246).—Contrary to Borsche and Feske (A., 1927, 661), 3 : 3′ : 5 : 5′-tetranitro-2 : 2′-dimethoxydiphenyl has m. p. 188—189°, whether prepared by the author's process (A., 1927, 453) or by that of Borsche and Scholten (A., 1917, i, 390). The low values recorded are due to the difficulty of purifying the material completely by crystallisation from boiling acetic acid; better results are obtained with alcohol as solvent.
H. WREN.

Oxidation in the benzene series by gaseous oxygen. III. Oxidation of α-phenylcarbinols. H. N. STEPHENS (J. Amer. Chem. Soc., 1928, **50**, 186—190; cf. A., 1927, 48).—The action of gaseous oxygen at about 100° on phenyl-methyl-, ethyl-, -dimethyl-, -*n*-propyl-, and -*iso*propyl-carbinol has been examined. In all cases except that of the last-named compound, small amounts of the direct oxidation products (ketones) were produced. In addition, dehydration takes place under the conditions applied, with formation, on the one hand, of ethers, and, on the other, of unsaturated hydrocarbons. In all cases except that of phenyldimethylcarbinol, from which *iso*propenylbenzene was obtained, the unsaturated hydrocarbons are immediately oxidised with formation of benzoic acid. All these reactions are prevented by the presence of a weight of water equal to that of the carbinol.
F. G. WILLSON.

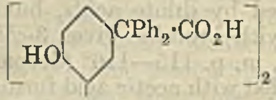
Tautomerism of hydroxytriarylcarbinols. L. C. ANDERSON and M. GOMBERG (J. Amer. Chem. Soc., 1928, **50**, 203—208; cf. A., 1925, i, 1269).—Examination of the absorption spectra of the two carbinol forms of *p*-hydroxytriphenylcarbinol and of *p*-hydroxy-*m*-tolyldiphenylcarbinol, and those of their respective fuchsones, in ether, supports the conclusion that each carbinol exists in both benzenoid and quinonoid tautomeric modifications.
F. G. WILLSON.

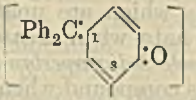
Basic triphenylmethane dyes. K. BRAND (I) [with A. MODERSOHN]; (II) [with G. SCHUCK] (J. pr. Chem., 1928, [ii], **118**, 97—137).—Further evidence that the colour changes observed when solutions of crystal-violet or malachite-green are gradually acidified are due to progressive conversion of the dimethylamino-groups into non-auxochromic dimethylammonium ions, is furnished by the study of the corresponding methylated quaternary salts. The methyl ether of *pp′p″*-hexamethyltriaminotriphenylcarbinol yields (*a*) with 1 mol. of methyl sulphate, a *monomethosulphate*, m. p. 234—236°, decomp. from 227°. The corresponding methiodide (Rosenstiehl, A., 1895, i, 377) is hydrolysed by boiling dilute acetic acid to iodine-green, $(NMe_2{\cdot}C_6H_4)_2C(C_6H_4{\cdot}NMe_3I)I$; (*b*) with 2 mols. of methyl sulphate, a mixture of products from which was obtained on one occasion an impure *dimethiodide*, which, after hydrolysis and removal of a little iodine-green gave a yellow aqueous, and an orange hydrochloric acid solution; (*c*) with 3 mols. of methyl sulphate a *trimethosulphate*, m. p. 223—224° (decomp.). The corresponding *trimethoperchlorate*, m. p. 303—

304° (decomp.), is hydrolysed by dilute acid to the colourless *substance* (I), $C(C_6H_4{\cdot}NMe_3ClO_4)_3OH$, m. p. 291—292° (decomp.), which gives with concentrated mineral acids carbonium salts similar in colour and stability to those of triphenylcarbinol. When the methyl ether (II) of *pp'*-tetramethyldiaminotriphenylcarbinol is successively treated with methyl sulphate (1 mol.) and sodium perchlorate, it affords a *methoperchlorate*, m. p. 167—168°, which is converted by boiling perchloric acid into the orange-red *compound* (III), $CPh(C_6H_4{\cdot}NMe_3ClO_4)_2ClO_4,H_2O$, m. p. 253—254° (decomp.). This is hydrolysed by water to the colourless *methoperchlorate* of *pp'*-tetramethyldiaminotriphenylcarbinol. The *dimethoperchlorate*, m. p. 295—296°, of the ether (II) is hydrolysed by dilute acid to the *dimethoperchlorate* (IV), m. p. 287—288°, of *pp'*-tetramethyldiaminotriphenylcarbinol, which gives halochromic solutions similar to those of triphenylcarbinol.

The *methosulphate*, decomp. 246°, and *methoperchlorate* (V), m. p. 217—218° (decomp.), of *p*-dimethylaminotriphenylcarbinol give yellow solutions in concentrated mineral acids, which are decolorised by addition of water. The carbinol is converted by oxalic acid into a mixture of the colourless oxalate (Baeyer and Villiger, A., 1904, i, 786) with an orange *salt* (VI), and by boiling methyl alcohol into its *methyl ether*, m. p. 90—91°, which forms a *methosulphate*, m. p. 159—164°, and a *methoperchlorate*, m. p. 247°. The ordinary Zeisel method is not applicable to triphenylmethane derivatives containing two or more trimethylammonium groups, since the latter also yield methyl iodide under these conditions. Correct results are, however, obtained by heating the substances with hydriodic acid at 100°. Although iodine-green gives no precipitate with neutral silver nitrate, it is quantitatively converted by sodium perchlorate into the corresponding *diperchlorate*. Conductivity measurements with iodine-green, tetramethyldiaminotriphenylmethane methiodide, crystal-violet, and (I), (III), (IV), and (V) above indicate that in each case all the acid radicals are ionogenic. Accordingly, formulæ (cf. Hantzsch, A., 1922, i, 24) of polyacid salts of triphenylmethane dyes in which acid radicals are included within the co-ordination complex are probably incorrect. The above carbonium salts fall into four groups of decreasing stability, containing (*a*) 3, (*b*) 2, (*c*) 1, and (*d*) 0 dimethylamino-groups. The colours (*a*) violet, (*b*) green, (*c*) orange-red [cf. (III) and (VI)], and (*d*) orange-yellow [cf. (I), (IV), and (V)], are independent of the number of trimethylammonium groups present and are similar to those of the corresponding polyacid salts of crystal-violet. H. E. F. Notton.

3 : 3'-Difuchsonyl and related compounds. A. Bistrzycki and W. Niederberger (Helv. Chim. Acta, 1928, **11**, 261—272).—Benzilic acid and 2 : 2'-dihydroxydiphenyl condense in acetic–sulphuric acid solution to form 2 : 2'-*dihydroxy*-5 : 5'-*dibenzhydryldiphenyl*-αα'-*dicarboxylic acid* (I), $+2H_2O$, m. p. 269—271° (decomp.), which is methylated by methyl sulphate forming *dimethyl* 2 : 2'-*dimethoxy*-5 : 5'-*dibenzhydryldiphenyl*-αα'-*dicarboxylate*, m. p. 260—261° (decomp.). Treatment of the acid with concentrated sulphuric acid affords *difuchsonyl tetrahydrate*, $C_{38}H_{26}O_2,4H_2O$, m. p. 308° (decomp.) after darkening,

(I.)



(II.)

which when treated with 2*N*-sodium hydroxide solution in ethereal solution affords a *tetrasodium* derivative, $C_{38}H_{26}O_4Na_4$. Successive treatment of a hot alcoholic solution of the tetrahydrate with 10% potassium hydroxide and 1—2% acetic acid furnishes 2 : 2'-*dihydroxy*-5 : 5'-*di*(α-*hydroxybenzhydryl*)*diphenyl*, $+2H_2O$, m. p. 308° (decomp.). 3 : 3'-*Difuchsonyl* (II) has m. p. 331° (decomp.) after previous darkening, and is reduced by zinc and acetic acid to 2 : 2'-*dihydroxy*-5 : 5'-*dibenzhydryldiphenyl*, m. p. 186—187° after softening. 2 : 2'-*Dimethoxy*-5 : 5'-*dibenzhydryldiphenyl*-αα'-*dicarboxylic acid*, m. p. 291° (decomp.), is obtained from 2 : 2'-dimethoxydiphenyl and benzilic acid, and gives when treated with concentrated sulphuric acid at 75°, 2 : 2'-*dimethoxy*-5 : 5'-*di*(α-*hydroxybenzhydryl*)*diphenyl*, m. p. 163—164° (decomp.). H. Burton.

Comparative migratory tendencies of acyclic radicals in the semi-pinacolic transpositions of phenyldialkylglycols. Their relation to affinity capacities. M. Tiffeneau and (Mlle.) J. Lévy (Compt. rend., 1928, **186**, 84—86).—The dehydration by sulphuric acid of phenyldialkyl glycols involves a semi-pinacolic transposition, with migration of one of the alkyl radicals. In the 13 cases studied, the migratory tendencies of the radicals were found as a rule to be inversely proportional to their affinity capacities. B. W. Anderson.

Catalytic action. XVII. New functions of reduced copper. II. S. Komatsu (Sexagint [Osaka celebration], Kyoto, 1927, 203—216).—Reduced copper as a catalyst for both dehydration and dehydrogenation stands between thoria and nickel. Three forms of reduced copper are described, distinguished by their action on menthol (cf. A., 1925, i, 687, 942).

Nitriles are obtained by passing a primary alcohol and ammonia over reduced copper (cf. A., 1925, i, 893). Copper with chlorine and benzene at 200° gives chiefly the hexachloride. Reduced copper converts unsaturated hydroaromatic compounds into a mixture of aromatic and saturated hydroaromatic compounds. It is also apparently capable of catalysing the keto–enol change, since inversion occurs with *l*-menthone (A., 1925, i, 943). C. D. Langford.

Catalytic action. XXI. Catalytic reduction of nitriles. S. Komatsu and S. Ishida (Mem. Coll. Sci. Kyoto, 1927, 331—337; cf. A., 1925, i, 893).—The reduction of benzonitrile by hydrogen in presence of reduced copper at 150—200° gives a mixture of benzaldimine, benzylamine, and dibenzylamine. The yield of bases is favoured by a low temperature (150°) and by those forms of reduced copper that are most active as oxidising catalysts. A rapid current favours the formation of aldimine. At a higher temperature the nitrile is decomposed to toluene and ammonia. The relative amounts of the products formed under different conditions are in agreement with the mechanism suggested by Braun, Blessing, and Zobel (A., 1923, i, 1087). The reduction of acetonitrile and *iso*valeronitrile gives no aldimine but only primary and secondary amines.

C. D. Langford.

α-Sulphophenylacetic acid. J. Brust (Rec. trav. chim., 1928, 47, 153—168).—Ammonium α-chloro- and α-bromo-phenylacetates react with ammonium sulphite in aqueous solution to form mainly mandelic acid, whilst with ethyl α-bromophenylacetate followed by hydrolysis with barium hydroxide solution a good yield of α-*sulphophenylacetic acid* $(+2H_2O)$, decomp. 140° after colouring at 130°, is obtained [*barium* $(+H_2O)$, *thallium* $(+H_2O)$, *cobalt* $(+H_2O)$, *nickel* $(+H_2O)$, *copper*, *aniline hydrogen*, m. p. 158°; *aniline*, o-*phenylenediamine*, decomp. 216°; *brucine hydrogen* $(+2H_2O)$, *brucine* $(+8H_2O)$, *strychnine hydrogen* $(+2H_2O)$, *strychnine* $(+5H_2O)$, and *quinine* $(+2H_2O)$ salts described]. Sulphonation of phenylacetic acid with sulphur trioxide or of phenylacetic anhydride with sulphuric acid yields p-*sulphophenylacetic acid* [*barium* $(+2H_2O)$, *calcium* $(+3H_2O)$, *lead* $(+2H_2O)$ salts], oxidised by chromic–sulphuric acids to *p*-sulphobenzoic acid. Fusion of this compound and *p*-sulphophenylacetic acid with potassium hydroxide furnishes *p*-hydroxybenzoic and *p*-hydroxyphenylacetic acids, respectively. l-α-*Sulphophenylacetic acid*, decomp. 225° [*sodium*, *sodium hydrogen*, *barium* $(+2H_2O)$, *cobalt* $(+4H_2O)$, *nickel* $(+2H_2O)$, *copper* $(+3H_2O)$, *aniline hydrogen*, m. p. 205°, and *aniline* salts], is obtained by decomposition of its brucine salt. Numerous values for the molecular rotations of the acid and its salts for different wave-lengths are given. d-*Sulphophenylacetic acid*, $[M]_D$ +36°, is obtained by the interaction of ammonium *l*-α-bromophenylacetate and ammonium sulphite.

When the normal aniline salt of α-sulphophenylacetic acid is boiled with excess of aniline there is produced the *aniline* salt, m. p. 242° (partial decomp.), of α-*sulphophenylacetanilide*, decomp. 205° [*barium* $(+6H_2O)$, *cobalt* $(+8H_2O)$, *nickel* $(+6H_2O)$, *copper*, *strychnine* $(+3H_2O)$, *brucine* $(+3H_2O)$, and *quinine* $(+2H_2O)$ salts described]. l-α-*Sulphophenylacetanilide*, $[M]_D$ −12° (*ammonium* salt, $[M]_D$ −14°), is obtained from the strychnine or quinine salts and racemises easily when heated. The *o*-phenylenediamine salt of α-sulphophenylacetic acid when heated at 180° yields 2-*benzylbenziminazole*-α-*sulphonic acid* [*barium* $(+6H_2O)$, *cobalt* $(+5H_2O)$, *nickel* $(+5H_2O)$, and *quinine* $(+2H_2O)$ salts]. Decomposition of the purified quinine salt with ammonia furnishes the *ammonium* salt $[M]_D$ −10°, which racemises quickly when heated. *l*-α-Sulphophenylacetic acid and *o*-phenylenediamine react to give the inactive glyoxaline derivative.

H. Burton.

Resolution of externally compensated *p*-nitrobenzoylalanine. W. M. Colles and C. S. Gibson (J.C.S., 1928, 99—108).—*p*-Nitrobenzoylation of alanine in potassium hydroxide solution at 7—10° affords dl-p-*nitrobenzoylalanine*, m. p. 194° [*silver*, *brucine* $(+4H_2O)$, and *cinchonidine* $(+3H_2O)$ salts, *ethyl* ester, m. p. 117·5—118°]. Since this compound has a great tendency to form partial racemates or series of mixed crystals of the diastereoisomeric salts with various alkaloids, the following method of resolution must be adhered to. Equivalent quantities of the acid and strychnine are mixed in ethyl alcohol at 50° and the crude *lAlB* salt which separates is crystallised from alcohol at 50° until pure. *Strychnine* l-p-*nitrobenzoylalanine* (+EtOH), $[\alpha]^{20}_{5461}$ (anhydrous salt) −48·8° in alcohol, when decomposed furnishes l-p-*nitrobenzoylalanine*, m. p. 167·5—168°, $[\alpha]^{20}_{5461}$ (ammonium salt) −51·66° in water, and −15·81° in alcohol. The crystals obtained from the alcoholic mother-liquor after separation of the crude *lAlB* salt are crystallised from much alcohol and finally from water. Decomposition of *strychnine* d-p-*nitrobenzoylalanine* $(+1{\cdot}5H_2O)$, $[\alpha]^{20}_{5461}$ −1·9° in alcohol, so obtained, gave d-p-*nitrobenzoylalanine*, m. p. 168·5—169°, $[\alpha]^{20}_{5461}$ (ammonium salt) +51·4° in water, +15·76° in alcohol (*ethyl* ester, m. p. 121—121·5°, $[\alpha]^{20}_{5461}$ +1·32° in alcohol) identical with a specimen prepared from *d*-alanine and *p*-nitrobenzoyl chloride.

For comparison with the above results *ethyl* dl-α-*naphthalenesulphonylalanine*, m. p. 104°, and *ethyl* d-α-*naphthalenesulphonylalanine*, m. p. 83·5—84°, $[\alpha]^{20}_{5461}$ −47·15° in alcohol, were prepared (cf. A., 1925, i, 137). There is no reversal of sign of the rotatory powers of the *p*-nitrobenzoyl derivatives as is the case with the α-naphthalenesulphonyl derivatives.

The test for amino-acids described by Waser and Brauchli (A., 1924, i, 1068) is more sensitive if the sodium carbonate solution is replaced by pyridine (cf. Ingersoll and Adams, A., 1923, i, 200).

H. Burton.

Derivatives of phenylanthranilic acid. IV. H. Goldstein and J. Vaymatchar (Helv. Chim. Acta, 1928, 11, 239—245; cf. A., 1926, 558; 1927, 1186).—2-Chloro-3 : 5-dinitrobenzoic acid reacts with *p*-phenylenediamine in boiling aqueous sodium acetate solution to form 4 : 6-*dinitro*-4′-*aminodiphenylamine*-2-*carboxylic acid*, decomp. 274°, which when reduced by stannous chloride and subsequently esterified yields *methyl* 4 : 6 : 4′-*triaminodiphenylamine*-2-*carboxylate*, m. p. 151°. 4 : 6 : 4′-*Trinitrodiphenylamine*-2-*carboxylic acid* [*methyl* ester, m. p. 220° (decomp.)] chars at 298° without melting. 4-*Aminodiacetyl*-m-*phenylenediamine*, m. p. 218°, condenses with 2-chloro-3 : 5-dinitrobenzoic acid giving 4 : 6-*dinitro*-2′ : 4′-*diacetamidodiphenylamine*-2-*carboxylic acid*, m. p. 255° (decomp.). From *p*-aminophenol and potassium 2-chloro-5-nitrobenzoate, in presence of boiling amyl alcohol, potassium carbonate, and copper powder, there is obtained 4-*nitro*-4′-*hydroxydiphenylamine*-2-*carboxylic acid*, m. p. 210°, reduced to 4-*amino*-4′-*hydroxydiphenylamine*-2-*carboxylic acid*, m. p. 213° (decomp.) (*methyl* ester, m. p. 164°, obtained from the chlorostannate of the amino-acid, and methyl-alcoholic hydrogen chloride). *Methyl* 4 : 6-*diamino*-4′-*hydroxydiphenylamine*-2-*carboxylate* has m. p. 162°.

H. Burton.

Electrochemical oxidation of β-phenylpropionic acid. F. Fichter and R. Senti.—See this vol., 253.

Ring closure of γ-phenyl-α-benzyl-*n*-butyryl chloride. H. Leuchs [with H. Köhler and G.

Grunow] (Ber., 1928, **61**, [*B*], 144—146; cf. von Braun and others, this vol., 174).—The ring closure leads to the production of a six-membered in preference to a five-membered group; the latter does not appear to be formed. Benzyl-β-phenylethylmalonic acid passes when heated into *γ-phenyl-α-benzyl*-n-*butyric acid*, m. p. 54°, b. p. 233—234°/12 mm. The acid is converted by 0·8 mol. of phosphorus pentachloride in the presence of chloroform into a mixture of the corresponding chloride (*γ-phenyl-α-benzyl*-n-*butyramide*, m. p. 133—134°) and 1-*keto-2-benzyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, b. p. 222—223°/12 mm., m. p. 53—54·5° [*semicarbazone*, m. p. 224—226° (slight decomp.) after softening at 218°]. The constitution of the latter compound is established by its preparation by hydrolysis of *ethyl* 1-*keto*-2-*benzyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*-2-*carboxylate*, m. p. 76—77°. H. Wren.

Co-ordination valency of aluminium in its salicylato-derivatives. G. J. Burrows and I. W. Wark (J.C.S., 1928, 222—229).—*Aluminosalicylic acid*, $H_2[(C_7H_4O_3)_2Al(OH)OH_2]$, is prepared by the interaction of hot aqueous solutions of potassium aluminium sulphate and sodium or ammonium salicylate, from aluminium chloride and salicylic acid in hot aqueous solution, from aluminium hydroxide and aqueous-alcoholic salicylic acid, and from salicylic acid and aluminium ethoxide in anhydrous alcohol. The acid is dibasic; the *sodium* (+1 and $2H_2O$ and +2MeOH), *barium* (+$2H_2O$), and *strychnine* salts are described. Resolution of the acid was not effected through the agency of several alkaloids. The co-ordination valency of aluminium in this complex is six. *Aluminium methyl* and *ethyl salicylates*, $(C_8H_7O_3)_3Al$ and $(C_9H_9O_3)_3Al$, and aluminium ethyl malonate, $(C_7H_{11}O_4)_3Al$, are obtained by the interaction of aluminium alkoxides and the appropriate ester. H. Burton.

Bismuth salicylates and citrates. P. Godfrin (J. Pharm. Chim., 1927, [viii], 6, 49—62).—The following crystalline bismuth salicylates and citrates have been prepared by slow crystallisation from a mixture of bismuth nitrate and the appropriate sodium salt in an aqueous solution of glycerol: bismuth salicylate, $(C_7H_5O_3)_3Bi,H_2O$; *sodium bismuth salicylate*, $(C_7H_5O_3)_2Bi_2,(C_7H_5O_3)Na,H_2O$; *bismuthyl acid salicylate*, $(C_7H_5O_3)_2Bi{\cdot}OH,\frac{1}{2}H_2O$; *bismuthyl salicylate*, $C_7H_5O_3BiO$; *bismuth citrate*, $(C_6H_5O_7)Bi,4H_2O$; *bismuthyl acid citrate*, $(C_6H_5O_7)_2Bi(OH)_3,xH_2O$. Certain *basic bismuth salicylates* have also been prepared: $(C_7H_5O_3BiO)_4Bi_2O_3,2H_2O$, as the final dissociation product of neutral bismuth salicylate in ether, and $(C_7H_5O_3BiO)_2Bi_2O_3,2H_2O$ as the final dissociation product of neutral bismuth salicylate in boiling water or alcohol. E. A. Lunt.

Bismuth salicylates and citrates. Picon (J. Pharm. Chim., 1927, [viii], 6, 307—309).—Experiments are described from which it has been deduced that neutral bismuth salicylate does not dissociate in aqueous solution, and it is therefore thought that the basic bismuth salicylate, $(C_7H_5O_3BiO)_2Bi_2O_3,2H_2O$, (cf. Godfrin, preceding abstract), does not exist. E. A. Lunt.

Carbomethoxy-derivatives of hydroxy-acids. A. McKenzie and M. S. Lesslie (Ber., 1928, **61**, [*B*], 153—163).—In the hope of establishing a general synthesis of benzoins, *r*-carbomethoxymandelyl chloride, m. p. 39—40° (cf. A., 1913, i, 1194), has been subjected to the action of benzene and aluminium chloride in the presence of carbon disulphide, benzene, or pyridine, whereby, however, phenyldeoxybenzoin, m. p. 134—135°, is produced. Analogously, r-*carbethoxymandelic acid*, m. p. 79—82°, prepared from *r*-mandelic acid and ethyl chloroformate in the presence of chloroform and dimethylaniline, is converted through its chloride into phenyldeoxybenzoin. Since benzoin is stable towards hydrogen chloride in hot benzene but is converted into phenyldeoxybenzoin, presumably through desyl chloride, if aluminium chloride is present, the change is represented: $CHPh(O{\cdot}CO_2Me){\cdot}COCl \longrightarrow CHPh(O{\cdot}CO_2Me){\cdot}COPh \longrightarrow CHPh(OH){\cdot}COPh \longrightarrow CHPhCl{\cdot}COPh \longrightarrow CHPh_2{\cdot}COPh$. *l*-Mandelic acid yields successively l-*carbomethoxymandelic acid*, m. p. 111—112°, $[\alpha]_D^{17}$ −137·6° in acetone (hydrolysed to *l*-mandelic acid without racemisation by sodium hydroxide), l-*carbomethoxymandelyl chloride*, m. p. 42—43°, $[\alpha]_D^{17}$ −138·1° in acetone, and phenyldeoxybenzoin. Carbomethoxymandelyl chloride is converted by an excess of magnesium phenyl bromide into triphenylethylene glycol, m. p. 167—167·5°, which affords phenyldeoxybenzoin when treated with sulphuric acid, thionyl chloride, or hydrochloric acid. *Carbomethoxybenzilic acid*, m. p. 94—95°, prepared by the action of methyl chloroformate on benzilic acid in the presence of chloroform and pyridine, is unexpectedly transformed by thionyl chloride into diphenylchloroacetic acid, m. p. 118—119°. r-*Carbomethoxyatrolactic acid*, m. p. 134—135°, yields the corresponding *chloride*, m. p. 88—89°, converted by aluminium chloride and benzene into αα-diphenylpropionic acid, m. p. 173—174° (*silver* salt). *l*-Atrolactic acid yields the corresponding *carbomethoxy-derivative*, m. p. 77—79°, $[\alpha]_D^{17}$ +33·2° in ethyl alcoholic solution, which is hydrolysed without appreciable racemisation by sodium hydroxide. r-*Carbomethoxy-α-hydroxy-β-phenylpropionic acid*, m. p. 97—98°, is described. H. Wren.

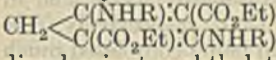
Dibromides of methylcoumaric and methylcoumarinic acids. M. Reimer and M. Howard (J. Amer. Chem. Soc., 1928, **50**, 196—203).—Treatment of methylcoumarinic or of methylcoumaric acid with bromine in carbon disulphide affords two isomeric dibromides, m. p. 177° (decomp.) (I), and m. p. 134° with slight decomposition and subsequent resolidification and then decomposition at 170° (II). Separation can be effected by fractional extraction with, and crystallisation from, toluene, in which solvent (II) gradually isomerises to (I) at the b. p. (cf. Biilmann and Lund, A., 1923, i, 218). Treatment of (II) with cold aqueous 50% potassium hydroxide affords α-bromo-*o*-methoxycinnamic acid, m. p. 171° (cf. Perkin, J.C.S., 1881, 39, 418), whilst (I) affords similarly a small proportion of an isomeric *α-bromo-o-methoxycinnamic acid*, yellow, m. p. 136° (III), together with α-bromo-*o*-methoxystyrene. Formation of (III) is favoured by substitution of alcoholic for aqueous alkali. Conversion of (III) into the isomeride of m. p. 171° is effected by exposure to sunlight in aqueous solution. Esterification of (III) cannot be effected by methyl-alcoholic hydrogen chloride, but the *methyl* ester, a yellow liquid, was obtained by the action of diazomethane. It is concluded that (III) is probably the *cis*-isomeride. Treatment of (II) with aqueous bromine affords a small proportion of αβ-5-tribromo-2-methoxycinnamic acid, m. p. 201°, which is converted by saturated methyl-alcoholic potassium hydroxide into two isomeric α-5-*dibromo-2-methoxycinnamic acids*, m. p. 163—164° (*methyl* ester, m. p. 94°), and m. p. 221° (*methyl* ester, m. p. 106—107°), respectively. Isomerisation of the former to the latter is effected by exposure to sunlight in benzene. Both isomerides yield 5-bromo-2-methoxyphenylpropiolic acid, decomp. 174°, when treated with boiling aqueous 10% potassium hydroxide. Treatment of both (I) and (II) with water affords the same α-bromo-β-hydroxy-2-methoxyphenylpropionic acid, m. p. 134°, which on treatment with aqueous bromine yields α-5-dibromo-β-hydroxy-2-methoxyphenylpropionic acid, m. p. 137°, with subsequent resolidification (IV) and m. p. 154° (V). Both (IV) and (V) yield the same *methyl* ester, m. p. 93—95°, and it is concluded that the two hydroxy-acids are dimorphic rather than isomeric. Treatment of (I) with cold methyl alcohol yields α-bromo-β-2-dimethoxyphenylpropionic acid, m. p. 118°, whilst (II) yields similarly the isomeride, m. p. 136° (cf. Werner, A., 1906, i, 180°). F. G. WILLSON.

Chlorobenzoylacetic esters. A. WAHL and J. ROLLAND (Compt. rend., 1928, 186, 37—39).—The action of nitrous vapours on methyl *o*-, *m*-, and *p*-chlorobenzoylacetates in presence of acetic anhydride and ether causes decomposition in each case with formation of the corresponding chlorobenzoic acid. Small amounts, however, of the respective αβ-diketonic esters are also formed, and the following derivatives have been isolated by treatment of the reaction mixture with phenylhydrazine: *methyl benzeneazo*-o-, -m-, and -p-*chlorobenzoylacetates*, m. p. 95—96°, 132°, and 90—91°, respectively, and 1-*phenyl*-3-o-, -m-, and -p-*chlorophenyl*-4 : 5-*diketodihydropyrazole*-4-*phenylhydrazones*, m. p. 195°, 166—167°, and 204°, respectively. B. W. ANDERSON.

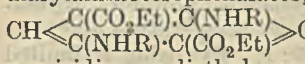
Derivatives of 2 : 3-hydroxynaphthoic arylamides. BRIT. DYESTUFFS CORP., LTD., J. B. PAYMAN, and H. WIGNALL.—See B., 1928, 118.

Direct substitution in the benzene nucleus. J. VAN ALPHEN (Rec. trav. chim., 1928, 47, 169—173).—Treatment of $\Delta^{2:6}$-dihydrophthalic acid with concentrated sulphuric acid at 60°, or in presence of acetic anhydride in the cold, yields phthalic acid or the anhydride. Cold absolute nitric acid or nitrogen peroxide in acetic acid solution gives similar results. When the acid is treated with bromine, Δ^{1}-3 : 6-dibromotetrahydrophthalic acid is produced, which when heated begins to decompose at 100°, phthalic anhydride begins to sublime at 160°, and at 200° decomposition into hydrogen bromide, water, and phthalic anhydride is complete. All the reactions are explained by 1 : 4-addition with subsequent elimination of hydrogen and the reacting constituent. These observations do not support Prins' objections (A., 1919, i, 71) to Holleman's addition theory of aromatic substitution. H. BURTON.

Constitution of ethyl succinylsuccinate and of ethyl *p*-dihydroxyterephthalate. D. MIGLIACCI (Gazzetta, 1927, 57, 914—923).—If the preparation of diethyl succinylsuccinate from diethyl succinate is not properly carried out, the mother-liquors yield a compound, m. p. 123—124°, which Gibbs and Brill (A., 1915, i, 648) regard as the ketonic form of diethyl succinylsuccinate. This compound is, however, diethyl *p*-dihydroxyterephthalate, since, on condensation with primary arylamines, it gives, not diethyl 2 : 5-diarylamino-$\Delta^{1:4}$-dihydroterephthalates,



$\mathrm{CH_2}\Big\langle\begin{matrix}\mathrm{C(NHR){:}C(CO_2Et)}\\ \mathrm{C(CO_2Et){:}C(NHR)}\end{matrix}\Big\rangle\mathrm{CH_2}$, but only diethyl 2 : 5-diarylaminoterephthalates,



$\mathrm{CH}\Big\langle\!\!\langle\begin{matrix}\mathrm{C(CO_2Et){:}C(NHR)}\\ \mathrm{C(NHR){\cdot}C(CO_2Et)}\end{matrix}\rangle\!\!\Big\rangle\mathrm{CH}$. Thus, the action of *p*-anisidine on diethyl succinylsuccinate in acetic acid, either with or without alcohol, yields *diethyl* 2 : 5-*di*-p-*anisidino*-$\Delta^{1:4}$-*dihydroterephthalate*, pale violet, m. p. 190—191°, whereas *p*-anisidine and Gibbs and Brill's ester, m. p. 123—124°, give *diethyl* 2 : 5-*di*-p-*anisidinoterephthalate*, orange-red, m. p. 171°.

Confirmation of Hantzsch's view that diethyl succinylsuccinate is rigidly enolic and diethyl *p*-dihydroxyterephthalate a quinol-*p*-dicarboxylic ester (A., 1917, i, 685) is obtained, since it is found possible (1) by oxidation by means of iodine (2 atoms), to pass from diethyl 2 : 5-di-*p*-anisidino-$\Delta^{1:4}$-dihydroterephthalate to diethyl 2 : 5-di-*p*-anisidinoterephthalate; (2) to convert the latter into a *dibenzoyl* derivative, m. p. 220°, and (3) by hydrolysis of the ester with potassium hydroxide, to obtain 2 : 5-*di*-p-*anisidinoterephthalic acid*, m. p. 276° (decomp.).

Diethyl 2 : 5-*di*-p-*phenetidino*-$\Delta^{1:4}$-*dihydroterephthalate*, m. p. 197°, *diethyl* 2 : 5-*di*-p-*phenetidinoterephthalate*, m. p. 180° (*dibenzoyl* derivative, m. p. 163°), and 2 : 5-*di*-p-*phenetidinoterephthalic acid*, $C_{24}H_{24}O_6N_2$, m. p. 280° (decomp.), are described. T. H. POPE.

Condensation of *cyclo*hexanealdehyde and malonic acid. S. S. G. SIRCAR (J.C.S., 1928, 54—57).—*cyclo*Hexanealdehyde condensed with malonic acid in presence of pyridine and piperidine (or diethylamine) forms β-cyclo*hexylacrylic acid*, b. p. 153—154°/11 mm., m. p. 57—58° (*silver* salt; *acid chloride*, b. p. 142°/12 mm.; *methyl* ester, b. p. 92—93°/15 mm.; *ethyl* ester, b. p. 119°/11 mm.; *amide*, m. p. 158—159°; *anilide*, m. p. 142°; *dibromide*). If condensation is effected in presence of a small amount of diethylamine, with subsequent heating, there is produced β-cyclo*hexylglutaric acid*, m. p. 153—154° [*silver* salt; *acid chloride*, b. p. 159—160°/12 mm.; *ethyl* ester, b. p. 118—120°/17 mm.; *methyl* ester, b. p. 106—108°/17 mm.; *diamide*, m. p. 190°; *dianilide*, m. p. 237° (decomp.); *anhydride*]. The *monoanilide*, m. p. 151°, of this acid when heated at 200° for a short time passes into the *anil*, m. p. 181°. When condensation takes place in alcoholic diethylamine there is obtained cyclo*hexane*spiro*butyrolactone*, b. p. 152—155°/15 mm. (the *silver* salt of the hydroxy-acid is described). Small amounts of β-*cyclo*hexylacrylic acid are also formed in both these condensations.

Oxidation of the αβ- and βγ-unsaturated ketones from *cyclo*hexanealdehyde and acetone (Kon, A., 1926, 952) with alkaline hypobromite yields β-*cyclo*hexylacrylic acid and a βγ-*acid* (*silver* salt), respectively. This last compound when oxidised with dilute potassium permanganate gives *cyclo*hexanone, whereas the former furnishes *cyclo*hexanealdehyde.

H. Burton.

Hydrolysis by alkalis of ethyl phenylethylmalonate. E. Tassilly, A. Belot, and M. Descombes (Compt. rend., 1928, 186, 149—151).—Hydrolysis of ethyl phenylethylmalonate with hot aqueous or alcoholic sodium hydroxide yields phenylethylmalonic acid and α-phenyl-α-ethylacetic acid in the proportions 4 : 1 and 1 : 9, respectively, the hydrolysis in alcoholic solution being completed much the more rapidly. Hydrolysis with powdered potassium hydroxide at the ordinary temperature gives the same acids in the ratio 4 : 1. By using a limited quantity of cold aqueous-alcoholic sodium hydroxide, *ethyl hydrogen phenylethylmalonate*, m. p. 94°, is obtained. B. W. Anderson.

3-Methyl-4′-*iso*propyldiphenyl-2 : 2′-dicarboxylic acid. H. P. Fogelberg (Annal. Acad. Sci. Fennicæ, 1927, A, 29, No. 4).—3-*Methyl*-4′-iso*propyldiphenyl*-2 : 2′-*dicarboxylic acid*, m. p. 188—189·5°, formed by the oxidation of retenequinone with hydrogen peroxide in glacial acetic acid, gives the *anhydride*, m. p. 111—112°, on treatment with acetyl chloride and acetic anhydride, yielding the *monoamide*, m. p. 196—197°, on warming with aqueous ammonia. The acid forms soluble alkali, barium, and calcium salts and insoluble silver, copper, and lead salts. G. A. C. Gough.

5-Bromo-2 : 4-dimethoxybenzoylacrylic acid and its esters. G. P. Rice (J. Amer. Chem. Soc., 1928, 50, 229—235).—Condensation of succinic anhydride with resorcinol dimethyl ether in carbon disulphide in presence of aluminium chloride (cf. Perkin and Robinson, J.C.S., 1908, 93, 506) affords, in addition to 2 : 4-dimethoxybenzoylpropionic acid, (I) (*ethyl* ester, m. p. 44°, with subsequent resolidification and m. p. 68·5°), 2-*hydroxy*-4-*methoxybenzoylpropionic acid* (*methyl* ester, m. p. 87°). Bromination of (I) in chloroform affords β-5-*dibromo*-2 : 4-*dimethoxybenzoylpropionic acid*, m. p. 165° (decomp.) (*methyl* ester, m. p. 103°; *ethyl* ester, m. p. 114·5°), and this, when treated with potassium acetate in glacial acetic acid at 100°, yields 5-*bromo*-2 : 4-*dimethoxybenzoylacrylic acid*, yellow, m. p. 208° (*methyl* ester, m. p. 138° after softening at about 129°, m. p. 129° after resolidification; *ethyl* ester, yellow, m. p. 115·5°). Treatment of the latter acid with aqueous sodium hyposulphite affords 5-*bromo*-2 : 4-*dimethoxybenzoylpropionic acid*, m. p. 187° (*methyl* ester, m. p. 117°). When ethyl 5-bromo-2 : 4-dimethoxybenzoylacrylate is exposed to sunlight, it is converted into two colourless *dimerides*, m. p. 266° and 129—130°, respectively. The former becomes yellow when kept in diffused daylight, and the latter is gradually depolymerised in molten camphor. Treatment of methyl 5-bromo-2 : 4-dimethoxybenzoylacrylate with methyl alcohol and a trace of concentrated aqueous potassium hydroxide at below 0° affords 5-*bromo*-α : 2 : 4-*trimethoxybenzoylpropionic acid*, m. p. 189°, together with its *methyl* ester, m. p. 117°, whilst boiling dilute hydrochloric acid yields 5-*bromo*-α-*hydroxy*-2 : 4-*dimethoxybenzoylpropionic acid*, m. p. 172°. 5-*Bromo*-β-*hydroxy*-2 : 4-*dimethoxybenzoylpropionic acid*, m. p. 179° (decomp.) (*methyl* ester, m. p. 134·5°), is obtained by treating β : 5-dibromo-2 : 4-dimethoxybenzoylpropionic acid with cold aqueous sodium carbonate. 5-*Bromo*-α-*ethoxy*-2 : 4-*dimethoxybenzoylpropionic acid*, m. p. 139—140°, and its *ethyl* ester, m. p. 97°, are obtained analogously to the corresponding α-methoxy-derivatives.

F. G. Willson.

Synthesis of 3 : 4 : 5-trimethoxy-*o*-phthalic acid. K. Feist and G. L. Dschu (Festschr. A. Tschirch, 1926, 23—29; Chem. Zentr., 1927, ii, 58).—(*a*) 3 : 4 : 5-Trimethoxybenzoic acid, m. p. 163—164° (from gallic acid, methyl sulphate, and sodium hydroxide) yields with chloral hydrate 3 : 4 : 5-trimethoxytrichlorophthalide, m. p. 71—72°, which by heating with methyl-alcoholic sodium hydroxide, diluting with water, evaporating off the alcohol, saturating with hydrogen chloride, and methylating the product with methyl sulphate yields 3 : 4 : 5-trimethoxyphthalidecarboxylic acid, m. p. 147—148° (with diazomethane, methyl ester, m. p. 121°). The acid, when heated at 2 mm., yields 3 : 4 : 5-trimethoxyphthalide, m. p. 134—135°, which on oxidation with potassium permanganate in sodium hydroxide solution affords 3 : 4 : 5-trimethoxy-*o*-phthalic acid, m. p. 163° (anhydride, m. p. 143°; methyl ester, m. p. 64—65°).

(*b*) Gallic acid trimethyl ether, when heated in chloroform solution with bromine and iron powder, yields bromogallic acid trimethyl ether, m. p. 148°; the mother-liquor contains a molecular compound of the two ethers. The latter with diazomethane affords the methyl ester, m. p. 33°, which by boiling in ethereal solution in presence of iodine with magnesium turnings yields 1-methyl-3 : 4 : 5-trimethoxy-*o*-phthalate, m. p. 138—141°, which with diazomethane gives the dimethyl ester.

A. A. Eldridge.

Di*cyclo*pentanone derivatives. N. J. Toivonen (Annal. Acad. Sci. Fennicæ, 1927, A, 29, No. 20; cf. A., 1920, i, 1017; J.C.S., 1901, 79, 786; 1920, 117, 1362).—Triethyl 4 : 5 : 5-trimethyl*cyclo*pentan-3-one-1 : 2 : 4-tricarboxylate yields 4 : 5 : 5-trimethyl*cyclo*pentan-3-one-1-carboxylic acid, m. p. 117—118°, on boiling with 20% sulphuric acid. This acid or its *triethyl* ester, b. p. 132·5—134·5°/14 mm., on oxidation with potassium permanganate yields γ-acetyl-γ-methyl-*n*-butane-αβ-dicarboxylic acid, m. p. 123—124° (*semicarbazone*, m. p. 138°; *anhydride*, m. p. 139—140°), which may in turn be oxidised to γ-methylbutane-αβγ-tricarboxylic acid, m. p. 157—158°, by sodium hypochlorite. Oxidation with nitric acid yields the final product directly. Fusion of γ-hydroxy-αββ-trimethylbutane-αβδ-tricarboxylic acid lactone (Perkin, Thorpe, and Walker, J.C.S., 1901, 79, 729) with potassium hydroxide yields trimethylsuccinic, formic, acetic, and propionic acids.

G. A. C. Gough.

Action of aniline on vanillin. P. CARRÉ and P. BARANGER (Bull. Soc. chim., 1928, [iv], 43, 73—74).—When melted with 1 mol. of aniline vanillin affords *vanillin-aniline*, $OH\cdot C_6H_3(OMe)\cdot CH(OH)\cdot NHPh$, m. p. 155—156°, converted at 115° into 4-hydroxy-3-methoxybenzylideneaniline, m. p. 156—157° [*hydrochloride*, m. p. 177° (decomp.)]. *Vanillin-aniline hydrochloride*, m. p. 143° (decomp.), is obtained by warming vanillin with aniline hydrochloride or by dissolving 4-hydroxy-3-methoxybenzylideneaniline in 18% hydrochloric acid. Both hydrochlorides when heated afford a *substance*, m. p. 196—198°. R. BRIGHTMAN.

Asarylaldehyde [2 : 4 : 5-trimethoxybenzaldehyde]. II. J. VAN ALPHEN (Rec. trav. chim., 1928, 47, 174—178; cf. *ibid.*, 1927, 46, 195).—Treatment of asarylaldehyde with absolute nitric acid in acetic anhydride at —10° affords 1-nitro-2 : 4 : 5-trimethoxybenzene, m. p. 130°, by displacement of the aldehydo-group. When this reaction is carried out in presence of a trace of concentrated sulphuric acid the product formed is 5-*methoxy*-p-*benzoquinone-2-aldehyde diacetate*, m. p. 145°. 2 : 4 : 5-*Trimethoxycinnamic acid*, m. p. 169°, obtained by heating asarylaldehyde and malonic acid in pyridine, is nitrated in acetic acid solution to 3 : 6-*dinitro*-2 : 4 : 5-*trimethoxycinnamic acid*, m. p. 166—167° (decomp.). H. BURTON.

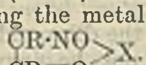
Campnospermonol, a ketonic phenol from *Campnospermum brevipetiolatum*. T. G. H. JONES and F. B. SMITH (J.C.S., 1928, 65—70).—Extraction of the oily exudate from *C. brevipetiolatum* with dilute sodium hydroxide solution and liberation of the dissolved phenol by carbon dioxide gives *campnospermonol*, $C_{27}H_{42}O_2$ or $C_{28}H_{44}O_2$, b. p. 260°/5 mm. (decomp.), $d^{15\cdot5}$ 0·9454, n_{D}^{20} 1·4925 [*acetate*, b. p. 255—260°/5 mm., $d^{15\cdot5}$ 0·9550, n_{D}^{20} 1·489; *oxime*, b. p. 240°/5 mm. (decomp.), $d^{15\cdot5}$ 0·9195, n_{D}^{20} 1·489]. *Campnospermonyl methyl ether* has b. p. 240°/5 mm., $d^{15\cdot5}$ 0·9342, n_{D}^{20} 1·496, $[R_L]_{\mathrm{D}}$ 128·8, iodine value 131 (*oxime*, b. p. 215°/4 mm., $d^{15\cdot5}$ 0·901, n_{D}^{20} 1·478), and when oxidised with potassium permanganate in acetone at 0° furnishes *m*-methoxybenzoic acid, formic, nonoic, and azelaic acids. Treatment of the methyl ether with ozone gives nonoaldehyde, formic and nonoic acids, and unrecognisable products.

Campnospermonyl methyl ether is reduced by sodium and alcohol, forming the corresponding *secondary alcohol*, b. p. 250°/5 mm., $d^{15\cdot5}$ 0·9191, whilst reduction with hydrogen in presence of platinum dioxide and ether gives *tetrahydrocampnospermonyl methyl ether*, m. p. 54° (*oxime*, m. p. 43°). Reduction of the ether with amalgamated zinc and hydrochloric acid furnishes an unsaturated *methoxyhydrocarbon*, $C_{28}H_{46}O$(?), b. p. 226°/5 mm., $d^{15\cdot5}$ 0·9093, n_{D}^{20} 1·495, which with hydrogen and platinum is reduced to a saturated *methoxyhydrocarbon*, $C_{28}H_{50}O$(?), m. p. 45°. Reduction of campnospermonyl acetate by hydrogen in presence of platinum dioxide affords *tetrahydrocampnospermonyl acetate*, m. p. 61°, from which is obtained *tetrahydrocampnospermonol*, m. p. 70°.

Oxidation of hydrocampnospermonyl methyl ether with potassium permanganate in boiling acetone gives *m*-methoxybenzoic, oxalic, and margaric acids, whilst treatment with amyl nitrite and sodium ethoxide yields an impure oximino-compound, from which by the action of phosphorus pentachloride, stearic acid was obtained. Campnospermonol is formulated as either β-*m*-hydroxyphenyl-$\Delta^{\alpha\mu}$-heneicosadien-δ-one,
$OH\cdot C_6H_4\cdot C(:CH_2)\cdot CH_2\cdot CO\cdot[CH_2]_7\cdot CH:CH\cdot[CH_2]_7\cdot Me$,
or β-*m*-hydroxybenzyl-$\Delta^{\alpha\mu}$-heneicosadien-δ-one,
$OH\cdot C_6H_4\cdot CH_2\cdot C(:CH_2)\cdot CH_2\cdot CO\cdot[CH_2]_7\cdot CH:CH\cdot[CH_2]_7\cdot Me$.
H. BURTON.

6-Acetyl-2-*iso*butyl-*m*-tolyl methyl ether and its nitration products. H. BARBIER (Helv. Chim. Acta, 1928, 11, 152—156).—2-*iso*Butyl-*m*-tolyl methyl ether and acetyl chloride react in presence of aluminium chloride and carbon disulphide to form 6-*acetyl*-2-iso*butyl*-m-*tolyl methyl ether*, b. p. 281°/730 mm., 155°/10 mm., m. p. 91°. Nitration of this with 92—95% nitric acid at —10° affords *nitro*-6-*acetyl*-2-iso-*butyl*-m-*tolyl methyl ether*, m. p. 97°, dinitro-2-*iso*butyl-*m*-tolyl methyl ether (I), m. p. 85° (musk ambrette, cf. Baur, A., 1894, i, 449), and *dinitro*-6-*acetyl*-m-*tolyl methyl ether* (II), m. p. 84°, together with a small amount of a substance, m. p. 96°. During the formation of (I) and (II) elimination of the acetyl and *iso*butyl groups, respectively, has occurred. *m*-Tolyl methyl ether and acetyl chloride yield 6-acetyl-*m*-tolyl methyl ether, b. p. 116°/4 mm., oxidised by 20% nitric acid to 5-methoxy-*o*-toluic acid, and nitrated by fuming nitric acid at 10° forming II. H. BURTON.

Hydrogenation of distyryl ketone and di-β-phenylethyl ketone. V. IPATIEV and N. ORLOV (J. Russ. Phys. Chem. Soc., 1927, 59, 537—539).—See A., 1927, 880.

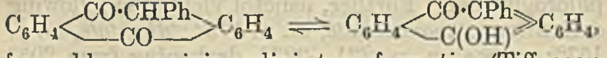
Constitution of the internally complex salts of the mono- and di-oximes of α-diketones. P. PFEIFFER and J. RICHARZ (Ber., 1928, 61, [*B*], 103—107; cf. Hieber and Leutert, this vol., 46).—Whereas the formation of metallic salts of mono- and di-oximes of α-diketones is readily explained if the α-oximes are regarded as *syn*-compounds, difficulties arise when Meisenheimer's view of their configuration is adopted (cf. A., 1922, i, 152). These are avoided by regarding the metal as attached to the nitrogen atom as in  $\begin{matrix}CR\cdot NO\\ CR{=}O\end{matrix}{>}X$. The complex nature of the salts is established by the isolation of the *compound* $[en_2\,Co(C_{14}H_{10}O_2N)]I_2$, by the successive action of hydroxoaquodiethylenediaminecobalt bromide (cf. A., 1927, 362) and potassium iodide on α-benzilmonoxime in aqueous alcohol. β-Benzilmonoxime does not react analogously. H. WREN.

Constitution of keto-enols from β-diketones. C. WEYGAND [with E. BAUER, H. GÜNTHER, and W. HEYNEMANN] (Annalen, 1927, 459, 99—122).—Attempts to prepare pairs of isomeric keto-enols of the types, $CPh(OH):CH\cdot COR$ and $CR(OH):CH\cdot COPh$ [R being (*a*) *p*-tolyl, (*b*) *p*-anisyl, (*c*) *p*-nitrophenyl, (*d*) *p*-bromophenyl], by hydrolysis of the corresponding methyl ethers or dimethylacetals yield only one product in each case. This is apparently homogeneous and is shown by bromine titration to contain 100% of enol, but determinations of its constitution by different chemical methods yield conflicting results (cf. Scheiber and Herold, A., 1914, i, 926; Claisen, A., 1926, 406). The tautomerism of these substances is thus closely similar to that of 5-phenyl-3-methylpyrazole. *p*-Anisyl αβ-dibromo-β-phenylethyl ketone is converted by boiling sodium methoxide into p-*anisyl α-bromostyryl ketone*, m. p. 126°, and by methyl alcohol and anhydrous sodium acetate into p-*anisyl β-methoxystyryl ketone*, m. p. 83—85°, identified by its ozonisation to methyl benzoate and anisic acid. This is hydrolysed by methyl-alcoholic hydrochloric acid to *p*-methoxydibenzoylmethane (I), m. p. 130—131°, and by acetic acid to a labile *isomeride*, m. p. 125—126°, similar to that of dibenzoylmethane (cf. A., 1926, 1248). Both isomerides are ozonised to phenyl- and anisyl-glyoxal, with benzoic and anisic acids. With hydroxylamine, (I) yields a single phenylanisyl*iso*oxazole, and with diazomethane principally the ether (II). Phenyl α-bromo-β-methoxy-β-anisylethyl ketone and sodium methoxide give *phenyl β* : p-*dimethoxystyryl ketone* (II), b. p. 165—170° [(*e*) in a cathode-ray vacuum], which is hydrolysed by acid to *p*-methoxydibenzoylmethane. *Phenyl α-bromo*-p-*methylstyryl ketone*, m. p. 65—66°, b. p. 225—228°/12 mm., prepared from phenyl αβ-dibromo-β-*p*-tolylethyl ketone and pyridine, is converted by sodium methoxide into *phenyl β-methoxy*-p-*methylstyryl ketone*, b. p. 145—150° (*e*), which is hydrolysed by acid to p-*methyldibenzoylmethane*, m. p. 84—85° (*copper* salt, m. p. 235·5°). Similarly *p*-tolyl αβ-dibromo-β-phenylethyl ketone affords successively p-*tolyl α-bromostyryl ketone*, m. p. 66—67°, b. p. 230—231°/11—12 mm., and p-*tolyl β-methoxystyryl ketone*, b. p. 140—145° (*e*), which is hydrolysed to the above *p*-methyldibenzoylmethane. With ozone the last yields benzoic and toluic acids, with hydroxylamine a mixture of *iso*oxazoles, and with diazomethane a mixture of ethers. Benzaldehyde and *p*-nitroacetophenone afford p-*nitrophenyl styryl ketone*, m. p. 146·5—147°, from which are prepared: a *dibromide*, m. p. 193·5—194°; p-*nitrophenyl α-bromostyryl ketone*, b. p. 153—155° (*e*), and p-*nitrophenyl β-methoxystyryl ketone*, m. p. 77°, b. p. 210° (*e*), which is hydrolysed to *p*-nitrodibenzoylmethane (Wieland, A., 1904, i, 432). *Phenyl α-bromo*-p-*nitrostyryl ketone*, m. p. 106°, b. p. 187° (*e*), obtained from the dibromide of phenyl *p*-nitrostyryl ketone, could not be converted into phenyl *p*-nitro-β-methoxystyryl ketone. The preparation of *phenyl* p-*bromostyryl ketone*, m. p. 123·5° (*dibromide*, m. p. 179·5°); p-*bromophenyl αβ-dibromo-β-phenylethyl ketone*, m. p. 184°; *phenyl α : 4-dibromostyryl ketone*, m. p. 131—131·5°; p-*bromophenyl α-bromostyryl ketone*, b. p. 136—143° (*e*); *phenyl* p-*bromo-β-methoxystyryl ketone* (III), b. p. 170° (*e*), and p-*bromophenyl ββ-dimethoxy-β-phenylethyl ketone* (IV), b. p. 176—180° (*e*), is described. (III) and (IV) are hydrolysed by acids to p-*bromodibenzoylmethane*, m. p. 94° (*copper* salt, m. p. 276°), of which a labile *form*, m. p. 86·5°, was obtained. H. E. F. Notton.

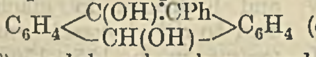
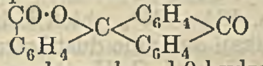
Additive character of heterogeneous conjugated systems. M. V. Ionescu (Bul. Soc. Stiinte Cluj, 1926, 3, 18—40).—See A., 1925, i, 1153.

Catalytic hydrogenation under pressure in presence of nickel salts. XII. Alkylated anthraquinones. J. von Braun, O. Bayer, and L. F. Fieser (Annalen, 1927, 459, 287—304).—The ease of hydrogenation of the side-nuclei in anthraquinone is considerably increased by α-alkylation, but scarcely affected by β-alkylation, whilst 2 : 3-dialkylation (in 1′ : 2′ : 3′ : 4′-tetrahydro-2 : 3-benzanthraquinone) protects the nucleus. The first product is invariably an alkylanthranol (cf. A., 1926, 172, 729). 1 : 4-Dimethylanthraquinone with 8 atoms of hydrogen in decahydronaphthalene at 180°, gives 1 : 4-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroanthranol*, m. p. 105—106° (*acetyl* derivative, m. p. 66—67°), and a little 1 : 4-*dimethyl*-(?)1 : 4-*dihydroanthranol*, m. p. 112—114°, which is oxidised by chromic acid to 1 : 4-dimethylanthraquinone. The tetrahydroanthranol is oxidised, first to 1 : 4-*dimethyl*-1 : 2 : 3 : 4-*tetrahydroanthraquinone*, m. p. 75°, then by permanganate to phthalic acid. It is further hydrogenated to 1 : 4-*dimethyl*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydroanthranol*, m. p. 83—84°, and finally to 1 : 4-*dimethyl*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydroanthracene*, m. p. 90—92°. Octahydrogenation of 1-methylanthraquinone yields an *oil*, b. p. 215—235°/14 mm. (traces of a bimolecular *product*, m. p. 235°), which is probably mainly 1-methyl-1 : 2 : 3 : 4-tetrahydro-9-anthranol, since 1-*methyl*-1 : 2 : 3 : 4-*tetrahydroanthraquinone*, m. p. 107—109°, may be isolated from its chromic acid oxidation product. It is further hydrogenated to 1-*methyloctahydroanthranol*, b. p. 202—203°/13 mm., and to 1-*methyl*-1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydroanthracene*, m. p. 64—66°, b. p. 170°/13 mm. Tetrahydrogenation of 2-methylanthraquinone affords a 2(3)-methylanthranol, m. p. 70—76°, which, like the product of Liebermann and Mamlock (A., 1905, i, 521), is probably a mixture of isomerides. Octahydrogenation yields 2-methylanthracene (10%), its reduction products, and an inseparable *mixture*, m. p. 5—40°, of 2(3)-methyltetrahydroanthranols (*acetyl* derivative, m. p. −5° to 20°), which is oxidised by chromic acid to a *mixture*, m. p. 45—70°, of 2-methyltetrahydroanthraquinones. The 2(3)-*methyl* 1 : 2 : 3 : 4 : 5 : 6 : 7 : 8-*octahydroanthranol*, m. p. 70—90°, b. p. 200—202°/14 mm., is also a mixture, but it is oxidised to a single 2-*methyloctahydroanthraquinone*, m. p. 155°. The course of hydrogenation of 2-methylanthraquinone is thus exactly similar to that of anthraquinone itself. 1′ : 2′ : 3′ : 4′-Tetrahydro-2 : 3-benzanthraquinone (I) (Schroeter, A., 1921, i, 861) is readily hydrogenated to 1′ : 2′ : 3′ : 4′-*tetrahydro*-2 : 3-*benzanthranol*, m. p. 142°, and reduced by zinc dust and ammonia to a small amount of an isomeric *tetrahydro*-derivative, m. p. 196°, which is oxidised to 2 : 3-benzanthraquinone, and 1′ : 2′ : 3′ : 4′ : 9 : 10-*hexahydro*-2 : 3-*benzanthranol*, m. p. 120°. This is decomposed by heating into 1′ : 2′ : 3′ : 4′-*tetrahydro*-2 : 3-*benzanthracene* (II), m. p. 233°, which is reduced by sodium and amyl alcohol to 1′ : 2′ : 3′ : 4′ : 9 : 10-*hexahydro*-2 : 3-*benzanthracene*, m. p. 128°. Octahydrogenation of the quinone (I) yields some of the anthracene (II) and 1′ : 2′ : 3′ : 4′ : 5 : 6 : 7 : 8-*octahydro*-2 : 3-*benzanthranol*, m. p. 159°, which is oxidised to the *octahydrobenzanthraquinone*, m. p. 264°. Its constitution has not been confirmed by oxidation, but the nature of further reduction products renders the above the most probable. The quinone (I) is reduced by 13 atomic proportions of hydrogen to a mixture of the impure 1′:2′:3′:4′:1:2:3:4:5:6:7:8-*dodecahydro*-2 : 3-*benzanthranol*, m. p. 129—130°, with the corresponding *dodecahydrobenzanthracene*, m. p. 82—83°, which is oxidised to pyromellitic acid, and by 11 atomic proportions to 1′ : 2′ : 3′ : 4′ : 5 : 6 : 7 : 8-*octahydro*-2 : 3-*benzanthracene*, m. p. 174°, which is more conveniently prepared by hydrogenating the anthracene (II). H. E. F. Notton.

A cyclic semipinacolin. J. W. Cook (J.C.S., 1928, 58—65).—The compound $C_{21}H_{14}O_2$, m. p. 133—134°, formed by the action of moist silver oxide on benzylideneanthrone dibromide (A., 1926, 1131) is shown to be a seven-membered ring compound,



$$C_6H_4\left<\begin{array}{c}CO\cdot CHPh\\ CO\end{array}\right>C_6H_4 \rightleftharpoons C_6H_4\left<\begin{array}{c}CO\cdot CPh\\ C(OH)\end{array}\right>C_6H_4,$$

formed by a semipinacolinic transformation (Tiffeneau and Orékhoff, A., 1921, i, 565). The compound furnishes an *oxime*, m. p. 191—193°, and a monoacetate; is reduced by zinc dust and ammonia into a *dihydro*-compound, m. p. 186—188° after sintering, probably  $C_6H_4\left<\begin{array}{c}C(OH)\vdots CPh\\ CH(OH)\end{array}\right>C_6H_4$ (*diacetate*, m. p. 154—156°), and by phosphorus and hydriodic acid to 9-benzyl-9 : 10-dihydroanthracene, showing that the semipinacolinic transformation is reversible. Oxidation of the semipinacolin with chromic–acetic acids yields 2-*benzoylbenzophenone*-2′-*carboxylic acid*, m. p. 228° (*methyl* ester, m. p. 165°). Treatment of this acid with boiling acetic anhydride and pyridine gives o-*benzoylphenylacetoxyphthalide*, m. p. 171—173° (cf. von Pechmann, A., 1882, 184; Graebe, A., 1900, i, 547), whilst reduction by zinc dust and sodium hydroxide solution or acetic acid did not yield satisfactory evidence. Treatment of the above acid with concentrated sulphuric acid at 160° affords the spirocyclic *lactone*,  $\begin{array}{c}CO\cdot O\\ |\\ C_6H_4\end{array}\!\!>C\left<\begin{array}{c}C_6H_4\\ C_6H_4\end{array}\right>CO$ (I), m. p. 238—239°, of 9-*o*-carboxyphenyl-9-hydroxyanthrone, which is reduced by tin and hydrochloric–acetic acids forming 9-o-*carboxyphenylanthrone*, m. p. 226—227°, or by zinc dust and ammonia yielding 9-o-*carboxyphenylanthracene*, m. p. 250—251°.

Magnesium *o*-tolyl bromide reacts with ethyl benzoate to form phenyldi-*o*-tolylcarbinol, which is oxidised by alkaline permanganate to triphenylcarbinol-2 : 2′-dicarboxylic acid, isolated as the *lactone*, m. p. 225—227°. Treatment of this compound with concentrated sulphuric acid at 160° affords (I). H. Burton.

Sulphonation of anthraquinone. Correction. H. E. Fierz-David (Helv. Chim. Acta, 1928, 11, 197—198).—β-Sulphonation of anthraquinone is effected with 30% oleum at 145°, and the yield of pure sodium anthraquinone-β-sulphonate is 64% (cf. A., 1927, 463). The solubility of this salt in water at 15° is 1 in 169. H. Burton.

Migration of the acyl group in partly acylated phenolic compounds. I. A. G. Perkin and R. C. Storey (J.C.S., 1928, 229—244; cf. A., 1925, i, 1159).—Methylation of 2 : 7-diacetylanthrapurpurin, m. p. 192—193° (lit. m. p. 175—178°), with excess of diazomethane and subsequent hydrolysis of the reaction product affords *anthrapurpurin 2-methyl ether*, m. p. 308—309° (7-*acetyl* derivative, m. p. 207°; 1 : 7-*diacetyl* derivative, m. p. 154—155°), together with *anthrapurpurin*-1-*methyl ether*, m. p. 299—300° (2 : 7-*diacetyl* derivative, m. p. 136—137°). 2 : 7-*Diethylcarbonatoanthrapurpurin*, m. p. 166—167°, gives 2 : 7-*diethylcarbonatoanthrapurpurin* 1-*methyl ether*, m. p. 120—121° (5 parts), and 1 : 7-diethylcarbonatoanthrapurpurin 2-methyl ether (2 parts) isolated as the phenolic ether. Benzoylation of 2 : 7-diacetylanthrapurpurin in presence of pyridine yields 2-*benzoyl*-1 : 7-*diacetylanthrapurpurin*, m. p. 201—203°, the acetyl group having migrated from position 2 to 1. Cautious hydrolysis of this compound gives 2-*benzoylanthrapurpurin*, m. p. 272—273°, which when methylated furnishes 2-*benzoylanthrapurpurin* 1 : 7-*dimethyl ether*, m. p. 201—203°, together with 1-*benzoylanthrapurpurin* 2 : 7-*dimethyl ether*, m. p. 209—211°. *Anthrapurpurin* 1 : 7-*dimethyl ether* (*acetyl* derivative, m. p. 175—176°) has m. p. 218—219°. 2-*Acetylpurpurin*, m. p. 179—180°, gives 1-*acetylpurpurin* 2 : 4-*dimethyl ether*, m. p. 189—190°, and 1-*acetylpurpurin* 2-*methyl ether*, m. p. 224—225° (1 : 4-*diacetyl* derivative, m. p. 170—172°). *Purpurin* 2 : 4-*dimethyl ether* has m. p. 186—189°, whilst purpurin 2-methyl ether has m. p. 232—233° and is also obtained from potassium purpurin and methyl iodide (J.C.S., 1899, 75, 447). 3-*Acetylpurpuroxanthin*, m. p. 144°, affords 3-*acetylpurpuroxanthin* 1-*methyl ether*, m. p. 154—155°, as the sole product, which is hydrolysed to *purpuroxanthin* 1-*methyl ether*, m. p. 311—313°.

Benzoylation of 2-acetylalizarin in presence of pyridine yields 2-*benzoyl*-1-*acetylalizarin*, m. p. 172—174°, which on hydrolysis gives 2-*benzoylalizarin*, m. p. 220—221°, also produced from potassium alizarin and benzoyl chloride. Methylation of this compound furnishes 1-*benzoylalizarin* 2-*methyl ether*, m. p. 266—268° (1 part), and 2-*benzoylalizarin* 1-*methyl-ether*, m. p. 203—205° (6 parts). 2-*Ethylcarbonatoalizarin*, m. p. 138—140° (*diethylcarbonato*-derivative, m. p. 150—151°), affords 1-*ethylcarbonatoalizarin* 2-*methyl ether*, m. p. 213—215° (1 part), and 2-*ethylcarbonatoalizarin* 1-*methyl ether*, m. p. 145—147° (3 parts), whilst from 2-p-*toluenesulphonylalizarin*, m. p. 218—219°, the corresponding 1-*methyl ether*, m. p. 176—177°, is obtained, no migration having occurred. 2 : 3-*Diethylcarbonatoanthragallol*, m. p. 174—175°, yields 2 : 3(or 1 : 2)-*diethylcarbonatoanthragallol* 1(or 3)-*methyl ether*, m. p. 125—127°, and 1 : 3-*diethylcarbonatoanthragallol* 2-*methyl ether*, m. p. 196—197°. From *diacetylgallacetophenone*, m. p. 107—108°, there were obtained 2 : 4-*diacetylgallacetophenone* 3-*methyl ether*, m. p. 150—151°, yielding gallacetophenone 3-methyl ether, m. p. 134—135° (cf. J.C.S., 1903, 83, 131), on hydrolysis, together with a compound (not isolated) yielding *gallacetophenone* 2(or 4)-*methyl ether*, m. p. 175°. *Di*-p-*toluenesulphonylgallacetophenone*, m. p. 152—153°, gives *di*-p-*toluenesulphonylgallacetophenone* 2(or 4)-*methyl ether*, m. p. 111—113°, exclusively.

The results show that with diazomethane the migration of the acetyl group approximates to 85%, the ethylcarbonato-group to 25%, the benzoyl to 20%; the *p*-toluenesulphonyl group does not migrate.

An explanation of these migrations is suggested involving the formation of a loose additive compound of diazomethane and the carbonyl oxygen.

H. BURTON.

Vat dyes [from benzanthronyl ethers]. I. G. FARBENIND. A.-G.—See B., 1928, 83.

New [acid] dyes of the anthracene series. I. G. FARBENIND. A.-G.—See B., 1928, 83.

Colour reactions of caoutchouc. H. PAULY (J. pr. Chem., 1928, ii, **118**, 48—52).—Caoutchouc of various origins and also guttapercha give practically all the colour reactions of the sterols. Buchard's reaction (bordeaux-red to reddish-violet coloration on addition of acetic anhydride and sulphuric acid to a solution in chloroform) is very sensitive towards quality and purity of the caoutchouc, and the change in the coloration on addition of perbenzoic acid varies with samples of different origin. The Buchard test also distinguishes amyrins from caoutchoucs. "Sodium-caoutchouc" gives a completely abnormal reaction (brownish-yellow). The Tschugaev–Golodetz reaction (A., 1908, ii, 330; violet coloration on dissolution in molten trichloroacetic acid, accelerated by a trace of formaldehyde) depends on the strongly acid character of the trichloroacetic acid and on the presence of the trichloromethyl group (trichloroethyl alcohol and anhydrous chloral dissolve caoutchouc, but give no coloration), and is probably given only by unsaturated caoutchoucs. Acyclic unsaturated hydrocarbons, *e.g.*, cold-polymerised isoprene, and isoprenedicarboxylic esters polymerised by light (Pauly and Will, A., 1918, i, 525), give none of the sterol colour reactions, whereas the diolefinic cyclic hydrocarbons give colorations with acetic acid or anhydride (Wallach's reaction). The sterols, amyrins, and resins which give colorations are all cyclic compounds, and a return to the old cyclic formula for caoutchouc is suggested.

Caoutchouc in chloroform solution yields an insoluble, saffron-yellow additive compound with stannic chloride.

C. HOLLINS.

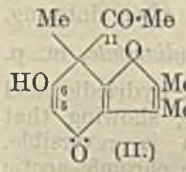
Saponin of *Primula* root. II. L. KOFLER and M. BRAUNER (Festschr. A. Tschirch, 1926, 351—356; Chem. Zentr., 1927, i, 3009).—*Primula elatior* saponin was obtained only in a gelatinous condition; it becomes yellowish-brown at 218° and has m. p. 224—225°. Its hæmolytic index is 50% greater than, and its toxicity half as great as, that of primulic acid. The differences between the saponin and that from *Primula veris* are described.

A. A. ELDRIDGE.

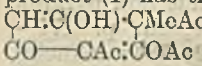
"Balanophorin." A. J. ULTÉE (Bull. Jard. bot. Buitenzorg, 1926, 8, No. 1, 3 pp.; Chem. Zentr., 1927, ii, 95).—Practically pure balanophorin, m. p. 77°, obtained by ethereal extraction, is identical with β-amyrin palmitate. β-Amyrin has m. p. 195°; acetate, m. p. 235°.

A. A. ELDRIDGE.

Constitution of usnic acid. C. SCHÖPF and K. HEUCK (Annalen, 1927, **459**, 233—286; cf. Kraus, Diss., Freiburg, 1925).—The observation that usnic acid contains 3 active hydrogen atoms (Zerewitinoff), and, like decarbousnic acid, is not a carboxylic acid but an enol, shows that Widman's formula (A., 1900, i, 235, 347; 1903, i, 96) is incorrect. Usnic acid is decomposed by concentrated alkali into the elements of acetoacetic acid and usnetic acid (Paternò, A., 1882, 1080; Salkowski, A., 1901, i, 152), which by heating is decarboxylated to usnetol, $C_{13}H_{14}O_4$. When this is ozonised in chloroform it affords a *substance* (I), $C_{13}H_{14}O_6$, m. p. 172°, which is readily hydrolysed by alkali to acetic acid (3 mols.) and methylphloroglucinol. Usnetol itself is hydrolysed by 50% potassium hydroxide at 185° to acetic acid (1 mol.) and 4 : 6-*dihydroxy*-2 : 3 : 7-*trimethylcoumarone*, m. p. 178° (decomp.) (*dibenzoate*, m. p. 135—136°), which is ozonised to 2 : 4-*dihydroxy*-6-*acetoxy*-5-*methylacetophenone*, m. p. 161—164°, whilst its *diacetate*, m. p. 148—149°, yields a resinous product which is hydrolysed by alkali to methylphloroglucinol. Further, usnetol yields the following derivatives: *monoacetate*, m. p. 173°; *diacetate*, m. p. 157°; *oxime*, m. p. 221—223°, darkening from 205° (*diacetate*, m. p. 126—127°); *phenylhydrazone*, m. p. 210—213°, and *monomethyl ether*, m. p. 127—128° (*oxime*, m. p. 184—185°; *phenylhydrazone*, m. p. 164—165°), and is reduced by palladium and hydrogen in glacial acetic acid to *dihydrousnetol*, m. p. 162° (*oxime*, m. p. 155—156°, and its *diacetyl* derivative, m. p. 132—134°). The constitution (II) for usnetol explains these and other reactions, acetylation attacking first the 6-hydroxyl, then the enolised acetyl group (11). The oxidation product (I) has therefore the formula,

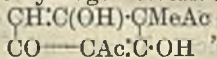


(II.)



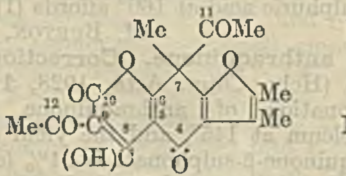
$$\begin{array}{l}\text{CH:C(OH)·CMeAc}\\ \text{CO——CAc:COAc}\end{array}$$

, which is confirmed by its hydrolysis by alcoholic hydrogen chloride to acetic acid and the *substance*,

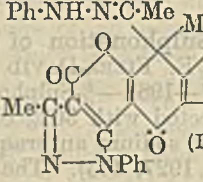


$$\begin{array}{l}\text{CH:C(OH)·CMeAc}\\ \text{CO——CAc:C·OH}\end{array}$$

, m. p. 168°. Usnetol methyl ether is ozonised to a *peroxide*(?), $C_{14}H_{16}O_7$, m. p. 124—126°, which is hydrolysed with difficulty by alkali and zinc dust to *substances*, $C_{12}H_{14}O_5$, m. p. 97—99°, and $C_{10}H_{12}O_4$, m. p. 195—197°, the constitutions of which are discussed. Usnetic acid is thus usnetol-5-carboxylic acid (*methyl* ester, m. p. 190—192°, and its *methyl ether*, m. p. 117—118°) and usnic acid (*phenylbenzylhydrazide*, m. p. 195°) has formula (III). Alternative *o*-quinonoid formulæ for usnetol and the corresponding structures for usnic acid are not excluded, but analogy with other naturally occurring phloroglucinol derivatives suggests that (III) is the most probable.



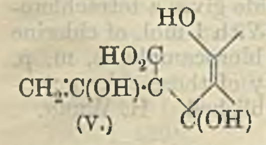
(III.)



(IV.)

The 7- and 9-acetyl radicals in usnic acid and its derivatives react readily in the enolic form; accordingly, with pyridine and acetic anhydride an 11 : 12-*diacetate*, m. p. 199—200° (d-*form*, m. p. 199—200°; $[\alpha]_D$ +205°), is formed. This is a monobasic acid, which shows that the 8-hydroxyl has remained unattacked. The anhydrobisphenylhydrazone, m. p.

265° (Widman, *loc. cit.*), is a pyrazole derivative (IV), and the monoxime anhydride is an *iso*oxazole of similar constitution. Unlike that of usnic acid, the lactone ring of the latter is opened by sodium methoxide giving 4′-carbomethoxy-3′-methyl-5 : 5′-*iso*oxazolylusnetol, m. p. 147° (A., 1900, i, 235). *i-anti*-Usnic acid oxime (A., 1903, i, 96) appears to be the corresponding carboxylic acid, whilst the monoxime, m. p. 243—244°, which shows no tendency to anhydride formation, is probably the 11-oxime. The isomerisation of usnic acid to usnolic acid (Stenhouse and Grove, J.C.S., 1881, **39**, 234), a dibasic, β-ketonic acid, is formulated as (III)⟶(V)⟶(VI). The formula (VI) is shown to explain a large number of its reactions.



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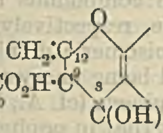
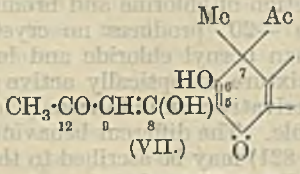


(VI.)



(VII.)

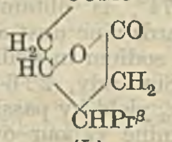
The constitution of decarbousnic acid (VII) follows from its mode of formation. It is confirmed by the hydrolysis and decarboxylation of diacetylusnic acid to 11 : 12-*diacetyldecarbousnic acid*, m. p. 112°. When decarbousnic acid or its diacetyl derivative is acetylated in presence of pyridine, 6 : 8 : 11 : 12-*tetraacetyldecarbousnic acid*, m. p. 189°, and a little of the 6 : 8 : 11-*triacetyl* derivative, m. p. 166°, are formed. The anhydrobisphenylhydrazone (1′-phenyl-3′-methyl-5 : 5′-pyrazolylusnetol-11-phenylhydrazone) and oxime anhydride (3′-methyl-5 : 5′-*iso*oxazolylusnetol) of decarbousnic acid and decarbousnol (9-decarboxyusnolic acid) are exactly analogous to the corresponding usnic acid derivatives. The formulæ given above are also supported by the behaviour of these derivatives with alkali and with ferric chloride and by many other reactions quoted from previous papers. The analogies between usnic acid and other naturally occurring phloroglucinol derivatives, *e.g.*, bergaptene (A., 1913, i, 192), albaspidin, lupulone, and cyanidin, are pointed out and their synthesis in the organism from simple aldehydes by means of aldol condensation, dehydration, and reduction is discussed. H. E. F. NOTTON.

Yeast ergosterol. II. F. REINDEL and E. WALTER (Annalen, 1928, **460**, 212—224).—α-Ergostanol (A., 1927, 241) contains an ethylenic linking and is therefore re-named α-ergostenol (tetrahydroergosterol). Owing to the ease with which oxidation occurs, neither the iodine value nor any other similar figure could be determined. Catalytic hydrogenation was unsuccessful. A method is given for the preparation of ergosterol from yeast fat. Ergosteryl acetate undergoes hydrogenation in ethereal solution in presence of platinum-black to give α-tetrahydroergosteryl acetate (formerly called α-ergostanyl acetate), which on hydrolysis affords α-ergostenol. Using platinum-black (Adam method) and ether, *α-ergostanyl acetate* (impure) results (the pure substance has m. p. 165—166°, $[\alpha]_D$ −7·5° in chloroform) and from this is obtained *α-ergostanol*, m. p. 150—151° practically inactive optically.

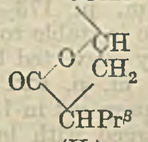
allo-α-Ergostanol (the former γ-ergostanol) is converted by phosphorus pentachloride into allo-*α-chloroergostan*, m. p. 119—120°, $[\alpha]_D$ +13·3° in chloroform, whilst the new α-ergostanol (m. p. 150—151°) similarly affords *α-chloroergostan*, m. p. 120—121°, $[\alpha]_D$ +22·8° in chloroform. Reduction of *allo*-α-chloroergostan with sodium in boiling amyl alcoholic solution gives a *hydrocarbon*, m. p. 84—85°, $[\alpha]_D$ +17° in chloroform, α-chloroergostan under similar conditions affording an isomeric *hydrocarbon*, m. p. 101—102°. Oxidation of the new α-ergostanol in glacial acetic acid solution at 70° with chromic oxide gives *α-ergostanone*, m. p. 174—175°, $[\alpha]_D$ +11·8° in chloroform [*ketazine*, m. p. 265° (decomp.); *oxime*, m. p. 225° (decomp.); *phenylhydrazone* m. p. 153—154°].

allo-α-Ergostanol similarly affords allo-*α-ergostanone*, m. p. 164°, $[\alpha]_D$ +34·9° in chloroform [*oxime*, m. p. 216°; *ketazine*, m. p. 155° (decomp.)]. *allo*-α-Ergostyl acetate, m. p. 144—145°, $[\alpha]_D$ +5·95°, produces no depression of the m. p. (144—145°) of γ-sitosyl acetate. Similarly, the above new hydrocarbon, m. p. 84—85°, $[\alpha]_D$ +17°, does not depress the m. p. of sitosan, m. p. 84—85°, $[\alpha]_D$ +28·5°. The m.-p. phenomena remain unexplained, but at the moment the two pairs of substances are not regarded as being identical.
E. E. TURNER.

Action of Beckmann's chromic acid mixture on monocyclic terpenes. T. A. HENRY and H. PAGET (J.C.S., 1928, 70—81).—α-Terpinene is oxidised by Beckmann's chromic acid mixture mainly to dimethylacetonylacetone, only traces of αδ-dihydroxy-α-methyl-δ-*iso*propyladipic acid being formed (J.C.S., 1921, **119**, 1714; 1923, **123**, 1878). *l*-Limonene is very slowly converted into 1 : 2 : 8-trioxyterpan and a ketolactone, $C_{10}H_{16}O_3$ (*semicarbazone*, m. p. 210°, $[\alpha]_D^{18}$ +1·28° in acetic acid), both of which have already been obtained by Wallach (Ann., 1893, **275**, 153) by the oxidation of terpineol, which therefore appears to be the first product of the action of chromic acid on limonene. α-Phellandrene is oxidised to *l-α-iso*propylsuccinic acid, thymoquinol, thymoquinone, and two *ketolactones*, $C_{10}H_{16}O_3$, b. p. 155—160°/1 mm., $[\alpha]_D^{20}$ +73·67° in water, +54·79° in benzene [*semicarbazone*, m. p. 183°, $[\alpha]_D^{21}$ +55·47° in acetic acid], and $C_9H_{14}O_3$, m. p. 48—50°, $[\alpha]_D^{20}$ +37·1° in water, −43·13° in benzene [*semicarbazone*, m. p. 187° (corr.) $[\alpha]_D^{20}$ +28·9° in alcohol or acetic acid]. The formulæ (I) and (II) are proposed respectively for these last-named compounds. The ketolactone (I) is oxidised by sodium hypobromite to a *dibasic acid*, $C_9H_{14}O_4$, m. p. 138°, $[\alpha]_D^{19}$ +15·99 in aqueous sodium hydroxide [*silver* salt; *ethyl* ester, b. p. 168—170°/17 mm., d_{19}^{19} 1·0046, $[\alpha]_D^{18}$ +18·05° in alcohol, n_D^{20} 1·4530], which undergoes further oxidation with potassium permanganate, giving *l-α-iso*-



(I.)



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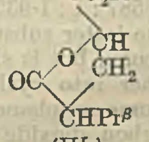


(III.)

propylsuccinic acid. The dibasic acid is alternatively formulated as β-*iso*propyl-αβ-dihydromuconic acid or 1-carboxy-2-*iso*propyl-*cyclo*propylacetic acid, the former structure being supported by molecular refraction of the diethyl ester, the latter by absence of reactivity with bromine. Oxidation of the keto-lactone (II) with sodium hypobromite gives bromoform, a small quantity of *substance*, m. p. 225° (decomp.), containing 31% of bromine, and a *lactone acid* (III), $C_8H_{12}O_4$, m. p. 58—60° (*silver* and *lead* salts), which undergoes further oxidation with potassium permanganate, giving *l*-α-*iso*propylsuccinic acid. Confusion exists in previously published data with regard to the physical constants of the optically active forms of the last-named acid. The *dl*-acid, m. p. 117° (anilic acid, m. p. 144°), is partly resolved by quinine (less soluble fraction of *quinine* salt has m. p. 206°) and by quinidine. Complete resolution is effected by fractionation of the easily dissociated *strychnine* salt, followed by conversion into the *brucine* salt, m. p. 144°, $[\alpha]_D^{20}$ —15·9° in chloroform. The pure *l*-acid has m. p. 94°, $[\alpha]_D^{20}$ —23·46° in water (anilic acid, m. p. 129°). Thymoquinone reacts with 1 mol. of semicarbazide, giving 4-hydroxy-3-methyl-5-*iso*propylbenzeneazoformamide (J.C.S., 1913, **103**, 1419) and, in addition, a *disemicarbazone*, existing in two stable yellow modifications, m. p. 237° and 257°, and one colourless labile form, m. p. 237°. The yellow modification, m. p. 237°, is obtained from each of these by crystallisation from boiling acetic acid.

p-Cymene, present as impurity in commercial phellandrene, is attacked exceedingly slowly by Beckmann's chromic acid mixture, yielding minute quantities of *p*-methylacetophenone. The mechanism of chromic acid oxidation of α-terpinene, *l*-limonene, and α-phellandrene is discussed. M. Clark.

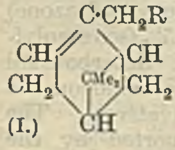
Crystalline dihalogen derivatives of pinene. G. Brus (Compt. rend., 1928, **186**, 87—89).—Neither the (orthorhombic) pinene dichloride, m. p. 173—174°, of Aschan nor the (monoclinic) dichloride of the author is isomorphous with (hexagonal) tricyclene dibromide. The constitutions of the two dichlorides thus remain unknown. B. W. Anderson.

Products of the addition of chlorine and bromine to pinene and their de-chlorination. O. Aschan (Ber., 1928, **61**, [*B*], 38—45).—Dry chlorine is led over the surface of well-stirred pinene kept below 0°, whereby a mixture of pinene hydrochloride and 2 : 6-*dichlorocamphane* (*pinene*-2 : 6-*dichloride*), rhombic-bipyramidal crystals, *a* : *b* : *c*= 0·8587 : 1 : 1·9320, m. p. 173—174°, is obtained. The latter substance is stable towards zinc dust and alcohol but is slowly converted by sodium in boiling ether into cyclene, m. p. 62°. Similarly, 2 : 6-dibromocamphane is prepared in 15% yield by passing carbon dioxide charged with bromine vapour over pinene cooled in a mixture of ice and salt. The chloride or, preferably, the bromide is slowly converted by freshly-prepared silver acetate in boiling glacial acetic acid into the unsaturated *ester*, $C_{10}H_{15}\cdot OAc$, b. p. 120—122°/15 mm., d_4^{20} 0·9894, n_D^{20} 1·47740 (corresponding *alcohol*, $C_{10}H_{16}O$, b. p. 212°), and a substance hydrolysed by alcoholic potassium hydroxide to the *glycol* or *ketol*, $C_{10}H_{18}O_2$, m. p. 132—133°.

Chlorine reacts violently with molten pinene hydrochloride or with the warm substance in the presence of antimony pentachloride, carbonisation occurring. In carbon tetrachloride a mixture of di- and tetrachlorocamphanes, m. p. 127—128°, appears to result, whereas when treated almost to saturation with chlorine in chloroform and carbon tetrachloride successively pinene hydrochloride gives a tetrachlorocamphane, m. p. 150—152°. With 1 mol. of chlorine in carbon tetrachloride a trichlorocamphane, m. p. 130°, results. The homogeneity of these chloro-compounds is not regarded as established. H. Wren.

Action of chlorine and bromine on nopinene. G. Brus (Compt. rend., 1928, **186**, 240—242).—The action of chlorine and bromine on nopinene at —15° to —20° produces no crystalline compounds other than bornyl chloride and bromide, respectively, the mixture of optically active stereoisomeric dihalogen derivatives simultaneously formed being uncrystallisable. The different behaviour of pinene (cf. A., 1925, i, 821) may be ascribed to the fact that in nopinene a third centre of asymmetry is formed on the first addition of 2 halogen atoms to the molecule. B. W. Anderson.

Influence of constitution on the rotatory power of optically active substances. XIX. H. Rupe and A. Héritier (Annalen, 1927, **459**, 171—194).—Myrtenol (I, R=OH), obtained by an improved process from French myrtle oil (yield 25%), is readily converted by phosphorus tribromide in ethereal solution into *myrtenyl bromide* (I, R=Br), b. p. 93°/9 mm., $[\alpha]_D$ +32·31°. The latter does not afford a magnesium derivative, but when the preparation of the latter is attempted, an 80% yield of *dimyrtenyl*, b. p. 173—174°/10 mm., d_4^{20} 0·9521, $[\alpha]_D^{20}$ +13·793°, is obtained. This property of myrtenyl bromide, however, allows of the ready substitution of bromine by hydrocarbon radicals. Thus, magnesium methyl iodide converts myrtenyl bromide into *methylmyrtenyl* (*homopinene*) (I, R=Me), b. p. 95·5—96°/62 mm., d_4^{20} 0·8697, $[\alpha]_D^{20}$ +33·962°. *Ethylmyrtenyl*, b. p. 73—73·5°/10 mm., d_4^{20} 0·8663, $[\alpha]_D^{20}$ +21·970°, n-*propylmyrtenyl*, b. p. 88—89°/10 mm., d_4^{20} 0·8624, $[\alpha]_D^{20}$ +21·632°, *phenylmyrtenyl*, b. p. 138—141°/12 mm., d_4^{20} 0·9712, $[\alpha]_D^{20}$ +29·486°, *benzylmyrtenyl*, b. p. 151—152°/10 mm., d_4^{20} 0·9633, $[\alpha]_D^{20}$ +16·182°, β-*phenylethylmyrtenyl*, b. p. 166—167°/10 mm., $[\alpha]_D^{20}$ —15·276°, or b. p. 167·5—168°/10·5 mm., $[\alpha]_D^{20}$ —4·5787°, n_α 1·52715, n_D 1·53116, n_β 1·54119, d_4^{20} 0·9574 (the second b. p. and [α] are probably the more accurate), and γ-*phenylpropylmyrtenyl*, b. p. 182·5—183·5°/10 mm., d_4^{20} 0·9522, $[\alpha]_D^{20}$ +4·957°, were prepared in a similar manner.



(I.)

Magnesium phenylethinyl bromide (obtained from phenylacetylene and magnesium ethyl bromide) and myrtenyl bromide afford *phenylethinylmyrtenyl* (I, R=·C⋮CPh), a yellow oil, b. p. 177·5—178·5°/10 mm. or 89—90° in a vacuum. It rapidly polymerises, has $[\alpha]_D^{20}$ +18·725°, n_α 1·55804, n_D 1·56336, n_β 1·57735, and d_4^{20} 0·9896. Phenylethinylmyrtenyl is reduced in boiling aqueous alcoholic solution by zinc–copper couple to *phenylethenylmyrtenyl* (I, R=$\cdot$CH:CHPh), b. p. 167·5—168·5°/10 mm., d_4^{20} 0·9683, $[\alpha]_D^{20}$ +13·050, n_α 1·54074, n_D 1·54534.

Myrtenyl bromide converts ethyl sodioacetoacetate into *ethyl myrtenylacetoacetate* (I, R=$\cdot CHAc\cdot CO_2Et$), b. p. 162—163·5°/11 mm. (*semicarbazone*, m. p. 122·2°, regenerating the pure ester when distilled in steam with oxalic acid). The ester, when hydrolysed with alcoholic sodium hydroxide, affords *homomyrtenyl methyl ketone* (I, R=$\cdot CH_2Ac$) (isolated first as the *semicarbazone*, m. p. 173°), b. p. 127—129°/12·5 mm., d_4^{20} 0·9516, $[\alpha]_D^{20}$ +26·719°.

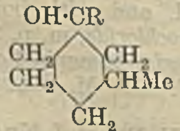
Myrtenal (I, R=$\cdot$CHO), b. p. 91·75—92°/12·5 mm., d_4^{20} 0·9898, has $[\alpha]_D^{20}$ +15·682 (cf. Semmler and Bartelt, A., 1907, i, 429).

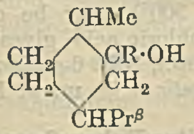
It was shown previously (Annalen, 1915, **409**, 327) that the esters of myrtenol with aliphatic and aromatic acids showed great regularities in their optical constants. Calculation from these results by Lowry and Dickson's method shows the esters to have anomalous rotatory dispersion. Adopting a new mode of calculation (the "end term formula"), however, the present authors find no anomaly (see original for mathematical part). Methyl-, ethyl-, *n*-propyl-, and phenyl-myrtenyl similarly exhibit normal rotation dispersion, but whilst benzylmyrtenyl is slightly anomalous, the phenylethyl and still more so the phenylpropyl derivative, exhibit marked anomaly of dispersion. This effect, due to the increasing distance of the phenyl group from the main nucleus, is intensified by unsaturation (phenylethenyl- and phenylethinyl-myrtenyl). Myrtenal has anomalous rotatory dispersion, but homomyrtenyl methyl ketone is normal.

The application of the new mode of calculation of rotatory dispersion to the case of pulegone shows that whilst pulegyl methyl ketone is an individual, pulegone is not (cf. Grignard and Savard, A., 1926, 408). E. E. Turner.

Influence of constitution on the rotatory dispersion of optically active substances. XX. H. Rupe and E. Kambli (Annalen, 1927, **459**, 195—217).—An improved method is given for the preparation of optically active 3-methyl*cyclo*hexanone from pulegone. Sodamide, followed by acetylene, converts the methyl*cyclo*hexanone into 3-*methyl*-1-*ethinyl*cyclo*hexanol* (I, R=$\cdot$C:CH), b. p. 76—78°/10 mm. The latter is a mixture of solid and liquid *isomerides* (proportions about 3—5 to 1). The solid has m. p. 47·5°, b. p. 79°/11 mm., $[\alpha]_D^{20}$ −12·46°, d_4^{20} 0·8826. The liquid, probably not free from the solid form, has b. p. 77—78°/10 mm., d_4^{20} 0·9439, and $[\alpha]_D$ −2·84°. A *tetrabromide* was obtained from the solid form, which, when reduced with zinc–copper couple in alcoholic solution, gave 3-*methyl*-1-*ethenyl*cyclo*hexanol* (I, R=$\cdot CH{:}CH_2$), b. p. 77°/11 mm., m. p. 32°, d_4^{20} 0·9238, $[\alpha]_D^{20}$ 1·04°. 3-*Methyl*-1-*ethyl*cyclo*hexanol* (I, R=Et), obtained from methyl*cyclo*hexanone and magnesium ethyl bromide has b. p. 75·5—76·5°/13 mm., d_4^{20} 0·9098, and $[\alpha]_D^{20}$ −2·68°.

(I.)





(II.)

Carvone is readily converted into tetrahydrocarvone in presence of alcohol, hydrogen, and nickel. The tetrahydro-compound, with sodamide and acetylene, gives 2-*ethinyl*-p-*menthan*-2-*ol* (II, R=$\cdot$C:CH), b. p. 104°/10 mm., d_4^{20} 0·9270, $[\alpha]_D^{20}$ −21·10° (*silver* derivative described). When reduced, the carbinol affords 2-*ethenyl*-p-*menthan*-2-*ol* (II, R=$\cdot CH{:}CH_2$), b. p. 103°/10 mm., d_4^{20} 0·9059, $[\alpha]_D^{20}$ −14·26°. 2-*Ethyl*-p-*menthan*-2-*ol*, from magnesium ethyl bromide and tetrahydrocarvone, has b. p. 106·5—107·5°/11 mm., d_4^{20} 0·9082, and $[\alpha]_D^{20}$ −29·07°. 2-*Phenylethinyl*-p-*menthan*-2-*ol* (II, R=$\cdot$C:Ph), from tetrahydrocarvone and magnesium phenylethinyl bromide, has b. p. 185—186°/10 mm., or 105° in a vacuum, d_4^{20} 0·9920, $[\alpha]_D^{20}$ −12·62°, and on reduction affords 2-*styryl*-p-*menthan*-2-*ol*, b. p. 173—174°/9 mm. or 102° in a vacuum, d_4^{20} 0·9601, and $[\alpha]_D^{20}$ −12·35°. When ω-bromostyrene, magnesium, ether, and tetrahydrocarvone were caused to interact, an *isomeric* styrylcarbinol, b. p. 103° in a vacuum, d_4^{20} 0·9695, $[\alpha]_D^{20}$ −36·19, and diphenylbutadiene were formed. 2-β-*Phenylethyl*-p-*menthan*-2-*ol* (II, R=$\cdot CH_2\cdot CH_2Ph$), from magnesium β-phenylethyl bromide and tetrahydrocarvone, has b. p. 175—176·5°/10 mm., d_4^{20} 0·9585, and $[\alpha]_D^{20}$ −5·60°.

Boiling formic acid or a mixture of glacial acetic and concentrated sulphuric acid converts the above phenylethinylmenthanol into 2-*phenacylidene*-p-*menthane*, b. p. 179—181°/10 mm. or 104° in a vacuum, d_4^{20} 0·9926, $[\alpha]_D^{20}$ −39·39° (*semicarbazone*, m. p. 156°).

The above 3-methyl-1-ethinyl*cyclo*hexanol, when boiled with mercuric oxide and dilute sulphuric acid, was converted into 1-*acetyl*-3-*methyl*cyclo*hexanol* (I, R=Ac), b. p. 105°/10 mm., d_D^{20} 0·9991, $[\alpha]_D^{20}$ 4·58° [*semicarbazone*, m. p. 210°, (decomp.)]. The similarly prepared 2-*acetyl*-p-*menthan*-2-*ol* (II, R=Ac) has b. p. 126°/11 mm., d_4^{20} 0·9662, and $[\alpha]_D^{20}$ −21·59° [*semicarbazone*, m. p. 212° (decomp.)].

The optical rotatory dispersion of most of the above-named substances was measured (6 lines). Methyl*cyclo*hexanone has the exceptionally high dispersion quotient of 3·42, and shows no appreciable anomaly. Tetrahydrocarvone (quotient 2·504) is also not anomalous. Of all the other compounds now described, only the β-phenylethylmenthanol exhibits anomalous dispersion. E. E. Turner.

Higher terpene compounds. XXXII. Addition reactions and the gentle permanganate oxidation of *d*-pimaric acid. L. Ruzicka and F. Balas (Annalen, 1928, **460**, 202—212).—The view previously held that *d*-pimaric acid contains one reactive and one only feebly reactive ethylenic linking is borne out by further work.

When potassium *d*-pimarate is oxidised with dilute potassium permanganate in aqueous solution, *dihydroxydihydro*-d-*pimaric acid*, $C_{20}H_{32}O_4$, m. p. 224° (decomp.), is formed (*diacetate*, m. p. 235°), together with a small quantity of an *isomeride*, m. p. 239° (decomp.). Using hydrochloric instead of acetic acid to precipitate the oxidation product, a third *substance*, m. p. 220—221°, is obtained.

d-Pimaric acid could not be caused to give a crystalline additive compound with bromine, but a *nitrosite*, pale greenish-yellow, m. p. 79—80° (decomp.), was obtained. Hydrogen chloride converts *d*-pimaric acid in cold dilute acetic acid solution into a mixture of three *hydrochlorides*, $C_{20}H_{31}O_2Cl$, respectively, melting at 232° (decomp.), 184° (decomp.), and 125° (decomp.), together with some other ill-defined derivatives containing chlorine. Repetition of the addition of hydrogen chloride to the acid, apparently under similar conditions, gave only the hydrochloride melting at 125°. At 100°, hydrogen chloride converts *d*-pimaric acid in glacial acetic acid solution rapidly into the hydrochloride melting at 184° (crystallographic data by Ulrich). Continued action of hydrogen chloride did not cause addition to the second ethylenic linking. The hydrochloride, m. p. 184°, was heated at 250° in quinoline solution; only *d*-pimaric acid was isolated from the product formed.

E. E. Turner.

Higher terpene compounds. XXXIII. Sesquiterpene compounds from camomile and milfoil oils. L. Ruzicka and E. A. Rudolph (Helv. Chim. Acta, 1928, **11**, 253—261; cf. Ruhemann and Lewy, B., 1928, 147).—There is obtained from camomile oil after removal of chamazulene (A., 1926, 299) a distillate of b. p. 110—140°/11 mm., which contains a monocyclic *hydrocarbon*, $C_{15}H_{24}$, having three double linkings. The constants of a fraction of b. p. 123—125°/12 mm., are d_4^{18} 0·8770, n_D^{19} 1·4941, α_D +3·6°. Treatment of six fractions of b. p. 105—118°/12 mm. to 125—130°/12 mm., from the above distillate, with hydrogen chloride in ether affords a small amount of a *trihydrochloride*, $C_{15}H_{27}Cl_3$, m. p. 55° (cf. Ruhemann and Lewy, *loc. cit.*) together with a liquid portion, which with alcoholic potassium hydroxide regenerates the hydrocarbon. This is dehydrogenated by sulphur into cadalene.

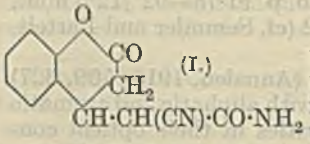
The alcohol fraction, b. p. 140—170°/11 mm., is treated successively with alcoholic potassium hydroxide, and phthalic anhydride in benzene. Decomposition of the hydrogen phthalate formed gives a small quantity of a compound, b. p. 150—160°/15 mm., probably $C_{15}H_{26}O$, and essentially a tricyclic alcohol. After removal of a further quantity of alcoholic substances by treatment with phthalic anhydride at 130°, the residue yielded a distillate, b. p. 150—160°, containing dicyclic alcohols, dehydrogenated into cadalene.

The sesquiterpenes, b. p. 115—125°/11 mm., from oil of milfoil do not give a crystalline hydrochloride, but are dehydrogenated into cadalene. The sesquiterpene alcohol fraction, b. p. 150—170°/11 mm., yields on treatment with phthalic anhydride in benzene a product, b. p. 155°/11 mm., probably a bicyclic alcohol mixture, dehydrated by formic acid into a *hydrocarbon*, $C_{15}H_{24}$, b. p. 120—125°/11 mm., d_4^{14} 0·9366, n_D^{14} 1·5045, which is tricyclic and contains one double linking. The remainder of the alcohol fraction, b. p. 160—165°/11 mm., consists of bicyclic alcohols, dehydrogenated into cadalene.

H. Burton.

Determination of valency requirements of alkyl groups. K. von Auwers and H. Düsterdiek.—See this vol., 305.

Reactivity of the double linking in coumarins and related αβ-unsaturated carbonyl compounds. I. Addition of cyanoacetamide to coumarins. T. R. Seshadri (J.C.S., 1928, 166—172).—The reactivity of the double linking in the hetero-ring of coumarin is exemplified by the ease with which addition of cyanoacetamide takes place with those coumarin derivatives which have no alkyl or halide substituent in the hetero-ring, but may have substituents in the benzene nucleus. The products of the reaction, which is carried out in hot alcoholic solution in the presence of a little piperidine, are 3 : 4-dihydrocoumarin-4-cyanoacetamides (I). The reactivity is ascribed to the presence of the double linking in a ring structure and to the degree of neutralisation of the ketonic properties of the carbonyl group by attachment to the singly-bound oxygen atom. The additive products may be hydrolysed to give a variety of compounds, the nature of which depends on the conditions. 3 : 4-*Dihydrocoumarin*-4-*cyanoacetamide*, m. p. 219—220°, yields with cold, concentrated hydrochloric acid, 3 : 4-*dihydrocoumarin*-4-*cyanoacetic acid*, m. p. 226—227°. With boiling, concentrated hydrochloric acid or potassium hydroxide solution, 3 : 4-*dihydrocoumarin*-4-*acetic acid*, m. p. 113—114°, is obtained. The last-named acid is further hydrolysed on keeping in cold, faintly acid, aqueous solution to β-o-*hydroxyphenylglutaric acid*, m. p. 160° (*disilver* salt), reconverted on heating or on boiling with hydrochloric acid into 3 : 4-dihydrocoumarin-4-acetic acid. Using similar experimental conditions, 7-*methyl*-3 : 4-*dihydrocoumarin*-4-*cyanoacetamide*, m. p. 245°, yields 7-*methyl*-3 : 4-*dihydrocoumarin*-4-*cyanoacetic acid*, m. p. 230—232°, and 7-*methyl*-3 : 4-*dihydrocoumarin*-4-*acetic acid*, m. p. 111—112°. This lactone acid is hydrolysed on keeping in cold, faintly acid solution to β-p-*methyl*-o-*hydroxyphenylglutaric acid*, m. p. 148—149°, reconverted into the parent lactone on fusion. 6-Nitro-3 : 4-dihydrocoumarin-4-cyanoacetamide, m. p. above 300°, yields with boiling hydrochloric acid, 6-*nitro*-3 : 4-*dihydrocoumarin*-4-*acetic acid*, m. p. 205° (decomp.), which with cold alkalis, gives yellow solutions containing salts of β-*m*-nitro-*o*-hydroxyphenylglutaric acid (*disilver* salt). 6-*Amino*-3 : 4-*dihydrocoumarin*-4-*cyanoacetamide*, m. p. 270° (*benzoyl* derivative, m. p. 300°), may be diazotised, and with boiling hydrochloric acid, gives the *hydrochloride*, m. p. 225° (decomp.), of 6-*amino*-3 : 4-*dihydrocoumarin*-4-*carbamylacetic acid*, m. p. 170—171°.



(I.)

M. Clark.

3-Nitrodiphenylene oxide. H. Ryan, J. Keane, and J. C. M'Gahon (Proc. Roy. Irish Acad., 1927, **37**, 368—372).—2 : 4-Dinitrodiphenyl ether is reduced to 4-*nitro*-2-*aminodiphenyl ether*, m. p. 107° (*acetyl* derivative, m. p. 118°), by a glacial acetic acid solution of stannous chloride containing hydrogen chloride. The nitroamine, when diazotised and heated with 50% sulphuric acid, gives, in 20—25% yield, 3-*nitrodiphenylene oxide*, m. p. 141°, which may be further nitrated to a *dinitrodiphenylene oxide*, m. p. 295°. The nitrodiphenylene oxides described by Ryan and Cullinane (A., 1924, i, 534) and by Borsche and Schacke (A., 1924, i, 161) are probably the 2- and the 1-nitro-compounds, respectively.

G. A. C. Gough.

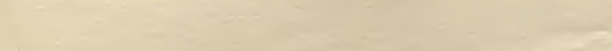
Odour and structure of certain cyclic acetals [alkylidene ethers]. R. R. Read, H. Lathrop, and H. L. Chandler (J. Amer. Chem. Soc., 1927, **49**, 3116—3119).—The following cyclic acetals were prepared by heating together equimolecular proportions of the appropriate αβ-diols and aldehydes under reflux for 6 hrs. on the steam-bath, with agitation and in presence of 5 drops of 40% sulphuric acid (cf. Fischer and Giebe, A., 1898, i, 167). *Methylene ethers*: of γ-phenoxypropane-αβ-diol, m. p. 40—43°, b. p. 138—139°/11 mm.; of α-phenylpropane-αβ-diol, b. p. 105—107°/12 mm.; of γ-phenylpropane-αβ-diol, b. p. 125—128°/16 mm., d_4^{20} 1·098; and of γ-*m*-tolylpropane-αβ-diol, b. p. 128—130°/15 mm., d_4^{20} 1·032. *Ethylidene ethers*: of γ-phenoxypropane-αβ-diol, m. p. 24°, b. p. 152—154°/11 mm.; of α-phenylpropane-αβ-diol, b. p. 116—118°/19 mm., d_4^{20} 1·032; of γ-phenylpropane-αβ-diol, b. p. 120—124°/16 mm.; of γ-*m*-tolylpropane-αβ-diol, b. p. 123—125°/13 mm., d_4^{20} 1·028; and of γ-*p*-tolylpropane-αβ-diol, b. p. 135—142°/17 mm., d_4^{20} 1·032. n-*Heptylidene ether* of γ-phenoxypropane-αβ-diol, b. p. 201—203°/12 mm. Few of the above possess any markedly agreeable odour, and none has an odour resembling that of jasmine.

F. G. Willson.

Stereoisomerism of disulphoxides and related substances. II. Derivatives of 1 : 4-dithian. E. V. Bell and G. M. Bennett (J.C.S., 1928, 86—92).—The stereoisomerism of the α- and β-dithian dioxides (A., 1927, 958) is further confirmed by a study of their reactions and of their derivatives, including in each case a *hydrochloride*, unstable *hydrobromide*, *mercurichloride*, *tetrabromide*, and *hexabromide*. The action of potassium sulphide on ββ′-dichlorodiethyl sulphone yield the structural isomeride, dithian monosulphone (Fromm and Ungar, A., 1924, i, 68), m. p. 203°, dimorphous. The corresponding reaction with ββ′-dichlorodiethyl sulphoxide yields *dithian monoxide*, m. p. 125° (*chloroplatinate*; *chloroaurate*), more conveniently prepared by controlled oxidation of dithian. This monosulphoxide gives rise to stereoisomeric *methyl sulphonium* salts, $SO<\genfrac{}{}{0pt}{}{C_2H_4}{C_2H_4}>\overset{+}{S}\cdot Me\}\overset{-}{X}$ (α-*picrate*, m. p. 187°, and β-*picrate*, m. p. 137°; α- and β-*chloroplatinates*; α-*iodide*) and to two *sulphoxide-sulphilimines*, $SO<\genfrac{}{}{0pt}{}{C_2H_4}{C_2H_4}>\overset{+}{S}\cdot\overset{-}{N}\cdot SO_2\cdot C_7H_8$ (α-, m. p. 230—234°, and β-, m. p. 176—177°). The bis-sulphilimine of dithian, $C_7H_8\cdot SO_2\cdot\overset{-}{N}\cdot\overset{+}{S}<\genfrac{}{}{0pt}{}{C_2H_4}{C_2H_4}>\overset{+}{S}\cdot\overset{-}{N}\cdot SO_2\cdot C_7H_8$ (Mann and Pope, J.C.S., 1922, 1052), has also been separated into two crystalline *isomerides* (α-, decomp. 250—255°, and β-, decomp. 200—210°).

M. Clark.

Pyrrolones. R. Lukeš (Chem. Listy, 1928, **22**, 1—12).—The action of Grignard reagents on various *N*-substituted succinimides leads to the production of pyrryl derivatives according to the following scheme:



$$\genfrac{}{}{0pt}{}{CH_2\cdot CO}{CH_2\cdot CO}>NR \rightarrow \genfrac{}{}{0pt}{}{CH_2\text{———}CO}{CH_2\cdot CR'(OH)}>NR \rightarrow \genfrac{}{}{0pt}{}{CH_2\cdot CO}{CH{:}CR''}>NR$$

Thus magnesium methyl bromide converts *N*-methylsuccinimide into 2-*hydroxy*-1 : 2-*dimethyl*-4-*pyrrolone*, m. p. 70°, and 1 : 2-*dimethyl*-4-*pyrrolone*, m. p. 62—63°, the latter product being identical with that obtained by the distillation of methylammonium lævulate. Similarly are prepared 1-*phenyl*-2-*methyl*-4-*pyrrolone*, m. p. 101°, 1-*ethyl*-2-*methyl*-4-*pyrrolone*, m. p. 33—34°, 1-*methyl*-2-n-*propyl*-4-*pyrrolone*, b. p. 145°/52 mm., and 1-*methyl*-2-n-*butyl*-4-*pyrrolone*, b. p. 148°/33 mm. The action of organic zinc derivatives is similar to that of magnesium; thus ethyl bromoacetate and *N*-methylsuccinimide in the presence of zinc yield the *ethyl* ester of 1-*methyl*-4-*pyrroloneacetic acid*, m. p. 123°.

R. Truszkowski.

Aliphatic β-aminoketones and related amino-alcohols. C. Mannich and W. Hof (Arch. Pharm., 1927, **265**, 589—598).—The benzoate of δ-dimethylaminobutan-β-ol, b. p. 60—62°/11 mm. (α-dimethylaminobutan-γ-ol, cf. Fourneau and Ramart-Lucas, A., 1919, i, 435), which has now been obtained by reducing δ-dimethylaminobutan-β-one (Mannich, A., 1917, i, 634), possesses pronounced anæsthetic properties. The reduction of the aminoketone to the amino-alcohol takes place smoothly by interaction with aluminium amalgam in moist ether. Analogues of the commercial product "Tutocaine" can be very simply prepared in this way, and the following is an account of results of further investigation. Acetone, paraformaldehyde, and piperidine hydrochloride, boiled together in alcohol solution, yield α-*piperidinobutan*-γ-*one*, b. p. 100—101°/11 mm. (*hydrochloride*, m. p. 167°; *picrate*, m. p. 107°; *oxime hydrochloride*, m. p. 201°). The ketone is reduced as described to α-*piperidinobutan*-γ-*ol*, an oil with a mouse-like odour, b. p. 102—103°/11 mm. (*hydrochloride*, m. p. 145°), the *benzoate hydrochloride* (m. p. 192°) of which is only weakly anæsthetic. By treating α-piperidinobutan-γ-one with magnesium methyl iodide, α-*piperidino*-γ-*methylbutan*-γ-*ol*, b. p. 115—116°/14 mm. (*hydrochloride*, m. p. 196°), is obtained, but the yield is poor.

Methyl ethyl ketone condenses with paraformaldehyde and dimethylamine (hydrochloride) to yield two products. Thus, condensation at the methyl group of the ketone gives α-*dimethylaminopentan*-γ-*one*, b. p. 103—104°/12 mm. (*chloroaurate*, m. p. 128°), and this compound forms about one fifth of the product; the remaining four fifths are the result of condensation at the methylene group, and so are composed of γ-dimethylaminomethylbutan-β-one (cf. Mannich and Curtaz, A., 1927, 231). This compound is readily reduced to γ-*dimethylaminomethylbutan*-β-*ol*, b. p. 65—67°/14 mm., of which the *hydrochloride* is very hygroscopic and the *benzoate hydrochloride*, m. p. 131°, is powerfully anæsthetic. The corresponding aminobenzoate hydrochloride is "Tutocaine," already referred to. When the same aminoketone is exhaustively methylated with methyl sulphate and the product, as quaternary base, distilled with steam, iso*propenyl methyl ketone*, b. p. 60—65° (*semicarbazone*, m. p. 176·5°), is obtained.

Methyl ethyl ketone, paraformaldehyde, and piperidine hydrochloride similarly yield γ-piperidinomethylbutan-β-one (Mannich and Curtaz, *loc. cit.*), the *oxime hydrochloride* of which has m. p. 167° (the m. p. of the hydrochloride of the aminoketone itself is now given as 150°). This aminoketone is reduced to *γ-piperidinomethylbutan-β-ol*, b. p. 112—114°/14 mm., which yields very hygroscopic salts and a *benzoate hydrochloride*, m. p. 178°, which is a potent anæsthetic.

Methyl propyl ketone, paraformaldehyde, and dimethylamine hydrochloride yield chiefly γ-dimethylaminomethylpentan-β-one (*picrate*, m. p. 123°; cf. Mannich and Bauroth, A., 1924, i, 947). *γ-Dimethylaminomethylpentan-β-ol*, b. p. 75—76°/13 mm., is obtained from the foregoing on reduction.

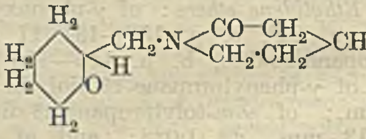
Pinacolin similarly condenses with paraformaldehyde and piperidine hydrochloride to give *α-piperidino-δδ-dimethylpentan-γ-one*, b. p. 116—119°/12 mm. (*hydrochloride*, m. p. 192°; *picrate*, m. p. 133°; *oxime hydrochloride*, m. p. 210°), which is reduced to *α-piperidino-δδ-dimethylpentan-γ-ol*, b. p. 121—123°/14 mm., of which the *hydrochloride*, m. p. 179—180°, and the *benzoate hydrochloride*, m. p. 186°, are described. The latter is a strong, persistent anæsthetic.

Allylacetone undergoes a similar condensation (with piperidine) to give γ-piperidinomethyl-Δ^{ϵ}-hexen-β-one (Mannich and Curtaz, *loc. cit.*), the hydrochloride of which is easily soluble in acetone, together with, in superior yield, a compound giving a hydrochloride sparingly soluble in acetone. This is *α-piperidino-*Δ^{ζ}*-hepten-γ-one*, b. p. 136°/16 mm. The *hydrochloride*, m. p. 157°, and the *hydrobromide*, m. p. 161°, are described. The aminoketone is reduced, like its congeners, to the carbinol, *α-piperidino-*Δ^{ζ}*-hepten-γ-ol*, b. p. 138°/14 mm., which is presumably a mixture of stereoisomerides, but yields a crystalline *benzoate hydrochloride*, m. p. 138°. This is almost devoid of anæsthetic properties.

Cocaine being derived, not from a simple amino-alcohol, but from the ester of an aminohydroxycarboxylic acid, an attempt was made to prepare an analogous compound along the above lines. Thus, ε-piperidino-γ-ketohexoic acid (Mannich and Bauroth, *loc. cit.*) was converted into the *ethyl* ester, b. p. 113—114°/14 mm. (*hydrochloride*, m. p. 117—118°). Unfortunately, when the compound is reduced with aluminium amalgam, it does not yield the ester of the corresponding hydroxy-acid, but the ethyl group is simultaneously removed, and the lactone, *ε-piperidino-γ-hydroxyhexoic lactone*, b. p. 174—176°/13 mm., *hydrochloride*, m. p. 213°, is obtained.

W. A. Silvester.

2-ω-Piperidinomethyl*cyclo*hexanone and related compounds. C. Mannich and P. Honig (Arch. Pharm., 1927, 265, 598—610).—The work of Mannich and Braun (A., 1920, i, 851; 1927, 659) has been extended in an attempt to obtain products with anæsthetic but not irritating properties. This has not been achieved. Diethylamine hydrochloride, formaldehyde, and *cyclo*hexanone readily yield *2-ω-diethylaminomethyl*cyclo*hexanone*, b. p. 117°/24 mm. (*hydrochloride*, m. p. 105—107°), which is reduced by aluminium amalgam in moist ether to *2-ω-diethylaminomethyl*cyclo*hexanol*, b. p. 119°/15 mm. This is presumably, like its lower homologue (*loc. cit.*), a mixture of stereoisomerides, but the *benzoate hydrochloride* can be purified without difficulty and then has m. p. 188—189° and is a powerful anæsthetic. *2-ω-Piperidinomethyl*cyclo*hexanone*, b. p. 130°/20 mm. (*picrate*, m. p. 127°), is prepared in a similar way. It is unstable and its behaviour has been examined in some detail. The *hydrochloride* crystallised from *iso*propyl alcohol has m. p. 161°, but then solidifies again at 165°, and melts at 227°. Actually a decomposition takes place: when the hydrochloride is heated for some time at 170°, it is converted into 2-methylene*cyclo*hexanone and piperidine hydrochloride. 2-ω-Piperidinomethyl*cyclo*hexanone yields normally a *cyanohydrin*, m. p. 67°, and an *oxime*, m. p. 113°. When it is oxidised with cold dilute potassium permanganate solution it yields adipic acid and a small proportion of a *compound*, $C_{12}H_{19}O_2N$, m. p. 75° (*semicarbazone*, m. p. 210—212°), which is not the piperidide of an acid and so is considered to have the constitution:



When 2-ω-piperidinomethyl*cyclo*hexanone is exhaustively methylated and distilled with steam it yields *N*-methylpiperidine and a *compound*, $C_{14}H_{20}O_2$, b. p. 163—165°/14 mm., which is not a diketone, for it yields a mono-*oxime*, m. p. 123°, and a *semicarbazone*, m. p. 206°. 2-ω-Piperidinomethyl*cyclo*hexanone is decomposed when heated with an excess of phenylhydrazine at 150—170°; ammonia, aniline, and piperidine are formed, and the residue contains tetrahydrocarbazole. Reduction in the usual way affords *2-ω-piperidinomethyl*cyclo*hexanol*, b. p. 141°/12 mm. (*picrate*, m. p. 127°), which is a mixture of two stereoisomerides, for the *benzoate hydrochloride*, originally of m. p. 175°, is separated by repeated recrystallisation into a product of m. p. 215° and a more soluble compound. It is a powerful anæsthetic. *2-ω-Tetrahydro*iso*quinolinomethyl*cyclo*hexanone* (*hydrochloride*, m. p. 161°), is obtained in a similar manner to its congener and on reduction yields *2-ω-tetrahydro*iso*quinolinomethyl*cyclo*hexanol*, b. p. 215—217°/14 mm. The *benzoate hydrochloride*, m. p. 205—206°, is a mixture of stereoisomerides with scarcely any anæsthetic potency. *2-ω-Dimethylaminomethyl-4-methyl*cyclo*hexanone*, b. p. 123—125°/30 mm. (*hydrochloride*, m. p. 145—146°), similarly yields *2-ω-dimethylamino-4-methyl*cyclo*hexanol*, b. p. 115—125°/20 mm., separable, as *hydrochloride*, into two isomerides, only one of which was obtained pure (m. p. 168—170°). The *benzoate hydrochloride* similarly gave a small sparingly soluble pure fraction, m. p. 212—214°, which was strongly anæsthetic. *2-ω-Piperidinomethyl-4-methyl*cyclo*hexanone*, b. p. 115°/15 mm., gives a *hydrochoride* which behaves like its lower homologue described above, *i.e.*, it melts at 155°, solidifies again at 162°, and melts again at 230°. *2-ω-Piperidinomethyl-4-methyl*cyclo*hexanol*, b. p. 147°/20 mm., is a mixture of isomerides. From menthone *dimethylaminomethylmenthone*, b. p. 120—135°/14 mm., is obtained. This can evidently be a mixture of structurally different isomerides and the *dimethylaminomethylmenthol*, b. p. 135—145°/18 mm., obtained by reduction must be a quite complex mixture. A *nitrate* is described, and the *benzoate hydrochloride* is eventually separated, by repeated recrystallisation, to give a pure sparingly soluble fraction of m. p. 239—241°, which is a powerful anæsthetic. W. A. SILVESTER.

Synthesis of unsaturated γ-ketonic amines and their reduction products. C. MANNICH and M. SCHÜTZ (Arch. Pharm., 1927, **265**, 684—695; cf. A., 1920, i, 851, and preceding abstract).—Styryl methyl ketone and its derivatives are now found to behave like other ketones in condensing with formaldehyde and secondary amines to give aminoketones. The yields are about 60% of the theoretical. The condensation takes place normally, *viz.*, at the terminal methyl group, and not in the aromatic nucleus (cf. Einhorn, A., 1906, i, 245). Piperidine hydrochloride, paraformaldehyde, and styryl methyl ketone yield ε-*piperidino*-α-*phenyl*-Δ^{α}-*penten*-γ-*one* (*hydrochloride*, m. p. 180·5°; *phenylhydrazone hydrochloride*, m. p. 188°, decomp.), which, like its analogues described below, is unstable in the free state, and, although solid when isolated, undergoes rapid change into a glue. Its constitution is proved by its giving benzoic acid when oxidised and also by its giving, on hydrogenation, a saturated ketone different from the branched chain isomeride described by Mannich and Curtaz (A., 1927, 231). This hydrogenation, in which palladised charcoal is used, yields in fact ε-*piperidino*-α-*phenylpentan*-γ-*one*, b. p. 170—180°/20 mm. The *hydrochloride*, m. p. 145°, the *oxime hydrochloride*, m. p. 159°, and the *phenylhydrazone hydrochloride*, m. p. 151°, are described. This ketonic amine is reduced by aluminium amalgam in moist ether to ε-*piperidino*-α-*phenylpentan*-γ-*ol*, b. p. 210—220°/25 mm. The *hydrochloride* has m. p. 108°. The *benzoate hydrochloride*, m. p. 174°, and the p-*nitrobenzoate hydrochloride*, m. p. 204°, are also described, and the first of these is a potent, persistent anæsthetic. The piperidinophenylpentenone is also converted by the action of bromine in chloroform solution into β-*bromo*-ε-*piperidino*-α-*phenyl*-Δ^{α}-*penten*-γ-*one*, of which the *hydrochloride* (m. p. 171°) and the *nitrate* (decomp. 102°) are described.

The following bases are prepared in a similar way to their analogues described above. ε-*Diethylamino*-α-*phenyl*-Δ^{α}-*penten*-γ-*one* (*hydrochloride*, m. p. 116·5°; *phenylhydrazone hydrochloride*, m. p. 168°), which gives first ε-*diethylamino*-α-*phenylpentan*-γ-*one* (*hydrochloride*, m. p. 72°; *phenylhydrazone hydrochloride*, m. p. 149°) and then ε-*diethylamino*-α-*phenylpentan*-γ-*ol*, b. p. 168—170°/15 mm., the *benzoate hydrochloride* (m. p. 128°) of which is a persistent anæsthetic. ε-*Piperidino*-α-3 : 4-*methylenedioxyphenyl*-Δ^{α}-*penten*-γ-*one* (*hydrochloride*, m. p. 185°; *phenylhydrazone hydrochloride*, m. p. 193°) is hydrogenated in glacial acetic acid by palladised charcoal to ε-*piperidino*-α-3 : 4-*methylenedioxyphenylpentan*-γ-*one* (*hydrochloride*, m. p. 155°; *oxime hydrochloride*, m. p. 169·5°), and this yields ε-*piperidino*-α-3 : 4-*methylenedioxyphenylpentan*-γ-*ol*, b. p. 235—240°/18 mm. (*hydrochloride*, m. p. 119°), of which the *benzoate hydrochloride* (m. p. 175—176°) is a weak anæsthetic with a bitter taste. ε-*Piperidino*-α-3 : 4-*dimethoxyphenyl*-Δ^{α}-*penten*-γ-*one* (*hydrochloride*, m. p. 188°; *phenylhydrazone hydrochloride*, m. p. 195°) gives ε-*piperidino*-α-3 : 4-*dimethoxyphenylpentan*-γ-*one* (*hydrochloride*, m. p. 133°) and then ε-*piperidino*-α-3 : 4-*dimethoxyphenylpentan*-γ-*ol*, m. p. 69°, b. p. 240—245°/18 mm., the *benzoate hydrochloride*, m. p. 188°, of which is also very weakly anæsthetic and bitter to the taste.

ε-*Diethylamino*-α-3 : 4-*methylenedioxyphenyl*-Δ^{α}-*penten*-γ-*one* (*hydrochloride*, m. p. 165°) gives likewise the corresponding saturated ketone which was reduced without purification to ε-*diethylamino*-α-3 : 4-*methylenedioxyphenylpentan*-γ-*ol*, b. p. 222—228°/18 mm., the *hydrochloride* (m. p. 125°) and *benzoate hydrochloride* (m. p. 98°) of which are described. ε-*Piperidino*-α-p-*anisyl*-Δ^{α}-*penten*-γ-*one* (*hydrochloride*, m. p. 186°) gives ε-*piperidino*-α-p-*anisylpentan*-γ-*one* (*hydrochloride*, m. p. 140°) and so ε-*piperidino*-α-p-*anisylpentan*-γ-*ol*, b. p. 270—275°/25 mm. (*hydrochloride*, m. p. 117°), of which the *benzoate hydrochloride*, m. p. 162°, is a weak anæsthetic. ε-*Diethylamino*-α-3 : 4-*dimethoxyphenyl*-Δ^{α}-*penten*-γ-*one hydrochloride*, m. p. 134°, was obtained in very poor yield, accompanied by a gummy by-product. W. A. SILVESTER.

Purification of pyridine and α-picoline [2-methylpyridine] by fractional distillation. A. L. WILKIE and B. D. SHAW (J.S.C.I., 1927, **46**, 469—471T).—Purification is effected by distilling the crude bases, after dehydration, through two fractionating columns of the Dufton type; the top portion of the first column and the whole of the second, being encased in hot-air jackets, may be maintained at any desired temperature. 500 C.c. of crude bases, after two distillations, yielded more than 270 c.c. of pure pyridine, b. p. 115·3°/760 mm., d_4^{25} 0·9778 (cf. Heap, Jones, and Speakman, B., 1922, 49A); the methiodide prepared without purification from this product had m. p. 116—117° (decomp.), whilst that from pyridine mixed with 5% of α-picoline softened at 100° and melted completely at 114°. α-Picoline, purified in the same manner, has b. p. 128—128·6°/760 mm., d_4^{25} 0·9401, methiodide, m. p. 226—228°. W. J. POWELL.

Quadrivalent vanadium. II. Co-ordination number of vanadium in complex vanadyl salts. E. PARISI (Gazzetta, 1927, **57**, 859—862; cf. A., 1927, 122).—The green compound, vanadyl benzoylacetonate (cf. Morgan and Moss, J.C.S., 1913, **103**, 87) gives, when washed with pyridine, a crystalline yellow compound, *pyridine vanadyl bisbenzoylacetonate*, $C_{25}H_{23}O_5NV$, m. p. 163°. Since the Werner co-ordination number of vanadium in the green compound is already six, it is suggested that the molecule of pyridine which is acquired "forms part of the external sphere": $[V(:O)(-O\cdot CMe:CH\cdot CPh:O---)_2]C_5H_5N$, the co-ordination number remaining unaltered; cf. copper acetylacetonate (Ley, A., 1915, i, 453). Similar *picoline* (m. p. 146°), *piperidine*, *quinoline* (greenish yellow, m. p. 184°), and *aniline* (greenish-grey, m. p. 212°) compounds are obtained. E. W. WIGNALL.

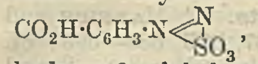
Nitro-2-acetamidopyridines. A. E. TSCHITSCHIBABIN and A. W. KIRSSANOV (Ber., 1928, **61**, [*B*], 206—207).—3-*Nitro-2-acetamidopyridine*, m. p. 135—136°, prepared by the action of boiling acetic anhydride on the base, is very readily hydrolysed by warm, dilute acids. Like 5-nitro-2-acetamidopyridine (Tschitschibabin and Pozdniakov, A., 1926, 845) it dissolves in dilute alkali hydroxide with formation of coloured, quinonoid salts. H. WREN.

Tautomerism in pyridine compounds. V. A. E. TSCHITSCHIBABIN (J. Russ. Phys. Chem. Soc., 1927, 59, 477—491).—See A., 1926, 1153.

Syntheses in the indole series. II. 5 : 6-Benz-4-carboline and its derivatives. W. O. KERMACK and R. H. SLATER (J.C.S., 1928, 32—45).—*o*-Nitrobenzyl chloride condenses with ethyl acetoacetate giving the compound $CO_2Et{\cdot}CAc(CH_2{\cdot}C_6H_4{\cdot}NO_2)_2$ (Ber., 1896, 29, 637) and a *substance*, m. p. 183° (decomp.), probably $NO_2{\cdot}C_6H_4{\cdot}CH_2{\cdot}CH(C_6H_4{\cdot}NO_2){\cdot}CHAc{\cdot}CO_2Et$. When dry hydrogen chloride is passed into an alcoholic solution of the phenylhydrazone, m. p. 153·5° (decomp.) (lit. 148—149°), of *o*-nitrophenylpyruvic acid, m. p. 130° (lit. 121°), both 3-o-*nitrophenylindole*-2-*carboxylic acid* (I), m. p. 276° (decomp.) [*potassium*, *calcium*, *barium*, *magnesium*, *lead*, and *zinc* salts; *brucine* salt, m. p. 230°, $[\alpha]_D^{18}$ −50·5° in chloroform], and 3-o-*nitrophenylindole* (II), m. p. 119°, may be isolated from the reaction product, the proportions depending on reaction conditions. The *ammonium* salt of (I) is decomposed at 270—280°, giving the compound (II). Reduction of (II) in alcoholic solution by iron filings and hydrochloric acid yields 3-o-*aminophenylindole*, m. p. 82° [*hydrochloride*, m. p. 288° (decomp.); *picrate*, m. p. 190°]. The formyl derivative of this base was not isolated but treated directly with phosphorus oxychloride in toluene solution, when 5 : 6-*benz*-4-*carboline* (III), m. p. 245°, was obtained. The compound (II) is reduced by zinc dust in acetic acid solution, giving a non-basic *substance*, m. p. about 265°. The compound (I) is reduced by zinc dust in acetic acid solution, giving 3-*keto*-3 : 4-*dihydro*-5 : 6-*benz*-4-*carboline*, m. p. above 316°, which is further reduced by zinc dust in a current of hydrogen to give the compound (III). 3-o-*Acetamidophenylindole*, m. p. about 158°, is converted by treatment with phosphorus oxychloride in toluene solution into 3-*methyl*-5 : 6-*benz*-4-*carboline*, m. p. 204—205° (*hydrochloride*; *picrate*; *chloroplatinate*). 3-o-*Propionamidophenylindole* is converted by a similar method into 3-*ethyl*-5 : 6-*benz*-4-*carboline*, m. p. 158° (decomp.). The phenylmethylhydrazone of *o*-nitrophenylpyruvic acid undergoes the Fischer indole reaction even in presence of dilute hydrochloric acid giving 3-o-*nitrophenyl*-1-*methylindole*-2-*carboxylic acid*, m. p. 234° (*calcium*, *barium*, *lead*, *zinc*, and *magnesium* salts), whence the following compounds were prepared: 3-*keto*-1-*methyl*-3 : 4-*dihydro*-5 : 6-*benz*-4-*carboline*, m. p. 302°; 3-o-*nitrophenyl*-1-*methylindole*, m. p. 98°; 3-o-*aminophenyl*-1-*methylindole*, m. p. 129° [*hydrochloride*, m. p. 246° (decomp.); *picrate*, m. p. 196°]; 3-o-*acetamido*-1-*methylindole*, m. p. 159°; 1 : 3-*dimethyl*-5 : 6-*benz*-4-*carboline*, m. p. 154°. An improved method of preparation for *o*-nitrophenylpyruvic acid is described.

M. CLARK.

Oxidation of quinoline-8-sulphonic acid. E. SUCHARDA (Kosmos, Bull. Soc. pol. Nat. Leopol, 1920—1921, 18 pp.; Chem. Zentr., 1927, i, 3005—3006).—Oxidation of quinoline-8-sulphonic acid with potassium permanganate yields potassium isatin-7-sulphonate and a *potassium* salt, (+H_2O), m. p. 248°, of an additive compound of quinoline-8-sulphonic acid and 2-amino-3-sulphobenzoic acid; the latter acid has m. p. 263°. Its solution in concentrated sulphuric acid yields with potassium nitrite the internal anhydride of 2-diazo-3-sulphobenzoic acid,



$$CO_2H{\cdot}C_6H_3{\cdot}N\lessdot\begin{matrix}N\\ |\\ SO_3\end{matrix}$$

, m. p. 150°, from which 2-hydroxy-3-sulphobenzoic acid (+2H_2O), m. p. 213° [barium (+H_2O) and sodium (+2·5H_2O) salts] is produced by treatment with hydrochloric acid. With formamide, 2-amino-3-sulphobenzoic acid yields 4-hydroxy-8-sulphoquinazolin. Isatin-7-sulphonic acid has m. p. 80° (+4H_2O), 197° (anhyd.).

A. A. ELDRIDGE.

2-Methylquinoline oxide and *s*-di-*o*-aminobenzhydrazide. G. HELLER, W. DIETRICH, and G. REICHARDT (J. pr. Chem., 1928, [ii], **118**, 138—148).—2-Methylquinoline-*N*-oxide, previously regarded as 4-keto-2-methyl-1 : 4-dihydroquinoline (cf. Heller and Sourlis, A., 1908, i, 913; Meisenheimer and Stotz, A., 1926, 77), yields with a mixture of phosphorus trichloride and phosphoryl chloride mainly a new *chloro*-2-*methylquinoline*, m. p. 39—40° (*picrate*, m. p. 158—159°; *hydrochloride*, decomp. 190—195°). The constitution of this oxide is further confirmed by the formation from 4-chloro-2-methylquinoline and perbenzoic acid of 4-*chloro*-2-*methylquinoline*-N-*oxide*, m. p. 135° (*picrate*, m. p. 145·5°; *hydrochloride*, m. p. 173—174°), for which a corresponding alternative formula is not possible. When phenazine-*N*-oxide is heated with phosphorus pentachloride and phosphoryl chloride at 160—165° it gives a mixture of chloro-derivatives from which fractions of m. p. 110°, 147°, and 237° were isolated, the last being apparently identical with the dichlorophenazine oxide of Bamberger and Ham (A., 1911, i, 684).

The compound previously regarded as 1 : 2-dinitroso-3-ketodihydroindazole (Heller and Köhler, A., 1923, i, 850) is shown by analysis and mol. wt. determination to be 3 : 3′-*bisbenzazimide*. It is hydrolysed by acetic and sulphuric acids to disalicylylhydrazide, and by alcoholic potassium hydroxide to a *substance*, m. p. 147°. The "3-hydroxyindazole" from which this is derived must, therefore, be *s*-*di*-o-*aminobenzhydrazide* [*hydrochloride*, m. p. 258° (decomp.), *diacetyl* derivative, m. p. 188°]. It is formed by reducing *s*-di-*o*-nitrobenzhydrazide with zinc dust and acetic acid. H. E. F. NOTTON.

Quinoline derivatives. H. JOHN [with F. KAHL]. **V. Synthesis of furfurylidene- and cinnamylidene-2-methylquinoline-4-carboxylic acids. VI. Synthesis of 2-styryl-3-alkylquinoline-4-carboxylic acids** (J. pr. Chem., 1928, [ii], **118**, 14—16, 17—19; cf. A., 1927, 1200)—V. Isatin is condensed with furfurylideneacetone [β-2-furylvinyl methyl ketone] to give 2-(β-2-*furylvinyl*)*quinoline*-4-*carboxylic acid*, m. p. 249° (19 *salts* described), and with cinnamylideneacetone (δ-phenylbutadienyl methyl ketone) to give 2-(δ-*phenylbutadienyl*)*quinoline*-4-*carboxylic acid*, m. p. 245—247° (*methyl* ester, m. p. 90—91°; *ethyl* ester, m. p. 70°; 20 *salts* described), reducible to the 2-δ-*phenylbutyl* compound, m. p. 142° (20 salts described). 6-*Bromo*-2-(δ-*phenylbutadienyl*)*quinoline*-4-*carboxylic acid*, m. p. 255—256° (20 *salts* described), is similarly obtained from 5-bromoisatin.

VI. 2-*Styryl*-3-*methylquinoline*-4-*carboxylic acid*, m. p. 274° (decomp.; *methyl* ester, m. p. 131°; 20 salts described), the 6-*bromo*-derivative, m. p. 248—250° (decomp.; 20 *salts* described), and 2-o-*hydroxystyryl*-3-*methylquinoline*-4-*carboxylic acid*, m. p. above 300° (20 *salts* described), are obtained from isatin or 5-bromoisatin and styryl ethyl ketone or *o*-hydroxystyryl ethyl ketone. C. Hollins.

Amides of α-phenylcinchoninic acid. S. Weil and A. Konówna (Rocz. Chem., 1927, 7, 467—469).—The following amides have been prepared by the action of α-phenylcinchoninyl chloride on various amines: with o-*phenetidine*, m. p. 138°, with *aminodimethylphenylpyrazolone*, m. p. 249°, with *piperazine*, m. p. 280°, and with *lysidine*, m. p. 160°.

R. Truszkowski.

Carbazine syntheses. IV. H. Goldstein and J. Vaymatchar (Helv. Chim. Acta, 1928, **11**, 245—249; cf. A., 1927, 1201).—Magnesium phenyl bromide and methyl 4 : 6 : 4′-triaminodiphenylamine-2-carboxylate react to give 1 : 3 : 7-triamino-5 : 5-diphenyldihydroacridine (not isolated), which is oxidised by ferric chloride into 1 : 7-diamino-5 : 5-diphenyldihydroacridine-3-imine (Kehrmann, Goldstein, and Tschudi, A., 1919, i, 552). Similarly methyl 4-amino-4′-hydroxydiphenylamine-2-carboxylate yields 7-amino-5 : 5-diphenyl-3-carbazone (Kehrmann and Brunner, A., 1926, 526). 7 : 9-*Diamino*-5 : 5-*diphenyl*-3-*carbazone*, violet, m. p. 227°, is obtained from methyl 4 : 6-diamino-4′-hydroxydiphenylamine-2-carboxylate. The diamino-compound described by Kehrmann and Tschui (A., 1925, i, 430) is probably 1 : 7-diamino-5 : 5-diphenyl-3-carbazone.

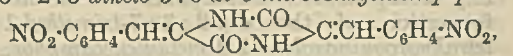
H. Burton.

Stereochemistry of carbonyldiamino-acids. C. Granachar and G. Wolf (Helv. Chim. Acta, 1928, **11**, 172—179).—When ethyl α-aminopropionate is treated with carbonyl chloride there are formed racemic- and meso-ethyl carbonyldi-α-aminopropionates, $CO(NH{\cdot}CHMe{\cdot}CO_2Et)_2$, having m. p. 153° (this vol. 74), and 85°, respectively. The meso-ester when treated with hydrochloric acid and ether yields α-5-*methylhydantoin*-3-*propionic acid*, m. p. 158—160°. Hydrolysis of the racemic- and meso-esters with alcoholic potassium hydroxide gives two *carbonyldi*-α-*aminopropionic acids*, m. p. 192—193° (decomp.) and 189—190°, which are probably identical, since treatment of both with diazoethane gives the racemic-ester. Resolution of the acid of m. p. 192—193° is effected through the *strychnine* salt, $[\alpha]_D$ −20·6° in water, from which l-*carbonyldi*-α-*aminopropionic acid*, m. p. 189—190°, $[\alpha]_D$ −21·0°, is obtained. H. Burton.

Condensation products of benzylideneacetophenone [phenyl styryl ketone] and some of its derivatives. L. C. Raiford and H. L. Davis (J. Amer. Chem. Soc., 1928, 50, 156—162).—Bromination of 4-acetamidoacetophenone in aqueous acetic acid affords 3-*bromo*-4-*acetamidoacetophenone*, m. p. 138—138·5°, from which 3-*bromo*-4-*aminoacetophenone hydrochloride*, m. p. 155—156°, and 3-*bromo*-4-*acetamidobenzoic acid*, m. p. 226—229°, were obtained by hydrolysis and oxidation respectively. Treatment of 4-acetamidoacetophenone with benzaldehyde in aqueous alcoholic sodium hydroxide yields 4-acetamidophenyl styryl ketone, m. p. 160—161° (cf. Giua and Bagiella, A., 1921, i, 730). 3-*Bromo*-4-*aminophenyl styryl ketone*, yellow, m. p. 146—147° (*diacetyl* derivative, m. p. 130—131°), and 3 : 5-*dibromo*-4-*aminophenyl styryl ketone*, m. p. 133—134° (*diacetyl* derivative, m. p. 173—174°), were prepared analogously. Treatment of phenyl styryl ketone with phenylhydrazine in glacial acetic acid affords the *phenylhydrazone*, m. p. 117—120°, which is converted into the corresponding pyrazoline, yellow, m. p. 135—136°, when boiled in glacial acetic acid (cf. Auwers and Voss, A., 1910, i, 70), the latter being also obtained if the phenylhydrazone is not separated from its reaction mixture immediately after its formation. The phenylhydrazone has a severe vesicant action on the skin. Treatment of 4-chlorophenyl styryl ketone with phenylhydrazine in cold glacial acetic acid yields directly 1 : 5-*diphenyl*-3-p-*chlorophenylpyrazoline*, orange, m. p. 129—130°. 1 : 5-*Diphenyl*-3-p-*acetamidophenylpyrazoline*, yellow, m. p. 241—242°, 1 : 5-*diphenyl*-3-(3′-*bromo*-4′-*aminophenyl*)-*pyrazoline*, m. p. 200·5°, 1 : 5-*diphenyl*-3-(3′ : 5′-*dibromo*-4′-*aminophenyl*)*pyrazoline*, orange, m. p. 180—181°, and 3-*phenyl*-5-p-*chlorophenyl*-1-p-*bromophenylpyrazoline*, m. p. 142—143°, are obtained analogously. Straus' conclusion that halogens have a stabilising effect on these hydrazones (cf. A., 1919, i, 41) is thus not confirmed. F. G. Willson.

Binary system "bromural"–"pyramidone." H. Sandqvist and W. Hök (Arch. Pharm., 1927, **265**, 705—707).—The m.-p. diagram for "bromural"–"pyramidone" mixtures has been constructed, using Rheinboldt's "thaw-melt" method (A., 1926, 25). No evidence of compound formation was obtained. The eutectic is at 75° (41% of "bromural"). W. A. Silvester.

Condensation of glycine anhydride with *o*-, *m*-, and *p*-nitrobenzaldehyde; formation of 3-aminohydrocarbostyryl and 2 : 5-diketo-3 : 6-di-o-nitrobenzylidenepiperazine. H. Ueda (Ber., 1928, **61**, [*B*], 146—151).—Glycine anhydride is converted by *o*-nitrobenzaldehyde in the presence of acetic anhydride and anhydrous sodium acetate at 115—125° into 2 : 5-*diketo*-3 : 6-*di*-o-*nitrobenzylidenepiperazine*,



$$NO_2{\cdot}C_6H_4{\cdot}CH{:}C{<}{\begin{matrix}NH{\cdot}CO\\CO{\cdot}NH\end{matrix}}{>}C{:}CH{\cdot}C_6H_4{\cdot}NO_2,$$

decomp. about 334—336°, which is reduced by red phosphorus and hydriodic acid (*d* 1·7) to 3-*amino*-2-*hydroxy*-3 : 4-*dihydroquinoline*, m. p. 149—150° [*hydriodide*, m. p. 291° (decomp.); *hydrochloride*, m. p. about 310° (decomp.); *picrate* (+$2H_2O$), m. p. 214° (decomp.); *benzoyl* derivative, m. p. 205°]. The base is converted by nitrous acid into 2-hydroxyquinoline. Similarly, glycine anhydride and *m*-nitrobenzaldehyde afford 2 : 5-*diketo*-3 : 6-*di*-m-*nitrobenzylidenepiperazine*, decomp. about 313°, converted by phosphorus and hydriodic acid into m-*aminophenylalanine*, decomp. 260° [*dihydriodide*; *copper* salt, m. p. 245° (decomp.); *compound*, $C_{23}H_{22}O_4N_4$, decomp. 204°, with phenylcarbimide]. Nitrous acid converts *m*-

aminophenylalanine into *dl-m*-hydroxyphenylalanine. Analogously, 2 : 5-*diketo*-3 : 6-*di*-p-*nitrobenzylidenepiperazine* is reduced to *dl-p*-aminophenylalanine [$+H_2O$, m. p. 256° (decomp.)], identical with the product of the nitration and subsequent reduction of phenylalanine; with phenylcarbimide it gives the *substance* $C_{23}H_{22}O_4N_4$, m. p. 236° (decomp.).

H. WREN.

Racemisation. VI. Action of alkali on peptides and on diketopiperazines. P. A. LEVENE and R. E. STEIGER (J. Biol. Chem., 1928, **76**, 299—318).—The previously observed (A., 1926, 852) racemisation of diketopiperazines in presence of alkali does not occur when the asymmetric carbon atom is tertiary (*e.g.*, in glycyl-*d-iso*valine anhydride) and must therefore be dependent on enolisation on this carbon atom. Such diketopiperazines show also greater resistance to hydrolysis. *Glycyl*-d-iso*valine* has $[\alpha]_D^{27}$ +1·7° in water; *glycyl*-d-iso*valine anhydride*, m. p. 269—270°, $[\alpha]_D^{27}$ +25° in aqueous pyridine. *Glycyl*-l-*phenylmethylaminoacetic acid* has $[\alpha]_D^{27}$ −82·8° in water; *glycyl*-d-*phenylmethylaminoacetic acid anhydride*, m. p. 297—298°, $[\alpha]_D^{28}$ +9·3 in aqueous pyridine. C. R. HARINGTON.

Stereochemistry of reduced quinoxalines. III. Resolution of externally compensated α- and β-2 : 3 : 7-trimethyl-1 : 2 : 3 : 4-tetrahydroquinoxalines. C. S. GIBSON, J. H. NUTLAND, and J. L. SIMONSEN (J.C.S., 1928, 108—116).—Reduction of 2 : 3 : 7-trimethylquinoxaline by the method described in A., 1927, 366, affords a mixture, separated by fractionation from light petroleum solution into dl-β-2 : 3 : 7-*trimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline*, m. p. 97—98° (*oxalate*, m. p. 138—140°; *diacetyl* derivative, m. p. 131°), and dl-α-2 : 3 : 7-*trimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline*, m. p. 71° (*diacetyl* derivative, m. p. 147°). The racemic *a*-compound yields a less soluble d-*base*-d-*tartrate* $+2H_2O$, $[\alpha]_{5461}^{20}$ +51·1°, whilst from the mother-liquors of this salt, the l-*base*-l-*tartrate* $+2H_2O$, $[\alpha]_{5461}^{20}$ −51·6°, is obtained. d-α-2 : 3 : 7-*Trimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline*, m. p. 61·5—62·5°, $[\alpha]_{5461}^{20}$ +117·5° (*di*-1 : 4-m-*nitrobenzoyl* derivative, $[\alpha]_{5461}^{20}$ −98·4°), and l-α-2 : 3 : 7-*trimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxaline*, m. p. 61·5—62·5°, $[\alpha]_{5461}^{20}$ −117·5° (*diacetyl* derivative, m. p. 164·5—165·5°, $[\alpha]_{5461}^{20}$ +164·3°, *hydrate*), are obtained from the tartrates. Resolution of the externally compensated β-compound is effected by the formation of the *d*-β-2 : 3 : 7-*trimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxalino*-1-d-*methylenecamphor*, m. p. 243—244°, $[\alpha]_{5461}^{20}$ +1312°, $[\alpha]_{5780}^{20}$ +1044°, and l-β-2 : 3 : 7-*trimethyl*-1 : 2 : 3 : 4-*tetrahydroquinoxalino*-1-l-*methylenecamphor*, m. p. 243—244°, $[\alpha]_{5461}^{20}$ −1307°, $[\alpha]_{5780}^{20}$ −1045°. Hydrolysis of these compounds with hydrochloric acid causes extensive racemisation of the bases, which were not obtained optically pure. Fractionation of the *oxalate*, m. p. 138—144° (decomp.), of the impure *d*-base and subsequent basification gave a dextrorotatory specimen of the *base*, m. p. 105—107°, $[\alpha]_{5461}^{20}$ +4·1°, whilst in a similar way, impure l-*base*, m. p. 105—108°, $[\alpha]_{5461}^{20}$ −3·6°, was obtained. The methylene camphor derivatives are not decomposed smoothly by titration in alcoholic solution with bromine. M. CLARK.

Contrast between iodine and bromine in glyoxaline substitution. H. PAULY and E. ARAUNER (J. pr. Chem., 1928, **118**, 33—52; cf. Pauly and Gundermann, A., 1909, i, 71; Pauly, A., 1910, i, 638).—The glyoxaline ring is peculiar in that bromination, like nitration and sulphonation, attacks the 4(5)-position, whilst iodination, like coupling with diazo-compounds, attacks the 2-position.

2-*Iodoglyoxaline*, m. p. 135—136° [*hydrogen oxalate*, m. p. 220°; *nitrate*, m. p. 136° (decomp.); *picrate*, m. p. 185°], prepared by reduction of di- or tri-iodoglyoxaline with boiling aqueous sodium sulphite, gives by bromination in alkali 4-*bromo*-2-*iodoglyoxaline*, m. p. 174°, and in chloroform with more bromine, 4 : 5-*dibromo*-2-*iodoglyoxaline*, m. p. 215·5°, isomeric with the 2 : 4-*dibromo*-5-*iodoglyoxaline*, m. p. 181° (*hydrochloride* and *nitrate* described), obtained by iodination of 2 : 4-dibromoglyoxaline. Pauly and Gundermann's "monoiodo-4-methylglyoxaline," m. p. 157° (*loc. cit.*), is an equimolecular mixture of the mono- and di-iodo-compounds. 2-Iodo-4-methylglyoxaline, m. p. 170—171° (*hydrogen oxalate*, m. p. 207°; *picrate*, m. p. 171°), is obtained pure by using half the theoretical amount of iodine, and 2 : 5-*di-iodo*-4-*methylglyoxaline*, m. p. 191—192° (*hydrochloride*, m. p. 220—222°), by using excess of iodine in dilute solution; the di-iodo-compound gives only the 2-iodo-compound on reduction with sodium sulphite. 5-*Bromo*-2-*iodo*-4-*methylglyoxaline*, m. p. 147—148° (*hydrochloride*, m. p. 211°), results from the bromination of 2-iodo-, or iodination of 5-bromo-4-methylglyoxaline. 4-*Iodo*-2-*methylglyoxaline*, m. p. 144—145°, cannot be obtained by direct iodination but is prepared from the di-iodo-derivative (Pauly, *loc. cit.*) and sodium sulphite. Pilocarpidine gives by iodination a mono*iodo*-compound, m. p. 161°, and a *di-iodo*-compound, m. p. 192°. C. HOLLINS.

Glyoxaline-4(5)-formaldehyde. W. HUBBALL and F. L. PYMAN (J.C.S., 1928, 21—32).—The following derivatives of glyoxaline-4(5)-formaldehyde (J.C.S., 1916, **109**, 186) have been prepared: *nitrate*, m. p. 165° (corr.); *hydrochloride*, m. p. 169—170° (corr.), hygroscopic; *anil*, m. p. 142—143° (corr.); *oxime*, m. p. 183—184° (corr.); *semicarbazone*, m. p. 223—224° (corr.) ($+H_2O$), and *sodium hydrogen sulphite compound*. The aldehyde fails to condense with acetone. With acetophenone it gives a poor yield of glyoxaline-4(5)-methylideneacetophenone isolated as picrate. With ethyl acetate, the *picrate* of *ethyl urocanate*, decomp. 250° (sintering from 230°), was isolated in a single instance. The aldehyde condenses readily with pyruvic acid and β-naphthylamine, giving 2-[*glyoxalinyl*-4(5)]-β-*naphthacinchoninic acid*, decomp. 300°, and with dimethylaniline, giving pp′-*tetramethyldiaminodiphenyl* [*glyoxalinyl*-4(5)]-*methane*, m. p. 190° (corr.), which, on oxidation, yields a dye closely resembling malachite-green. The aldehyde, like *o*- and *p*-hydroxybenzaldehydes and pyrrole-2-aldehyde, fails to undergo many of the reactions characteristic of benzaldehyde. This behaviour is attributed either to the presence of an acidic group (·OH or :NH) or to stability in the tautomeric hydroxymethylene form. The preparation of *N*-methyl derivatives, in which conformity to the benzaldehyde type might be expected, was therefore attempted. Methylation of glyoxaline-4(5)-formaldehyde gives a very poor yield of 1-*methylglyoxaline-5-formaldehyde* (I) [*picrate*, m. p. 170° (corr.); *nitrate*, m. p. 175° (corr., decomp.)] unaccompanied by the isomeric 1-methylglyoxaline-4-formaldehyde. Reduction of the compound (I), which shows a normal Cannizzaro reaction, gives 1 : 5-dimethylglyoxaline, whilst the products of oxidation and of reaction with potassium hydroxide solution are isolated respectively as the *picrate* of 1-*methylglyoxaline-5-carboxylic acid*, m. p. 198—199° (corr., decomp.), and 1-*methyl-5-hydroxymethylglyoxaline picrate*, m. p. 166° (corr.). Methylation of methyl glyoxaline-4(5)-carboxylate gives *methyl* 1-*methylglyoxaline-5-carboxylate*, m. p. 68—70° (corr.) [*picrate*, m. p. 171° (corr.)], together with a very small quantity of *methyl* 1-*methylglyoxaline-4-carboxylate*, m. p. 171—172° (corr.), and of the dimethylated quaternary base isolated as 4(5)-*carboxy*-1 : 3-*dimethylglyoxalinium picrate*, m. p. 220—221° (corr.). Oxidation of 4(5)-methyl-5(4)-hydroxymethylglyoxaline by nitric acid yields 4(5)-*methylglyoxaline*-5(4)-*formaldehyde* (II), m. p. 167° (corr.) [*picrate*, m. p. 180—181° (corr.)], with 4(5)-methylglyoxaline-5(4)-carboxylic acid as by-product. Methylation of (II) gives 1 : 4-*dimethylglyoxaline-5-formaldehyde* (III), m. p. 70° (corr.) ($+H_2O$) [*picrate*, m. p. 212—213° (corr.)], alternatively obtained by oxidation of 1 : 4-dimethyl-5-hydroxymethylglyoxaline. Oxidation of (III) gives 1 : 4-*dimethylglyoxaline-5-carboxylic acid*, m. p. 205—206° (corr., decomp.) [*picrate*, m. p. 186—187° (corr.) ($+H_2O$)], which is converted by decarboxylation into 1 : 4-dimethylglyoxaline. The carbonyl group thus behaves like the nitro-group in directing the formation predominantly of substances in which the carbonyl and methyl groups are in the 5 : 1-position (A., 1924, i, 1112). M. CLARK.

Formation of 2-methylbenziminazoles. M. A. PHILLIPS (J.C.S., 1928, 172—177).—Nitration of diacetyl-*o*-phenylenediamine yields 4-nitrodiacetyl-*o*-phenylenediamine (I), m. p. 255° (Ladenburg, Ber., 1884, **17**, 150, gives m. p. 227°), oriented by reduction and acetylation to 1 : 2 : 4-triacetamidobenzene (II) Reduction of the compound (I) and of 2-nitrodiacetyl-*m*-phenylenediamine with iron powder and acetic acid yields 4-*aminodiacetyl*-o-*phenylenediamine*, m. p. 205° (which reacts normally with nitrous acid), and 2-*aminodiacetyl*-m-*phenylenediamine*, m. p. 250°, respectively. Derivatives of mono- or di-acetyl-*o*-phenylenediamine are converted by boiling with 3*N*-hydrochloric acid into substituted 2-methylbenziminazoles. The monoacetyl derivative appears to be formed as an intermediate in the formation of the ring compound from the diacetyl derivative, since *o*-aminoacetanilide may be isolated as well as 2-methylbenziminazole when diacetyl-*o*-phenylenediamine is hydrolysed in this way. 2-Methylbenziminazole is formed when *o*-phenylenediamine is boiled with 3*N*-hydrochloric acid and acetic anhydride, whereas the diacetyl derivative only is produced in the absence of the mineral acid. Compound (I) yields 5-nitro-2-methylbenziminazole with boiling sodium hydroxide solution as well as with hydrochloric acid. Compound (II) on treatment with hydrochloric acid followed by addition of acetic anhydride gives 5-acetamido-2-methylbenziminazole (*hydrochloride*, m. p. 325°, dimorphous, described as the base by Gallinek (Ber., 1897, **30**, 1912), also formed by reduction and subsequent acetylation of 5-nitro-2-methylbenziminazole. When the compound (II) is treated with hydrochloric acid alone, it yields the dihydrochloride of 5-amino-2-methylbenziminazole. M. CLARK.

Determination of valency requirements of alkyl groups. K. VON AUWERS and H. DÜSTERDIEK (J. pr. Chem., 1928, **118**, 53—66; cf. von Auwers and Wegener, A., 1924, i, 534).—The scission of (mono)semicarbazones of 4-methyl-1-alkylcoumaranones by semicarbazide is a better criterion of the valency requirements of the 1-alkyl groups than the experiments previously described (*loc. cit.*). The order of decreasing "unsaturation" as now determined is Me, Et, Bu^{α}, Pr^{α} (cf. Me, Pr^{α}, Bu^{α}, Et, *loc. cit.*). The preparation of monosemicarbazones of the 1-methyl and 1-ethyl compounds presents no difficulty. 4-*Methyl*-1-*propylcoumaranone semicarbazone*, m. p. 179°, and the corresponding 1-*butyl* compound, m. p. 204°, on the other hand, are not easily obtained, fission of the ring occurring before formation of the monosemicarbazone. For the same reason, direct formation of the disemicarbazone is no indication of relative valency requirements of the alkyl substituents, but the conclusions previously reached as to the effect of position and number of substituent groups on the stability of the coumaranone ring are not invalidated.

The interaction of silver anthranilate with alkyl halides (Karrer, A., 1919, i, 339) might be expected to give alkyl esters or *N*-alkylated acids according to the degree of unsaturation of the alkyl group. Exactly similar results, however, are obtained with methyl, ethyl, propyl, and allyl iodides, the *N*-alkylated acid being the main product.

When indazole and an alkyl halide are heated together, the 2-derivative is formed almost exclusively; the silver salt method gives almost exclusively the 1-derivative. In presence of alkali, 1- and 2-isomerides are obtained, usually in about equal proportions; with *iso*propyl, allyl, and benzyl bromides, however, the 1-derivative predominates (A., 1921, i, 806; 1924, i, 992; 1925, i, 73). Extension of these observations to ethylene bromohydrin, γ-phenylallyl bromide and iodide, *n*-butyl bromide and iodide, *iso*amyl bromide, and *o*- and *p*-nitrobenzyl chlorides and iodides, confirms the dependence of the behaviour of indazole towards alkyl halides on the degree of unsaturation of the alkyl group. Alkylation in presence of alcoholic alkali at 80—100° gives 1- and 2-isomerides in the ratios: *n*-butyl, 1 : 1; *iso*amyl, 1 : 1; γ-phenylallyl, 3 : 1; *o*- or *p*-nitrobenzyl, 5 : 3. The following compounds are described: 2-butylindazole methiodide, m. p. 176—177°; 2-iso*amylindazole methiodide*, m. p. 155°; 2-methylindazole *iso*amyliodide, m. p. 125°; 2-β-*hydroxyethylindazole*, m. p. 102° (*methiodide*, m. p. 139°); 2-β-*iodoethylindazole*, m. p. 70° [reducible to 2-ethylindazole (picrate, m. p. 154°)]; 2-γ-*phenylallylindazole*, m. p. 103° (*picrate*, m. p. 167°); 1-γ-*phenylallylindazole*, m. p. 86—87° (*picrate*, m. p.

127·5—128·5°; *methiodide*, m. p. 172°); 1-o-*nitrobenzylindazole*, m. p. 80—82°; 1-p-*nitrobenzylindazole*, m. p. 122° (*picrate*, m. p. 133°). C. HOLLINS.

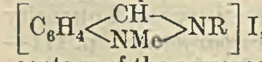
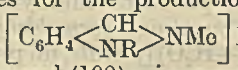
Indazole derivatives. K. VON AUWERS and H. KLEINER (J. pr. Chem., 1928, **118**, 67—90).—Some miscellaneous observations are recorded. 5-Nitroindazole, m. p. 207°, is obtained almost quantitatively from indazole and cold fuming nitric acid. Sulphonation is best performed with 5 parts of 20% oleum at 100° and gives a 46·5% yield of *indazole*-5(?)-*sulphonic acid*, m. p. 269—270° (*sulphonyl chloride*, m. p. 90—94°), which is converted by alkaline fusion into 5(?)-*hydroxyindazole*, m. p. 177—179° (*diacetate*, m. p. 91—91·5°). 5- and 7-Diazoindazoles could not be converted into the corresponding hydroxy-compounds.

By interaction with β-halogenoaliphatic esters indazole yields mainly 3-indazyl derivatives. *Ethyl* β-2-*indazylpropionate*, b. p. 206—207°, $d_4^{15\cdot2}$ 1·1453 (*picrate*, m. p. 126·5—127°; free acid, m. p. 148—149°), and β-1-*indazylpropionic acid*, m. p. 105·5—106·5°, are obtained from ethyl β-chloropropionate; β-2-indazylpropionic acid is also synthesised from 2-β-hydroxyethylindazole by way of the 2-β-*bromoethyl* (m. p. 60—60·5°) and 2-β-*cyanoethyl* derivatives. From indazole and ethyl α-bromobutyrate an ester, b. p. 170—180°/14 mm., is obtained, hydrolysable to α-2-*indazylbutyric acid*, m. p. 143—145°, which by decarboxylation yields 2-propylindazole (picrate, m. p. 151—152°). α-2-*Indazylphenylacetic acid*, m. p. 177° (decomp.), similarly gives 2-benzylindazole. By heating indazole with ethyl α-bromo-β-phenylpropionate at 200° there results 2-β-phenylethylindazole, m. p. 73° (*picrate*, m. p. 158—159°; *methiodide*, m. p. 171·5—172·5°), which is also obtained from indazole and β-phenylethyl bromide at 195°, or, with the 1-*isomeride*, m. p. 77—78° (*picrate*, m. p. 115—116°; *methiodide*, m. p. 184°), from the same components in presence of hot alcoholic alkali; from silver indazole and phenylethyl iodide the 1-isomeride only is obtained. 2-γ-*Phenylpropylindazole*, b. p. 227°/16 mm. (*picrate*, m. p. 121—122°; *methiodide*, m. p. 128—129°), and the 1-*isomeride*, m. p. 45—46° (*picrate*, m. p. 91—92°; *methiodide*, m. p. 141—143°), are formed in equal amounts from indazole, sodium ethoxide, and γ-phenylpropyl bromide; *p*-methylbenzyl bromide, b. p. 110°/15 mm., gives 2-p-*methylbenzylindazole*, m. p. 90—91° (*picrate*, m. p. 157—158°; *methiodide*, m. p. 165—166°), and a smaller quantity of the 1-*isomeride*, m. p. 43—44° (*picrate*, m. p. 127—129°; *methiodide*, m. p. 165°), the mixed oils distilling at 210—220°/15 mm. From 2-β-bromoethylindazole by the action of alcoholic alkali there is obtained 2-*vinylindazole*, b. p. 138°/15 mm., d_4^{20} 1·1065 (*picrate*, 128·5—129°; *methiodide*, m. p. 167°). Ethyl 1-indazylacetate yields a *methiodide*, m. p. 121—122°.

o-Toluoyl chloride reacts with indazole in well-cooled ether to give the 1-*derivative*, m. p. 91—92°, completely converted by heating for 2 hrs. into the 2-*isomeride*, m. p. 64—66°, also obtained directly at 110°; the former, but not the latter, is hydrolysed at once by hydrogen chloride in dry ether. 1-m-*Toluoylindazole*, m. p. 70—71°, 1-p-*toluoylindazole*, m. p. 92·5°, and 2-p-*toluoylindazole*, m. p. 87—88°, are described. 1(or 2)-*Indazylphenylthiocarbamide*, m. p. 102—103° (*methyl ether*, m. p. 59—60°; *acetyl* derivative, m. p. 117°) is obtained from indazole and phenylthiocarbimide. Indazole does not react with carbon disulphide.

From 6-nitroindazole, ethyl chloroacetate, and sodium ethoxide *ethyl* 6-*nitro*-1(or 2)-*indazylacetate*, m. p. 117—118° (free *acid*, m. p. 217—218°), is obtained. 6-Nitroindazole reacts with benzyl chloride at 130—180° to give 6-*nitro*-1(or 2)-*benzylindazole*, m. p. 124—125° (no methiodide), reducible to a diazotisable *amine*, m. p. 136—137°.

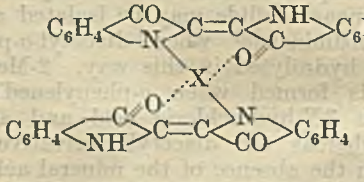
C. HOLLINS.

Tenacity of organic radicals towards nitrogen. K. VON AUWERS, H. DÜSTERDIEK, and H. KLEINER (Ber., 1928, **61**, [*B*], 100—103; cf. A., 1925, i, 1100).—The decomposition of indazolium salt,  $\left[C_6H_4{<}{}^{CH}_{NMe}{>}NR\right]I$, has been studied, the percentage of the corresponding 2-alkylindazole produced being placed in parentheses after the name of the radical *R*: methyl (8); β-phenylethyl (30); ethyl (34); γ-phenylpropyl (37); β-hydroxyethyl (43); *iso*propyl (52); *n*-butyl (54); *n*-propyl (55); *iso*amyl (57); vinyl (0); Δ^{β}-propenyl (0); benzyl (0); *p*-methylbenzyl (0); *o*-chlorobenzyl (0); *p*-chlorobenzyl (0). The similar series for the production of 1-alkylindazoles from salts,  $\left[C_6H_4{<}{}^{CH}_{NR}{>}NMe\right]I$, is as follows: ethyl (100); *n*-propyl (100); *iso*propyl (100); *iso*amyl (100); β-phenylethyl (100); γ-phenylpropyl (100); *p*-chlorobenzyl (93); methyl (92); Δ^{β}-propenyl (83); benzyl (77); *p*-methylbenzyl (75); *o*-chlorobenzyl (71); styryl (? 33). The relatively feeble union of methyl is remarkable; beyond propyl, increase in weight of the radical does not appear to be accompanied by increased tenacity. The relative tenacities of the benzyl, β-phenylethyl, and γ-phenylpropyl groups does not appear to be explicable by the accepted theories of valency demand of the component atoms. Contrary to previous observations (*loc. cit.*), 2-ethylindazole is not produced by decomposition of 1 : 2-diethylindazolium iodide.

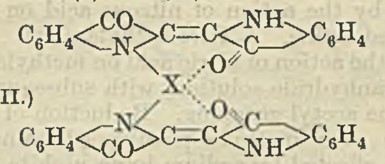
H. WREN.

Constitution of the metallic complexes of indigotin. R. KUHN and H. MACHEMER (Ber., 1928, **61**, [*B*], 118—127).—Indigotin, when treated with magnesium methyl iodide according to Zerewitinov, evolves 2 mols. of methane; hence the hydrogen atoms of both imino-groups are active. The copper and zinc compounds of indigotin, on the other hand, contain only two active hydrogen atoms for each atom of metal and therefore for two indigotin residues. Complex formation occurs therefore in such a manner that the bivalent metal replaces two active hydrogen atoms. These observations are incompatible with the constitution assigned to these compounds by Kunz and co-workers (A., 1923, i, 155,

(I.)



1134; 1925, i, 1318; 1927, 366) and leave only a choice between (I) and (II).



(II.)

These structures are in harmony with the observations that the zinc and copper compounds afford indigotin and the metal as ion without evolution of gas when acted on by warm 5% hydrochloric acid and that the sodium derivative gives sodium hydroxide, indigotin, and no gas when treated with water. Similarly the red silver salt of 2-methylindolyl-2′-methylindolidenemethane has the composition $C_{19}H_{15}N_2Ag$ instead of $C_{19}H_{16}N_2Ag$ ascribed by Kunz (*loc. cit.*), since it evolves one mol. of methane whereas the free base evolves two. The applicability of magnesium methyl iodide to the elucidation of structural problems with complex salts is established by experiments with diacetyldioxime and its nickel derivative, cupferron and its copper and iron salts.

The production of metallic compounds from indigotin and the acetates of heavy metals involves, according to Kunz, a complicated decomposition of the salt according, for example, to the equation $2Ac{\cdot}OCu = 2Cu + 3Ac{\cdot}OH + C + CO_2$. This change has not been observed at temperatures at which complex formation occurs and, further, the amount of acetic acid produced is equivalent to that of the dye taken and not to that of the excess of acetate employed. Thus ethyl indigotinmalonate readily affords the *copper* compound, $C_{42}H_{26}O_8N_4Cu$, and the corresponding *cobalt* and *silver* derivatives, in each of which the imino-hydrogen atom is replaced by metal. The production of the zinc and copper complexes from the metal and indigotin in solvents of high b. p. is confirmed but the change occurs only when a large excess of metal containing oxide or carbonate is used, when air is present or the solvent takes part in the change. Pyrophoric copper does not react with solutions of indigotin or ethyl indigotinmalonate in pyridine or xylene at 100°, 125°, 150°, or 175° if oxygen is completely excluded. H. Wren.

2 : 2′-Dipyridylamine and its nitro-derivatives. A. E. Tschitschibabin and W. A. Preobrashensky (Ber., 1928, 61, [*B*], 199—206; cf. Tschitschibabin and Zeide, A., 1915, i, 590; Steinhäuser and Diepolder, A., 1916, i, 740).—2 : 2′-Dipyridylamine is prepared in 45% yield by heating a mixture of equivalent amounts of 2-aminopyridine and its hydrochloride for 40—50 hrs. with exclusion of atmospheric moisture. It exists in two polymorphic forms, m. p. 95° and 84°, obtained by crystallisation from water and anhydrous ether, respectively. The latter form is usually obtained by sublimation of either variety and generally passes into the former when melted and allowed to solidify. Nitration of 2 : 2′-dipyridylamine in concentrated sulphuric acid usually affords a mixture of nitro-derivatives, but by suitably controlling the quantity of nitric acid and the temperature the following compounds may be made the main products of the change: (1) 5-*nitro*-2 : 2′-*dipyridylamine*, m. p. 196—197°, obtained by use of a 10% excess of nitric acid at 0° and synthesised from 2-aminopyridine and 2-chloro-5-nitropyridine at 67—80°; (2) 5 : 5′-*dinitro*-2 : 2′-*dipyridylamine*, by use of a 10% excess of nitric acid at 0° and from 2-chloro-5-nitro- and 5-nitro-2-aminopyridine; (3) 3 : 5 : 5′-*trinitro*-2 : 2′-*dipyridylamine*, m. p. 197°, from 5-nitro- or 5 : 5′-dinitro-2 : 2′-dipyridylamine and the calculated quantity of nitric acid in hot sulphuric acid solution; 3 : 5 : 3′ : 5′-*tetranitro*-2 : 2′-*dipyridylamine*, m. p. 140—141°, not obtained in any of the processes described above but prepared by prolonged nitration of 2 : 2′-dipyridylamine at 100° or from 3 : 5 : 5′-trinitro-2 : 2′-dipyridylamine. 3 : 3′-*Dinitro*-2 : 2′-*dipyridylamine*, m. p. 179—180°, is obtained from the mother-liquors of the preparation of trinitrodipyridylamine and from 2-chloro-3-nitropyridine and 3-nitro-2-aminopyridine. Introduction of a fifth nitro-group could not be effected. The ease with which the nitro-compounds, even if containing only a single nitro-group, dissolve in solutions of alkali hydroxide with the formation of deeply-coloured salts shows that the pyridine has a much greater tendency than the benzene nucleus to pass into the quinonoid form. The dinitrodipyridylamine of Wibaut and La Bastide (this vol., 75) appears to be a mixture of isomerides.

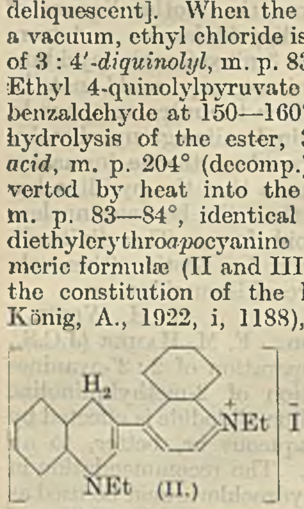
H. Wren.

ψ-Cyanine condensation. F. M. Hamer (J.C.S., 1928, 206—215).—The preparation of 2 : 2′-cyanines (ψ-cyanines) by condensation of 2-methylquinoline alkiodide with 2-iodoquinoline alkiodide is effected by addition of alkali to an aqueous or, better, to an absolute-alcoholic solution. The recommendation in the literature, that dilute hydrochloric acid be used as solvent with the object of increasing the stability of 2-iodoquinoline alkiodide, is based on a misapprehension, since this solvent decreases its stability. By use of 4-methylquinoline alkiodide, or 2-methylbenzthiazole alkiodide, instead of 2-methylquinoline, *iso*cyanines and thio-ψ-cyanines, respectively, are obtained. This method of preparation confirms the formulæ previously assigned to these compounds. By use of substituted indolenine quaternary salts containing a reactive 2-methyl group, dyes of a new type, the indo-ψ-cyanines, are prepared. The ψ-cyanines, like the other cyanines, act as photographic sensitisers. Their nomenclature is discussed. The following are described: 2-iodoquinoline ethiodide, m. p. 205° (decomp.) (lit. 220°); 1 : 6-dimethyl-2-quinolone, m. p. 82—84°, b. p. 205°/15 mm. (lit. m. p. 90°); 2-*iodo*-6-*methylquinoline methiodide*, m. p. about 225° (decomp.); 1 : 1′-dimethyl-ψ-cyanine iodide, m. p. 245—246° (decomp.); 1(1′)-*methyl*-1′(1)-*ethyl*-ψ-*cyanine iodide*, m. p. 261—262° (decomp.); 1 : 1′: 6- and 1 : 1′ : 6′-*trimethyl*-ψ-*cyanine iodides*, m. p. about 220° (decomp.) and 183° (decomp.); 1 : 6 : 1′ : 6′-*tetramethyl*-ψ-*cyanine iodide*, m. p. about 250° (decomp.); 1 : 1′-*diethyl*-ψ-*cyanine iodide*, m. p. 277° (decomp.); 6(6′)-*methyl*-1 : 1′-*diethyl*-ψ-*cyanine iodide*, m. p. 258° (decomp.); 1 : 1′-*diethyl*-5 : 6(5′ : 6′)-*benz*-ψ-*cyanine iodide*, m. p. 273° (decomp.); 1 : 1′-*dimethyl*-5 : 6-(5′ : 6′)-*benz*-ψ-*cyanine iodide*, m. p. about 266° (decomp.); 1′ : 2-*dimethylthio*-ψ-*cyanine iodide*, m. p. about 272—276° (decomp.); 1′-*methyl*-2-*ethylthio*-ψ-

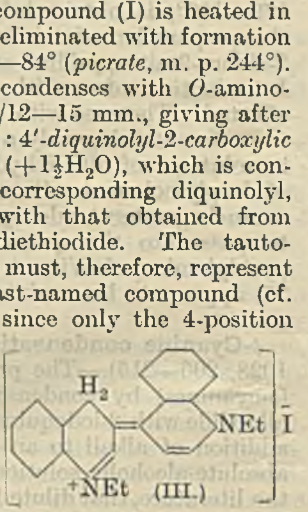
cyanine iodide, m. p. about 266° (decomp.); *2-methyl-1′-ethylthio-ψ-cyanine iodide*, m. p. about 261—264° (decomp.); *1 : 3 : 3 : 1′-tetramethylindo-ψ-cyanine iodide*, m. p. 247° (decomp.); *3 : 3-dimethyl-1 : 1′-diethylindo-ψ-cyanine iodide*, m. p. about 222° (decomp.). Photographic data are given.

M. Clark.

Cyanine dyes. X. Constitution of the *apo*-cyanines. W. H. Mills and H. G. Ordish (J.C.S., 1928, 81—86).—Oxidation of diethylerythro*apo*cyanine quaternary salts (G.P. 154,448) with iodine or potassium permanganate yields the corresponding salts of 3 : 4′-diquinolyl [diethiodide, m. p. 198°; dichromate, m. p. 211° (cf. Kaufmann and others, A., 1911, i, 721); *diethochloride* (I), m. p. 121°, deliquescent]. When the compound (I) is heated in a vacuum, ethyl chloride is eliminated with formation of *3 : 4′-diquinolyl*, m. p. 83—84° (*picrate*, m. p. 244°). Ethyl 4-quinolylpyruvate condenses with *O*-aminobenzaldehyde at 150—160°/12—15 mm., giving after hydrolysis of the ester, *3 : 4′-diquinolyl-2-carboxylic acid*, m. p. 204° (decomp.) (+1½H_2O), which is converted by heat into the corresponding diquinolyl, m. p. 83—84°, identical with that obtained from diethylerythro*apo*cyanine diethiodide. The tautomeric formulæ (II and III) must, therefore, represent the constitution of the last-named compound (cf. König, A., 1922, i, 1188), since only the 4-position for the last hydrogen atom will leave a conjugated chain of unsaturated linkings between the two nitrogen atoms. Ethyl 2-quinolylpyruvate condenses with *o*-aminobenzaldehyde yielding, after hydrolysis of the ester, *2′ : 3-diquinolyl-2-carboxylic acid*, m. p. 175° (decomp.), converted by heat into 2′ : 3-diquinolyl. The constitution of the last-named compound, advanced by Carlier and Einhorn (cf. A., 1891, 93) is thus confirmed.



(II.)



(III.)

M. Clark.

Triazole compounds. II. Methylation of 1-hydroxy-1 : 2 : 3-benztriazoles. O. L. Brady and C. V. Reynolds (J.C.S., 1928, 193—202).—1-Hydroxy-1 : 2 : 3-benztriazole (I) (*acetyl* derivative, m. p. 98°; *benzoyl* derivative, m. p. 77°) is prepared by boiling *sodium-*o*-nitrophenylhydrazine sulphonate* with potassium hydroxide or by the action of hydrazine on *o*-bromonitrobenzene. It yields 1 : 2 : 3-benztriazole when reduced with phosphorus and hydriodic acid, or when boiled with excess of hydrazine. Methylation of (I) with methyl sulphate and aqueous alkali, or with methyl iodide and sodium ethoxide, yields a mixture of *1-methoxy-1 : 2 : 3-benztriazole*, m. p. 89°, and *1-methyl-1 : 2 : 3-benztriazole-1-oxide* (II), m. p. 145°.

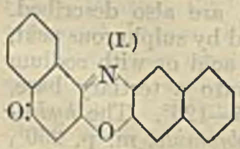
The proportion of *O*-methyl ether, the predominating product in either method of preparation, is greater in the second of these. Compound (II) is obtained alone by the action on (I) of methyl sulphate or methyl iodide followed by hydrolysis. Reduction of (II) with phosphorus and hydriodic acid gives 1-methyl-1 : 2 : 3-benztriazole, identical with that obtained by the action of nitrous acid on methyl-*o*-phenylenediamine. *o*-Nitromethylaniline was prepared by the action of nitric acid on methylacetanilide in acetic anhydride solution, with subsequent hydrolysis of the acetyl grouping. Reduction of the nitro-group to give methyl-*o*-phenylenediamine is conveniently effected by sodium hyposulphite. 1-Hydroxy-6-methyl-1 : 2 : 3-benztriazole (III) (*acetyl* derivative, m. p. 138°; *benzoyl* derivative, m. p. 129—130°), prepared by methods analogous to those described for (I), gives, on reduction, 6-methyl-1 : 2 : 3-benztriazole. Methylation of (III) with methyl sulphate and aqueous alkali or with methyl iodide and sodium ethoxide yields a mixture of *1-methoxy-6-methyl-1 : 2 : 3-benztriazole*, m. p. 50°, and *1 : 6-dimethyl-1 : 2 : 3-benztriazole-1-oxide* (IV), m. p. 169°, the proportion of *O*- to *N*-derivative being less in this case than in methylation of the compound (I). The variation in the *O*/*N* ratio is ascribed to the weaker acidity of (III), caused by introduction of the methyl group into the benzene nucleus and by the fact that *O*-methylation is ionic, whereas *N*-methylation is molecular in type (cf. A., 1926, 1142). By heating (III) with methyl sulphate, only (IV) is obtained. Compound (IV) yields on reduction *1 : 6-dimethyl-1 : 2 : 3-benztriazole*, m. p. 75°. To confirm the supposition that methylation of (I) and (III) causes the formation of the 1-*N*-methyl derivative, 1 : 6-dimethyl-1 : 2 : 3-benztriazole was synthesised from 4-nitro-*m*-tolylmethyl ether (for which an improved method of preparation is described). The ether, when heated with methylamine, yields 4-nitro-3-methylaminotoluene, which gives 4-amino-3-methylaminotoluene on reduction with sodium hyposulphite. Reaction of the diamine with nitrous acid gives 1 : 6-dimethylbenztriazole, identical with that formed by reduction of (IV). To eliminate the possibility of tautomerism, *3 : 6-dimethyl-1 : 2 : 3-benztriazole*, m. p. 50°, was prepared from 3-nitro-4-methylaminotoluene by reduction and diazotisation. It is distinct from 1 : 6-dimethyl-1 : 2 : 3-benztriazole.

M. Clark.

Sulphoxytriazines [ketothiontetrahydro-1 : 2 : 4-triazines]. J. Bougault and L. Daniel (Compt. rend., 1928, 186, 151—152).—Thiosemicarbazones of α-ketonic acids readily undergo cyclisation with loss of water under treatment with alkalis forming ketothiontriazines analogous to the diketotriazines similarly obtained (cf. Bougault, A., 1915, i, 598), the yields being almost theoretical. *6-Phenyl-*, m. p. 256°, *6-benzyl-*, m. p. 194°, and *6-β-phenylethyl-5-keto-3-thion-2 : 3 : 4 : 5-tetrahydro-1 : 2 : 4-triazine*, m. p. 210°, have been thus prepared. Ketothiontriazines have a stronger acid reaction than diketotriazines, and, like these, give mono- and di-esters (only the latter have been obtained in a pure condition). Whilst diketotriazines, treated with sodium hypobromite, yield a dibromo-derivative of the amide of the parent α-ketonic acid, with evolution of nitrogen, ketothiontriazines give a different (unidentified) product, without evolution of gas; but they are decomposed with effervescence by alkali hypochlorites, the benzylketothiontriazine yielding phenylacetic acid, and the β-phenylethyl compound β-phenylpropionic acid. B. W. ANDERSON.

***iso*Oxazoline oxides.** E. P. KOHLER (J. Amer. Chem. Soc., 1928, **50**, 221—228; cf. A., 1927, 262).—Treatment of the lower-melting isomeride of α-bromo-γ-nitro-β-phenylpropiophenone with a methyl-alcoholic suspension of sodium carbonate affords three isomeric 1-*nitro*-2-*benzoyl*-3-*phenyl*cyclo*propanes*, m. p. 95° (cf. Kohler and Engelbrecht, A., 1919, i, 582), 88°, and 142°, respectively. The higher-melting isomeride of the first-named substance yields similarly, in addition to the *cyclo*propane derivatives, *α-hydroxy-γ-methoxy-γ-oximino-β-phenylpropiophenone* (+1Me_2CO), m. p. (solvent-free) about 190° (decomp.) [*acetate*, m. p. 185° (decomp.)] (I), from which the corresponding *hydroxamic acid*, m. p. 160° (decomp.), is obtained by treatment with cold aqueous alkali. The latter is isomerised in solution to β-hydroxy-γ-oximino-αγ-diphenyl-*n*-butyric acid (*loc. cit.*), whilst potassium acetate and acetic acid in methyl alcohol convert (I) into the corresponding methyl ester, the mechanism of the formation of this ester from the bromonitroketone, previously reported, being thus explained. When either of the above oximino-derivatives is heated with methyl alcoholic hydrochloric acid, trans-β-*benzoyl*-α-*phenylacrylic acid*, m. p. 202°, is obtained. This was synthesised as follows: bromination of β-benzoyl-α-phenylpropionic acid yields two isomeric β-*bromo*-derivatives, m. p. (decomp.) 195° and 208°, respectively, the former containing ether of crystallisation, and yielding, on treatment with aqueous sodium carbonate, the above benzoylphenylacrylic acid, together with an indifferent *compound*. F. G. WILLSON.

Azoxines. IV. H. GOLDSTEIN and A. WARNÉRY (Helv. Chim. Acta, 1928, **11**, 250—253; cf. A., 1926, 1159; 1927, 63).—Condensation of 3-amino-β-naphthol with 2-hydroxy-1 : 4-naphthaquinone yields the *dinaphthazoxone* (I), m. p. 276—277°, together with 2-(3-*hydroxy*-β-*naphthyl*)-*amino*-1:4-*naphthaquinone*, m. p. 205°. With the same amino-naphthol and 2-hydroxy-1 : 4-naphthaquinone-4-imine, there is formed a *dinaphthoxazime* (I; O:=NH:), chars at 238—240° (*acetyl* derivative, m. p. 238°; N-*phenyl* derivative, m. p. 257°, obtained from 2-hydroxy-1 : 4-naphthaquinone-4-anil).



H. BURTON.

2-(Aminophenyl)benzthiazoles. H. HAUSER (Helv. Chim. Acta, 1928, **11**, 198—209).—Reduction of 4 : 4′-dichloro-2 : 2′-dinitrodiphenyl disulphide with aqueous sodium sulphide yields 4-chloro-*o*-aminothiophenol. Treatment of this with *p*-nitrobenzoyl chloride and subsequent reduction of the nitrothiazole produced with iron and hydrochloric acid gives 5-*chloro*-2-p-*aminophenylbenzthiazole*, m. p. 183—184° (all m. p. are corr.). Similarly, there have been prepared 5-*chloro*-2-m-*aminophenyl*-, m. p. 158—159°; 5-*chloro*-2-o-*aminophenyl*-, m. p. 161—162°; 5-*bromo*-2-p-*aminophenyl*-, m. p. 188—189°; 6-*chloro*-2-p-*aminophenyl*-4-*methyl*-, m. p. 150—151°; 6-*chloro*-2-p-*aminophenyl*-4-*methoxy*-, m. p. 220—221°; 6-*ethoxy*-2-p-*aminophenyl*-, m. p. 199·5—200·5°; 4 : 6-*di-chloro*-2-p-*aminophenyl*-, m. p. 198°; 4 : 6 : 7-*tri-chloro*-2-p-*aminophenyl*-, m. p. 224—225°; 5-*chloro*-2-(2′-*chloro*-5′-*aminophenyl*)-, m. p. 176—177°, and 5-*chloro*-2-(4′-*chloro*-3′-*aminophenyl*)-*benzthiazoles*, m. p. 164·5—165·5°.

With Epsilon acid as the secondary component *dyes* have been prepared from the above bases and 2-*p*-aminophenylbenzthiazole. The positions of the absorption bands for aqueous solutions of the dyes are given. Introduction of chlorine into the aminophenylbenzthiazole molecule has no effect on the depth of shade of the dye as is the case with methyl-substituted compounds (Bogert and Allen, A., 1927, 679). H. BURTON.

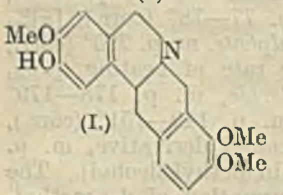
Nor-*d*-ψ-ephedrine, an alkaloid from *Ephedra* species. S. SMITH (J.C.S., 1928, 51—53; cf. A., 1927, 1094).—The Chinese drug Ma Huang contains, in addition to *d*-ψ- and *l*-ephedrines and *l*-methylephedrine, a fourth alkaloid, *nor*-d-ψ-*ephedrine*, $OH\cdot CHPh\cdot CHMe\cdot NH_2$, m. p. 77—78° (corr.), $[\alpha]^{20}_{5461}$ +32·2° in methyl alcohol [*sulphate*, m. p. 295° (corr., decomp.), dependent on the rate of heating, $[\alpha]^{20}_{5461}$ +42·9° in water; *hydrochloride*, m. p. 178—179° (corr.); *hydrogen tartrate*, m. p. 149—151° (corr.), $[\alpha]^{20}_{5461}$ +43° in water; *dibenzoyl* derivative, m. p. 156—157° (corr.), $[\alpha]^{20}_{5461}$ +28° in methyl alcohol]. The constitution follows from formation of *d*-ψ-methylephedrine methiodide on treatment with methyl iodide. N-*Benzoylnor*-d-ψ-*ephedrine*, m. p. 132° (corr.), $[\alpha]^{20}_{5461}$ +58·3° in methyl alcohol, obtained by partial hydrolysis of the dibenzoyl derivative, yields, when warmed with dilute hydrochloric acid and alcohol, or kept for some time in acetone solution with hydrogen chloride, O-*benzoylnor*-d-ψ-*ephedrine hydrochloride*, m. p. 244—245° (corr., decomp.), $[\alpha]^{20}_{5461}$ −32·5° in water, from which the original *N*-benzoyl derivative is regenerated on treatment with alkali.

M. CLARK.

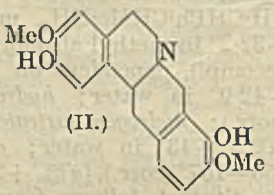
Preparation of coniine and conhydrine. F. CHEMNITIUS (J. pr. Chem., 1928, **118**, 25—28).—The finely-ground hemlock seeds (0·4—0·5% total alkaloids), mixed with wood-wool, are moistened with 15% aqueous sodium hydroxide and extracted four times with warm ether in a copper vessel. The concentrated extract is acidified with 50% acetic acid and the solvent is distilled off. After cooling the residues, solidified fat is removed from the surface and rejected after extraction of traces of alkaloids with 10% acetic acid. The total acetic acid solutions are shaken with ether to remove colouring matter, excess of 35% sodium hydroxide solution is added, and the alkaloids extracted with ether are fractionally distilled, using a wide condenser tube. The fraction up to 165° is converted into coniine salts, at 166—174° "coniine purum" of commerce distils, and the distillate above 174° is refractionated for coniine purum and conhydrine. Coniine hydrochloride, m. p. 220°, and hydrobromide, m. p. 211°, are obtained by the action of alcoholic acid on the base in alcohol, precipitation with ether, and recrystallisation from alcohol–ether. C. HOLLINS.

Preparation of pilocarpine. F. CHEMNITIUS (J. pr. Chem., 1928, **118**, 20—24).—Crude pilocarpine, extracted from *Pilocarpus pinnatifolius* (which should give by analysis at least 0·4% total alkaloids), is purified by crystallisation of the nitrate, m. p. 175°, from 90% alcohol. The pure base, m. p. 34°, gives a hydrochloride, m. p. 200°, neutral sulphate, salicylate, and valerate. C. HOLLINS.

Two new alkaloids from *Corydalis cava*. J. GADAMER, E. SPÄTH, and E. MOSETTIG (Arch. Pharm., 1927, **265**, 675—684).—Knörck (Dissertation, Marburg, 1926) isolated two new alkaloids from *Corydalis cava*. The first of these (0·01 g. was available for examination) has m. p. 240—241° (new determination, in evacuated tube, as are all the other m. p.'s recorded below); it also contains three methoxyl groups, and resembles, but is not identical with, corybulbine or corypalmine. These properties suggest that the compound in question is the hitherto unknown iso*corypalmine* (d-*tetrahydrocolumbamine* or 2-*hydroxy*-3 : 9 : 10-*trimethoxytetrahydroprotoberberine*) of formula (I).



(I.)



(II.)

The base (cf. Späth and Mosettig, A., 1927, 368) obtained from *d*-canadine (cf. Gadamer and Voss, A., 1910, i, 415) was methylated by treatment with diazomethane, and by working more carefully than previously (Späth and Mosettig, *loc. cit.*) a higher proportion of trimethoxy-compound was obtained. The *d*-tetrahydrocolumbamine eventually isolated had m. p. 239—241° and was identical with Knörck's product. The identity was confirmed by preparing l-*tetrahydrocolumbamine*, m. p. 241—242°, in a similar way from the *lævo*-isomeride of the dihydroxy-compound. In this preparation, *l*-corypalmine, m. p. 235—237°, was isolated as the second product. An equimolecular mixture of *d*- and *l*-tetrahydrocolumbamine reproduced the *racemic* compound, m. p. 221—222°, of natural origin.

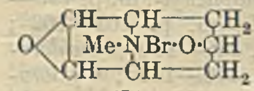
Knörck's second base had m. p. 192—193° and actually contained only two methoxyl groups, not three as originally supposed. It was smoothly and completely methylated with diazomethane to give *d*-tetrahydropalmatine. The compound was ethylated with diazoethane and the product oxidised without isolation. Mild oxidation gave 6-methoxy-7-ethoxy-1-keto-1 : 2 : 3 : 4-tetrahydro*iso*quinoline, together with (from the liquors after further oxidation) 5-methoxy-4-ethoxyphthalic acid (isolated as its ethyl imide). More drastic oxidation gave two acids, which were isolated, and separated as their ethyl imides, viz., 5-methoxy-4-ethoxy- and 4-methoxy-3-ethoxy-phthalic acids. Knörck's second base is therefore 2 : 9-dihydroxy-3 : 10-dimethoxy-tetrahydroprotoberberine (II). Efforts to synthesise this compound have as yet been unsuccessful.

W. A. SILVESTER.

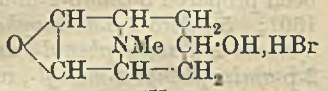
ψ-Scopine and scopoline. M. POLONOVSKI and M. POLONOVSKI (Compt. rend., 1928, **186**, 147—149).—ψ-Scopine is oxidised by chromic acid giving methylamine, *m*-hydroxybenzaldehyde, and an amorphous phenolic *substance*. As the former two compounds are degradation products of scopinium bromide (cf. Polonovski, A., 1927, 888), ψ-scopine is probably first oxidised to a scopinone salt, which at once alters to the tautomeric scopinium form, which then breaks down into the products mentioned. Scopoline does not form these oxidation products; moreover, it is not affected by the action of sulphuric and acetic acids at 160°, whereas ψ-scopine thus treated undergoes partial conversion into scopoline, and in addition yields an amorphous *substance*, analogous to that mentioned above. The following compounds are described: *benzoyl-ψ-scopine*, m. p. 142° (*hydrochloride*, m. p. 216°; *picrate*, m. p. 104°; *chloroaurate*, m. p. 220°); *acetyltropyl-ψ-scopine*; *tropyl-ψ-scopine* (amorphous *picrate* and *chloroaurate*); Nor-*ψ-scopine*, m. p. 184° (*hydrochloride*, m. p. 262°; *picrate*, m. p. 225°; *chloroaurate*, m. p. 220°); and *ψ-scopylphenylurethane*; m. p. 229°, neutral to litmus (*hydrochloride*, m. p. 244°; *chloroaurate*, m. p. 210°). The corresponding isomeric *scopolinylphenylurethane* is alkaline to litmus, and has a *hydrochloride*, m. p. 226°.

B. W. ANDERSON.

Amino-oxides of alkaloids. IV. Transformation of a derivative of the *N*-oxide of scopolamine into a quaternary scopinium derivative. M. POLONOVSKI and M. POLONOVSKI (Bull. Soc. chim., 1928. [iv], **43**, 79—97).—The formation of the amine-oxide, O:N:R·O·CO·R′, is the main result of the action of hydrogen peroxide on alkaloids of the tropan group (cf. A., 1925, i, 828; 1926, 1160), but hydrolysis with formation of the linkings N:R·OH, and, secondarily, O:N:R·OH, may also occur. Thus the mother-liquors after the separation of the hydrobromide of scopolamine *N*-oxide afford a quaternary *bromide*, m. p. 209—210°, in which the basic nitrogen atom is linked with three carbon atoms and an ether oxygen atom, :NBr·O·. For the new base which could not be isolated on account of its instability, the name *scopinium* is proposed; the *nitrate*, m. p. 213°, and *chloride*, m. p. 187°, are also described. Scopinium bromide is not reduced by sulphurous acid, but with zinc and hydrochloric acid or with sodium amalgam is converted (+2H) into a tertiary base, *ψ-scopine*, $C_8H_{13}O_2N$, m. p. 125—126°. The *hydrochloride*, m. p. 257—258°, *hydrobromide*, m. p. 250°, *picrate*, m. p. 234°, *chloroaurate*, m. p. 239—240°, *chloroplatinate*, m. p. 223°, d-*hydrogen tartrate*, m. p. 181°, $[\alpha]_D$ +13·5°, *methiodide*, m. p. 249° (decomp.), and N-*oxide*, m. p. 213° (decomp.) (*hydrobromide*, m. p. 192°, *hydrochloride*, m. p. 185°, and *picrate*, m. p. 210°), are described. The *acetyl* derivative, a basic oil gives a *picrate*, m. p. 187°, and *chloroaurate*, m. p. 203°. The above properties of ψ-scopine, its stability in acid and alkali media (the base is recovered unchanged after boiling for 6 hrs. with sodium in amyl alcohol), and its optical inactivity agree with a scopic rather than a scopoline formula, the reduction of scopinium bromide (I) to ψ-scopine (II) being represented:



(I.)



(II.)

Further support for the scopic structure for scopinium bromide is afforded by its degradation with silver oxide or sodium hydroxide or sodium carbonate into methylamine and *m*-hydroxybenzaldehyde, neither *o*- nor *p*-hydroxybenzaldehyde being formed, whereas a scopolinium structure should afford *p*-hydroxybenzaldehyde. *ψ*-Scopine is thus regarded as a diastereoisomeride of scopine, and its formation from scopolamine *N*-oxide is analogous to the transformation of tropine into *ψ*-tropine through tropinone. Scopoline chloroaurate has m. p. 235·7°, its *N*-oxide (anhydrous), m. p. 244° (hydrochloride, m. p. 191°, hydrochloride, m. p. 192°, picrate, 204—205°). R. BRIGHTMAN.

Preparation of colchicine. F. CHEMNITIUS (J. pr. Chem., 1928, **118**, 29—32).—Details are given for the extraction of colchicine and colchiceine from the seeds or other parts of meadow saffron. C. HOLLINS.

Occurrence of harmine in a South American liane (yagé). F. ELGER (Helv. Chim. Acta, 1928, **11**, 162—166).—Harmine, m. p. 263—264° (lit. 257—259°), is extracted from the bark (1·7%) and the wood (0·8%) of the yagé. Telepathine (Hamet, Compt. rend., 1927, **184**, 1266) and yageine are identical with harmine. H. BURTON.

Determination of morphine in opium. R. EDER (Festschr. A. Tschirch, 1926, 392—409; Chem. Zentr., 1927, i, 3213).—The opium (1 part) is extracted by Helfenberger's method with water (8—10 parts), and the total alkaloids (except narceine) in the extract are precipitated with so much alkali (*e.g.* 0·2617 g. of sodium carbonate) as leaves the least possible amount of morphine in solution. If much calcium is present, ammonia solution is employed. The other alkaloids are separated from morphine by shaking the alkaline liquid with benzene. The results are identical with those obtained by Helfenberger's method. A. A. ELDRIDGE.

Vanillin and piperonal as reagents for alkaloids. L. VAN ITALLIE and A. J. STEENHAUER (Arch. Pharm., 1927, **265**, 696—698).—Vanillin and piperonal behave like other aldehydes in giving sensitive colour reactions with certain alkaloids, viz., *apo*morphine, aspidospermine, cevadine, codeine, and morphine. Reddish-violet or blue colours are produced when a small quantity of the alkaloid in warm alcohol is treated, *e.g.*, with the aldehyde and dilute sulphuric acid. W. A. SILVESTER.

Analogous organic compounds of phosphorus and arsenic. C. S. GIBSON and J. D. A. JOHNSON (J.C.S., 1928, 92—99).—Phenylmethylphosphinic acid readily forms the *acid chloride*, b. p. 155°/11 mm., 167°/22 mm., *methyl* ester, b. p. 137°/11 mm., *ethyl* ester, b. p. 143°/11 mm. (the parachor corresponds with the existence of a semipolar double linking), and *anilide*, m. p. 142°. Phenylmethylphosphinyl chloride reacts with benzoic acid giving benzoyl chloride. With *o*-ethylaminobenzoic acid, it gave in one instance a *compound*, m. p. 186°, containing nitrogen and phosphorus, and, in another instance, an unstable *compound*, m. p. 168°, reverting to the acid. The arsinic acid grouping in phenylmethylarsinic acid (for which a new method of preparation is described) behaves differently. The ethyl ester is not obtained by treatment of the silver salt with ethyl iodide. With thionyl chloride, the acid yields phenyldichloroarsine and probably methyl chloride. Phenylmethylchloroarsine also reacts with thionyl chloride giving phenyldichloroarsine. Diphenylchloroarsine and diphenylarsinic acid give definite crystalline additive *compounds*, $Ph_2AsCl,SOCl_2$ and $Ph_2AsO\cdot OH,SOCl_2$, respectively. These are decomposed, when heated under reduced pressure, with formation of phenyldichloroarsine and chlorobenzene in either case. The mechanism of the action of thionyl chloride on secondary arsinic acids is discussed. M. CLARK.

Guaiacol cacodylate. A. ANGELETTI (Giorn. Farm. Chim., 1927, **76**, 165—172; Chem. Zentr., 1927, ii, 1346).—Besides the compound, $AsMe_2O\cdot OH,OH\cdot C_6H_4\cdot OMe$, which is completely decomposed in aqueous solution, there is a eutectic, m. p. 18°, containing 87·3% of guaiacol. A. A. ELDRIDGE.

Constitution of the supposed *N*-methylenesulphurous acid derivatives of amines. I. Oxidation by an alkaline solution of iodine. G. NEWBERY and M. A. PHILLIPS (J.C.S., 1928, 116—126).—Reduction of a mixture of sodium 4-aminophenylarsinate and sodium phenylarsinate with sodium hyposulphite affords 4-*aminoarsenobenzene* (*hydrochloride*), whilst similar treatment of the former salt gives 4 : 4′-diaminoarsenobenzene. The solubility of this base in hydrochloric acid differs from that prepared by Kashima (A., 1925, i, 1195) using hypophosphorous acid reduction. Nitration of ethenyl-*o*-aminophenol in sulphuric acid at 10—20° yields crude 5-*nitroethenyl*-o-*aminophenol*, m. p. 150—151°, which is hydrolysed by boiling hydrochloric acid giving 5-nitro-*o*-aminophenol together with a small amount of the 4-nitro-isomeride, and is reduced by iron powder and aqueous acetic acid, forming 5-*aminoethenyl*-o-*aminophenol*, m. p. 147°. Details are given for the preparation of 3-amino-4-hydroxyarsenobenzene, 4-amino-2-hydroxyphenylarsinic acid (cf. Hewitt and King, A., 1926, 746), 5-amino-2-hydroxyphenylarsinic acid, 4-amino-3-hydroxyphenylarsinic acid, and 4 : 4′-diamino-3 : 3′-dihydroxyarsenobenzene. Sodium 3 : 3′-diamino-4 : 4′-dihydroxyarsenobenzene-*NN*′-dimethylenesulphite prepared by the action of excess of formaldehyde and sodium hydrogen sulphite on 3 : 3′-diamino-4 : 4′-dihydroxyarsenobenzene (cf. Christiansen, A., 1923, i, 1148; Voegtlin and Johnson, *ibid.*, 70) and its *isomeride* obtained from the diamino-compound and excess of sodium formaldehyde hydrogen sulphite, yield acids having different physical and pharmacological properties. *Sodium* 3 : 3′-*diamino*-4 : 4′-*dihydroxyarsenobenzene*-N-*monomethylenesulphite* and *sodium* 4 : 4′-*diaminoarsenobenzenedimethylenesulphite* are described.

Treatment of an aqueous solution of the hydrochlorides of 19 bases (including the above) with aqueous formaldehyde (2 mols. for each amino-group) and sodium hydrogen sulphite, with subsequent determination of nitrogen, arsenic, total sulphur, and oxidisable sulphur by alkaline iodine (cf. Elvove, B., 1926, 27), shows that in the compounds containing the *o*-aminophenol grouping the combined sulphur is not oxidised. It is suggested that in this class of compounds the grouping $NH\cdot CH_2\cdot SO_3Na$ is present, whilst in the oxidised compounds the grouping $NH\cdot CH_2\cdot O\cdot SO_2Na$ exists. H. Burton.

Diphenylamine- and triphenylamine-arsenic acids. I. Action of arsenic acid on diphenylamine. H. Lieb and O. Wintersteiner [with W. Frost] (Ber., 1928, **61**, [*B*], 107—116).—Arsenic acid does not react smoothly when heated with pure diphenylamine, whereas controllable change occurs when a preserved specimen of the base is used. Previous boiling of the amine under atmospheric pressure or treatment with air at 100°, or addition of nitrobenzene, glacial acetic acid, concentrated hydrochloric acid, or water, but not of xylene, causes reaction to occur smoothly. Optimum conditions are found in the use of 12 g. of arsenic acid, 10 g. of diphenylamine, and 1·5 c.c. of water at 100° and finally at 140—145°. The products are (1) *p*-phenylaminophenylarsinic acid (diphenylamine-*p*-arsinic acid), decomp. 286° [Burton and Gibson (A., 1926, 419) record m. p. 265°]; the *ammonium*, *disodium* ($+8H_2O$), and *magnesium* salts are described: (2) *diphenylamine*-pp′-*diarsinic acid*, $NH[C_6H_4\cdot AsO(OH)_2]_2$, decomp. 330—340°; (3) occasionally *bisdiphenylaminearsinic acid*, $(NHPh\cdot C_6H_4)_2AsO\cdot OH$. Diphenylamine-*p*-arsinic acid cannot be acetylated; attempts to arsenate acetyldiphenylamine were unsuccessful. Reduction of diphenylamine-*p*-arsinic acid by hypophosphorous acid to *di*-p-*phenylaminoarsenobenzene* is best effected by rapid dissolution of the organic compound in an excess of 50% hypophosphorous acid on the water-bath and preservation of the rapidly cooled solution at the atmospheric temperature during some hours. Reaction very readily proceeds further with the production of polyarsenides. Similar reduction of diphenylamine-*pp*′-diarsinic acid affords pp′-*di-phenylaminoarsenobenzene*-p″p‴-*diarsinic acid*, $As_2[C_6H_4\cdot NH\cdot C_6H_4\cdot AsO(OH)_2]_2$, readily soluble in ammonia and sodium carbonate solutions; the *magnesium* salt is described. H. Wren.

Active hydrogen atoms of hæmin. R. Kuhn and M. Furter (Ber., 1928, **61**, [*B*], 127—131).—Hæmin from different sources and purified by different methods invariably evolves 3 mols. of methane when acted on by magnesium methyl iodide according to Zerewitinov at temperatures not exceeding 40° (cf. Kuhn and co-workers, A., 1927, 784; Fischer, A., 1926, 630; 1927, 1099). Dimethylhæmin contains only one active hydrogen atom. The third active hydrogen atom of hæmin which does not find expression in Fischer's formula, is due to a hydrogen atom which, with the chlorine atom of the FeCl group, is lost as hydrogen chloride. Under the influence of Grignard's reagent in pyridine, hæmin loses all its chlorine which is quantitatively found in the ionised condition after addition of water. Pyridine in the absence of magnesium methyl iodide does not cause a similar change and iron is only replaced in traces. The compound, $C_{34}H_{31}O_4N_4Fe$, obtained by the action of aniline on hæmin contains only two active hydrogen atoms. H. Wren.

Action of aniline dyes on albumin, caseinogen, and gelatin. M. A. Rakusin (Biochem. Z., 1928, **192**, 167—171).—Proteins form compounds with both acid and basic dyes which are irreversible in boiling water. The compounds of protein with basic dyes are reversible in alcohol. Albumin (different from caseinogen) gives with acid dyes compounds which are irreversible in boiling alcohol and are often true chemical compounds. Caseinogen behaves as an amphoteric body. In the dyeing of albumin both the biuret complex and the free NH_2 groups take part. P. W. Clutterbuck.

Rapid determination of carbon and hydrogen in organic compounds. II. E. Berl, A. Schmidt, and K. Winnacker (Ber., 1928, **61**, [*B*], 83—91; cf. A., 1926, 749).—The lead chromate employed must be dried at 550—600° to ensure complete removal of water; the dry substance is extraordinarily hygroscopic. Complete desiccation of some varieties of lead chromate is not effected at 200°.

The formation of higher oxides of nitrogen during the combustion of nitrogenous compounds appears to depend, not on the state of oxidation of nitrogen in the compound, but on the ratio, C : N. It is not observed with nitrobenzene, nitroacetanilide, chlorodinitrodiphenylamine, or thiocarbanilide, but occurs with thiocarbamide and guanidine nitrate. The apparatus described previously (*loc. cit.*) is modified by lengthening the combustion tube and introducing a layer of lead peroxide heated at 180° in an air bath. If carbon dioxide is determined volumetrically, the gas burette must be cleansed frequently from traces of grease; this can be obviated by adding a few drops of "Nekal" solution to the acidified, saturated salt solution or by using a 20—25% solution of glycerol saturated with sodium chloride (the vapour tension of these solutions is 80% of that of water).

The combustion of liquids of relatively low b. p. is described in detail. H. Wren.

Pregl's micro-analytical method for determination of carbon and hydrogen. H. D. K. Drew and C. R. Porter (J.S.C.I., 1928, **47**, 17—21T).—Calcium chloride is shown to be unsuitable as a drying or an absorbing agent in the combustion apparatus of Pregl. Phosphorus pentoxide mixed with glass wool is found to be ideal for the purpose (cf. Kemmerer and Hallett, A., 1927, 269; B., 1927, 958). Details of procedure are given for the filling of the drying and absorbing tubes and for carrying out analyses. Possible sources of error are examined experimentally. It is established that each filled combustion tube is characterised by a "normal" blank value and a "permanent" blank value, these values being the amounts of moisture delivered to the absorption tubes during blank runs when the tube is in a condition for carrying out analyses and when it is at maximum desiccation, respectively. A simple method of obtaining the normal state is given. The new carbon dioxide-absorbing tube lasts for about twenty analyses, as against about four for Pregl's tube. The results of analyses are exact and are free from fluctuations.

Direct Nesslerisation of Kjeldahl digestions. H. M. Chiles (J. Amer. Chem. Soc., 1928, **50**, 217—

221).—The ammonia in Kjeldahl digestions, up to a concentration of 20 mg. nitrogen per 100 c.c., can be determined colorimetrically by direct Nesslerisation, in presence of up to 5—8 g. of sodium or potassium sulphate, provided 5 c.c. of gum arabic solution, prepared as follows, be added per 100 c.c. of solution to be tested. Powdered gum arabic (10 g.) is stirred into ammonia-free water (190 c.c.) and the solution shaken for 10 min. with Permutite powder (4 g.). The slightly turbid liquid is decanted, and the treatment with Permutite repeated if it gives more than a faint coloration with Nessler solution. If reduction of the Nessler reagent is observed, the gum arabic solution is treated with about one tenth of its volume of the reagent, kept until clear, and decanted. Standard solutions for comparison should be prepared with salt contents as nearly as possible equal to those of the solutions to be determined. F. G. Willson.

Volumetric determination of amino-nitrogen. K. Linderstrøm-Lang (Compt. rend. Lab. Carlsberg, 1927, **17**, No. 4, 1—17).—The methods of Van Slyke and Folin for determining amino-groups in amino-acids are uncertain. It is deduced theoretically that such groups can be accurately titrated if use is made of the correct indicator in an appropriate solvent. A satisfactory method is described, which consists of titrating the free amino-acids in aqueous acetone solution (200 c.c. of acetone, 10 c.c. of water) with tenth normal 90% alcoholic hydrochloric acid, using naphthyl-red (benzeneazo-α-naphthylamine) as indicator, preferably at its most acid colour change (corresponding with p_H 4·8 in water). All the nitrogen can be determined in this way in amino-carboxylic acids, diamino-carboxylic acids, amino-dicarboxylic acids, the corresponding hydroxy-acids, proline and hydroxyproline, two thirds in histidine, half in asparagine, arginine, tryptophan, and dipeptides, and one third in creatine and guanidine, but the basic groups in aromatic amino-acids, amino-sulphonic acids such as taurine, and certain other weakly basic groups are not titrated. Incidentally the preparation of pure naphthyl-red, m. p. 124°, from diazoaminobenzene and α-naphthylamine is described in detail. S. Coffey.

Volumetric determination of organic substances completely oxidisable by sulphuric acid-chromic acid mixtures in presence of silver nitrate. H. Cordebard and V. Michl (Bull. Soc. chim., 1928, [iv], **43**, 97—106; cf. Simon, A., 1922, ii, 593).—Owing to the stability of acetic acid towards oxidising agents application of the sulpho-chromic acid method to acetates and acetyl derivatives yields untrustworthy results. Fairly trustworthy values are, however, obtained in presence of silver chromate. The present method involves the volumetric determination of the excess of chromate and hence addition of silver chromate as such is not desirable. The substance is dissolved in a slight excess of a solution of potassium dichromate and silver nitrate equivalent to the amount of silver dichromate necessary for the oxidation of the acetic acid likely to be produced added. The mixture is boiled under a reflux condenser after addition of an equal volume of concentrated sulphuric acid. The excess of chromate is determined by titration with a solution of ferrous sulphate, after precipitation of the silver with sodium chloride. J. S. Carter.

Analysis of brominated cresols. J. Buxton and H. J. Lucas (J. Amer. Chem. Soc., 1928, **50**, 249—252).—A slow reaction between alcohol and bromate in acid solution may affect the accuracy of Francis and Hill's method (A., 1925, ii, 163) of determining brominated cresols, and this source of error is eliminated by using aqueous acetic acid instead of alcohol as solvent. In the determination of total bromine by Robertson's method (J.C.S., 1912, **107**, 902), for which a modified apparatus is described, fading of the ferric thiocyanate end-point is avoided by boiling the solution with 1 c.c. of *N*-ferric nitrate solution before acidification, by which means the hydrogen peroxide is decomposed. A further 9 c.c. of ferric nitrate solution is added after acidification. F. G. Willson.

Determination of aromatic aldehydes by titration with benzidine acetate solution. P. N. van Eck (Pharm. Weekblad, 1928, **65**, 82—84).—The aldehyde is dissolved in glacial acetic acid, an acetic acid solution of blood added as indicator, and the mixture titrated with the benzidine acetate solution. The end-point is determined by bringing a drop of the mixture on to filter-paper damped with hydrogen peroxide, the blue coloration of the blood–benzidine–peroxide reaction appearing only after all the aldehyde has reacted. Benzaldehyde does not give a good end-point, since it forms a green reaction product with benzidine. S. I. Levy.

Determination of small quantities of benzoic and cinnamic acids, with some notes on the colorimetric determination of salicylic acid. J. R. Nicholls (Analyst, 1928, **53**, 19—29).—Benzoic acid may be determined by partial oxidation to salicylic acid by adding 1 c.c. of iron solution (50 c.c. of *N*-ferric chloride and 13 c.c. of *N*/10-sulphuric acid to 100 c.c.) to an aliquot part of a neutral solution containing not more than 4 mg. of benzoic acid to 15 c.c. of water, together with 1 c.c. of 0·1% hydrogen peroxide. After heating to boiling, 0·5 c.c. of *N*-sodium hydroxide solution is added, the whole filtered hot into a 50 c.c. Nessler tube, and the precipitate washed with hot water. The filtrate is cooled, diluted to the mark, and 1 drop of iron solution added; the colour is matched by adding a 0·01% solution of salicylic acid to a blank carried out in an identical manner. The salicylic acid may also be determined by Jorissen's test. Under these conditions a constant proportion (slightly more than 10%) of the benzoic acid is oxidised to salicylic acid, but appreciable quantities of salts other than nitrates must be absent. Cinnamic acid, if present, may be quantitatively oxidised to benzoic acid in neutral or alkaline solution with potassium permanganate. D. G. Hewer.

Determination of mercury salicylate and lactate. A. Jonesco-Matiu and C. V. Bordeiano (J. Pharm. Chim., 1927, **6**, 300—307).—A volumetric method for the analysis of mercuric salicylate and lactate is described, based on the oxidation of the salt with a mixture of 1 part of nitric acid and 2 parts of sulphuric acid, and the subsequent titration of the mercury with sodium chloride solution, using the precipitate formed on adding a small quantity of sodium nitroprusside as an indicator. The method is accurate to 1%. E. A. LUNT.

Determination of the amino-group in nitroarylamines. II. Determination of nitrotoluidine, nitronaphthylamine, and nitroarsanilic acid. N. SEMIGANOVSKY (Z. anal. Chem., 1927, **72**, 295—298).—The amino-group content of nitrotoluidines, nitroacetotoluidides, nitroacetnaphthalides (other than *m*-nitroarylamines), and nitroarsanilic acid has been successfully determined by the author's method (A., 1927, 1062). Dinitroarylamines cannot thus be analysed; thus 3 : 4-dinitrophenol when boiled with alkali yields 7% of its nitrogen as ammonia.

F. S. HAWKINS.

Morphine reaction of Pellagris and Vulpius. L. EKKERT (Pharm. Zentr., 1928, **69**, 1—6, 19—22).—The procedure may be much simplified; it is only necessary to heat the substance or its solution with a little concentrated sulphuric acid until the original red coloration deepens finally to brown, dilute with water, and extract separate portions with ether, chloroform, and ethyl acetate, respectively. The colour changes at various dilutions with water and these solvents are described; they are due to the formation and oxidation of *apo*morphine. The colour changes observed with several morphine derivatives and allied alkaloids are described. S. I. LEVY.

Alkaloid ferrocyanides and their analytical applications. M. GADREAU (J. Pharm. Chim., 1927, [viii], **6**, 145—151).—Methods for the quantitative determination of strychnine and of brucine, and for the separation and determination of mixtures of these two alkaloids are described. The methods are based on determinations as ferrocyanides and the difference in the time required to precipitate strychnine and brucine ferrocyanide is made the basis of the separation. It is suggested that owing to the solubility of certain alkaloid ferrocyanides, morphine, codeine, eserine, etc., hydroferrocyanic acid cannot be regarded as a specific reagent for tertiary amines.

E. A. LUNT.

Biochemistry.

Effect of over-breathing and of breathing high concentrations of carbon dioxide on urinary excretion of water and chlorides. G. E. SIMPSON and A. H. WELLS (J. Biol. Chem., 1928, **76**, 171—184).—The urinary excretion of water and chlorides is increased by over-breathing and decreased by breathing air containing more than 4% of carbon dioxide. C. R. HARINGTON.

Respiratory proteins of blood. I. Copper content and minimum mol. wt. of hæmocyanin of *Limulus polyphemus*. A. C. REDFIELD, T. COOLIDGE, and M. A. SHOTTS. **II. Combining ratio of oxygen and copper in bloods containing hæmocyanin.** A. C. REDFIELD, T. COOLIDGE, and H. MONTGOMERY (J. Biol. Chem., 1928, **76**, 185—196, 197—205).—I. The hæmocyanin of *Limulus polyphemus* contains 0·173% of copper, which gives a minimum *M* of 36,700; since ultra-filtration experiments indicate that *M* lies between those of hæmoglobin and pseudoglobulin the true value of *M* is probably 73,400, and the substance contains two atoms of copper per molecule.

II. In the hæmocyanins of nine species, oxygen is combined with copper in the atomic ratio of 1 : 1.

C. R. HARINGTON.

Hæmoglobin and iron in blood under tropical conditions. H. MENGERT-PRESSER (Med. dienst volksgezondh. Nederlandsch-Indie, 1926, 240—260; Chem. Zentr., 1927, ii, 277).—Higher values were obtained for natives than for Europeans.

A. A. ELDRIDGE.

Composition of the blood of various human races and some analyses of pathological blood. W. F. DONATH (Med. dienst volksgezondh. Nederlandsch.-Indie, 1926, 261—277; Chem. Zentr., 1927, ii, 276).—The iron content of the blood of natives is higher than that of Europeans, which again is higher than that of Europeans in Europe. In general, lower values are observed in disease, particularly in tuberculosis. The iron of the blood is associated exclusively with the erythrocytes. A. A. ELDRIDGE.

Sulphur content of various proteins. E. KAISER (Biochem. Z., 1928, **192**, 58—66).—The sulphur content of the globin of the hæmoglobin of cat is 0·97—0·98%, of ox 0·59—0·60%, of horse (5 samples) 0·58—0·60% (1 sample), 0·49%, and of dog 0·50—0·73%. No sulphur is lost in elimination of the globin and the different sulphur contents of the different hæmoglobins obtained by Valer (this vol., 191) are thus confirmed. Globulins precipitated by Hammersten's method contain rather more sulphur than when precipitated by ammonium sulphate.

P. W. CLUTTERBUCK.

Clinical methods for the determination of hæmoglobin. E. M. F. ITHURRAT and V. MORERA (Rev. asoc. med. Argentina, 1926, **39**, 401—426; Chem. Zentr., 1927, ii, 305).—Newcomer's method is recommended, although Bürker's method is more accurate. A. A. ELDRIDGE.

Methæmoglobin formation. I. Effect of certain gases, acids, and alkalis on the production of methæmoglobin by chemicals. II. Methæmoglobin production by chemicals *in vivo*. C. SUZUKI (Folia pharmacol. japon., 1927, **4**, 156—179, 180—194).—I. The production of methæmoglobin in fresh rabbit's blood *in vitro* by potassium chlorate, pyrogallol, hydroxylamine perchlorate, potassium nitrate, and aniline hydrochloride is promoted by carbon dioxide and acids, and inhibited by alkali. Except for pyrogallol, the effects are more marked in blood hæmolysed by water.

II. *In vivo* (mice), the effects are less pronounced. That of potassium chlorate and potassium nitrate is not influenced by acids. CHEMICAL ABSTRACTS.

Equilibria involving oxidation of hæmoglobin to methæmoglobin. J. B. Conant and N. D. Scott (J. Biol. Chem., 1928, **76**, 207—222).—The extent of oxidation of hæmoglobin to methæmoglobin by various reversible oxidising agents has been observed spectrophotometrically; the results confirm both the view (A., 1925, i, 455) that the hæmoglobin–methæmoglobin system is reversible and the value previously obtained for the oxidation–reduction potential of this system. Whereas the value of *n* in the electrochemical equation relating to the equilibrium should be 1 or 4 according as hæmoglobin has *M* 16,700 with 1 atom of iron or 66,800 with 4 atoms of iron, spectroscopic observations of the equilibrium between hæmoglobin and naphtholsulphonate-indophenol, and of that between carboxyhæmoglobin and potassium ferricyanide, indicate an actual value for *n* of 2. C. R. Harington.

Determination of methæmoglobin. J. B. Conant, N. D. Scott, and W. F. Douglass (J. Biol. Chem., 1928, **76**, 223—227).—The method of Conant and Fiesen (A., 1925, i, 456) has been modified by substituting titanous tartrate as a reducing agent for the β-anthraquinolsulphonate formerly employed. C. R. Harington.

Reduction of hæmin by cysteine. W. Cremer (Biochem. Z., 1928, **192**, 426—427).—When cysteine and hæmin are mixed in an atmosphere of carbon monoxide, 1 mol. of carbon monoxide is absorbed per mol. of hæmin. P. W. Clutterbuck.

Independence of the displacement of the absorption bands, and changes of absorption in hæmatoporphyrin solutions. Cause of the variability of the spectrum of acid hæmotoporphyrin with concentration of acid. A. Tethi (Biochem. Z., 1928, **192**, 105—117).—Absorption of light by hæmatoporphyrin dissolved in different media may be very different quantitatively even when the solutions behave similarly in respect to absorption maxima. The variation of the spectra of acid hæmatoporphyrin with the concentration of the acid depends on the fact that the spectrum of the less strongly acid solutions is additively composed of the spectra in neutral and in pure acid solution. P. W. Clutterbuck.

Independence of the displacement of absorption bands and of the changes of absorption of light in different solutions of pigments. V. Zilzer (Biochem. Z., 1928, **192**, 118—122).—The displacement of the absorption bands and changes in the degree of absorption of light by pigments in media of different chemical nature can be quite independent of one another. Using various pigments (hæmatoporphyrin, rhodamine-B, patent-blue, phloxin, quinoline-blue) and alcohol and 0·1*N*-potassium hydroxide as media, it is shown that the region of maximum absorption can be different with almost identical strength of absorption, or inversely the maximum may have the same position and yet the absorption be different or both the position of the maximum and the degree of absorption may be different. P. W. Clutterbuck.

Phosphorus in the metabolism of blood-sugar. G. Florence and T. Zola (Bull. Soc. Chim. biol., 1927, **9**, 1244—1252).—High levels of blood-sugar are associated with a concentration of organic phosphorus higher, and of inorganic phosphorus lower than normal. W. O. Kermack.

Blood-sugar after vagus irritation. J. Lehmann (Skand. Arch. Physiol., 1927, **52**, 169—186; Chem. Zentr., 1927, ii, 1362).

Effect of brewers' yeast extract on the combined sugar of the blood. M. Bufano (Arch. Farm. sperim., 1927, **44**, 22—31).—The proportion of total sugar in the blood of rabbits to which extract of brewers' yeast is administered subcutaneously shows no uniform variation, any increase observed being in the free sugar and any decrease in the combined sugar. The amount of the free sugar may either diminish or increase slightly. In some cases the combined sugar gradually but completely disappears, whilst in others it tends after a time to revert to its original quantity. The amount of the extract administered is without influence on the results. The observations made emphasise the excessive lability of combined sugar *in vivo* towards the enzymes of brewers' yeast and seem to justify the conclusion that similar lability of the sugar in presence of the little-known endogenous enzymes may be the cause of the variations occurring in the combined sugar content of the blood of both healthy and diseased organisms. T. H. Pope.

Determination of the reducing substance in blood. S. Jonsell, E. Jorpes, and N. Sikström (Acta med. Skand., 1926, **63**, 446—477; Chem. Zentr., 1927, ii, 305).—Hagedorn and Jensen's method, in which the error is 1·58%, is preferred. A. A. Eldridge.

Determination of protein-sugar. H. Bierry (Compt. rend. Soc. Biol., 1927, **96**, 606—609; Chem. Zentr., 1927, i, 2759).—Plasma (10 c.c.), distilled water (14 c.c.), and sulphuric acid (*d* 1·84, 2 c.c., diluted 1 : 4) are heated at 120° in an autoclave for 30 min.; when cold, the mixture is treated with sodium carbonate and mercuric chloride (dropwise), then sodium carbonate to a violet coloration of purple bromocresol paper, filtered, and the mercury removed with zinc powder or copper borings, and the sugar determined by Bertrand's method. A. A. Eldridge.

Determination of sugar, uric acid, urea, and creatinine in 1 c.c. of blood. E. S. Rose (J. Amer. Pharm. Assoc., 1928, **17**, 41—42).—The blood is freed from protein and the sugar, uric acid, and urea are determined in the filtrate by slight modifications of the Folin–Wu methods. Creatinine is determined colorimetrically by the reduction of alkaline sodium picrate solution. E. H. Sharples.

Blood-ammonia, its formation and physiological behaviour. J. K. Parnas (XII Int. Cong. Physiol., 1926, 124—126; Chem. Zentr., 1927, i, 2918—2919).—The non-colloidal nitrogenous substance which, by ferment action, yields ammonia directly the blood is withdrawn from the blood-vessels, is present in rabbit's blood to the extent of 2 mg. per 100 c.c., and in human blood to a much smaller extent. The formation of ammonia is independent of the content or addition of amino-acids or urea, but is related to p_H, temperature, and dilution. For the uterine veins of pregnant rabbits the increase of ammonia content is significant. Only portal blood contains relatively much ammonia. Anoxæmia increases the ammonia content. During death blood-ammonia increases on account of anoxæmia; after death further increase is due to its production from its precursor. A. A. ELDRIDGE.

Ammonia of human blood. E. ADLER and K. SCHWERIN (Klin. Woch., 1927, **6**, 1188—1189; Chem. Zentr., 1927, ii, 709—710).—The ammonia content (actual) of human blood 5—6 min. after withdrawal is 0·02 mg. per 100 c.c., whilst that (virtual) of sterile blood kept at 37° for 24 hrs. is 2 mg. Violent muscular exercise has no effect on the values, but individuals with marked cyanosis or moribund give high actual values (0·091 mg.). Blood-ammonia values are independent of the variations in urinary ammonia elimination. Insulin does not influence the blood-ammonia value; in four of five cases of carcinoma low virtual and fairly high actual values were obtained. A. A. ELDRIDGE.

Test for ergothioneine and its determination in simple solution and in blood-filtrates. G. HUNTER (Biochem. J., 1928, **22**, 4—10).—When a solution of sodium carbonate and sodium acetate, mixed with a solution containing ergothioneine, is added under specified conditions to a diazotised sulphanilic acid solution, a clear yellow colour develops. On addition, after 30 seconds, of strong sodium hydroxide solution to this mixture a red colour with a purple tinge is produced. By this specific test ergothioneine can be detected in a dilution of about one in five millions. Quantitative results can be obtained by matching against standards made from known amounts of ergothioneine or against phenol-red standards. Determinations of ergothioneine have been carried out on bloods from various animals. The protein-free blood-filtrates are prepared by the tungstic acid method of Folin and Wu. S. S. ZILVA.

Micro-determination of adenine nucleotide content of blood. M. V. BUELL and M. E. PERKINS (J. Biol. Chem., 1928, **76**, 95—106).—Whole blood is freed from proteins with tungstic acid; adenine nucleotide is precipitated from the filtrate with excess of uranyl nitrate; the precipitate is hydrolysed with dilute sulphuric acid, the solution freed from uranium, and the adenine precipitated as the silver compound in presence of gelatin; the resulting solution is compared nephelometrically with a similarly treated standard solution of adenine. The error of the method is 2—3%. Figures are given for the adenine nucleotide content of the bloods of various species, the amounts ranging from 2—3 mg.% for ox blood to 60—90 mg.% for pigeon blood.

C. R. HARINGTON.

Determination of amino-acids in blood: Folin's method. S. H. EDGAR (Biochem. J., 1928, **22**, 162—167).—Figures have been obtained with Folin's colorimetric method (A., 1922, ii, 540) which varied according to the alkalinity of the solutions. The relative rates of change have been investigated. The rate of increase of the amino-acid-nitrogen falls gradually to give a constant value at an alkalinity higher than that used by Folin. S. S. ZILVA.

Determination of oxalic acid in blood, urine, etc. J. KHOURI (Bull. Soc. Chim. biol., 1927, **9**, 957—960).—See A., 1927, 689.

Composition of the blood of children. G. DE TONI (Clin. pediatr., 1926, **8**, 449—493; Chem. Zentr., 1927, ii, 276).—A system of analytical methods is described. A. A. ELDRIDGE.

Inorganic substances in human blood. I. Cation and anion content of normal serum. W. H. JANSEN and A. M. LOEW (Deuts. Arch. klin. Med., 1927, **154**, 195—220; Chem. Zentr., 1927, i, 3099).—Average, minimum, and maximum values (mg.%) for human blood are: (cations) sodium 320, 315, 350; potassium 20, 18, 22; calcium 10·2, 9·4, 11·0; magnesium 2·34, 1·8, 2·8; (anions) chlorine 360, 335, 370; phosphorus 13, 10·1, 14·5; sulphur 141·5, 117, 166·6; ratio sodium : potassium 16·5, calcium : magnesium 4·0—5·0; potassium : calcium 2·0. At an average carbon dioxide tension of 40 mm. the carbonic acid capacity is 118·6 mg.% CO_2. The chloride : hydrogen carbonate quotient is 2·2.

A. A. ELDRIDGE.

Calcium, magnesium, and potassium content of muscular tissue and blood. M. CAHANE (Compt. rend. Soc. Biol., 1927, **96**, 1168—1169; Chem. Zentr., 1927, ii, 709).—In old animals (guinea-pigs, rabbits, dogs, cats) the calcium content of the muscular tissue and blood is subnormal, and that of magnesium less markedly so, whilst the potassium content undergoes no regular change. A. A. ELDRIDGE.

Variations in serum-calcium. P. MEGLITZKY (Z. ges. exp. Med., 1927, **55**, 13—16; Chem. Zentr., 1927, ii, 589).—In hunger, the serum-calcium of cats rises to 180% of the normal value, and later falls to subnormal values. Nephrectomy causes a rapid increase, followed by a premortal fall. Mercuric chloride poisoning and splenectomy cause a fall.

A. A. ELDRIDGE.

Condition of serum-calcium and its pathological significance. K. KLINKE (Klin. Woch., 1927, **6**, 791—794; Chem. Zentr., 1927, i, 3203).—Calcium is present in serum in the following forms: ionised; soluble complex or molecular salt; salt adsorbed on protein. The three forms are not only in equilibrium, but also are related chemically.

A. A. ELDRIDGE.

Condition of calcium in serum. A. NITSCHKE (Biochem. Z., 1928, **192**, 123—127).—The equilibrium constant of saturated solutions of calcium hydrogen carbonate, determined in dialysis experiments by application of the Donnan theory, is $K=[Ca^{\cdot\cdot}][HCO_3']/[H^{\cdot}]=2570$ at 37°. The ionised calcium at p_H 7·35, HCO_3' 67·2 vol.-% is therefore 14·5 mg.-%. The equilibrium constant for a similar solution of calcium phosphate at 37° is $K=[Ca^{\cdot\cdot}][HPO_4']/[H^{\cdot}]=67\times10^{-7}$. In serum at p_H 7·35, phosphorus content 3·7 mg.-%, and calcium content 10 mg.-%, the calcium is present 2·4 mg. as molecular calcium hydrogen phosphate, 5·6 mg. in the ionised form, and about 2 mg. as protein-calcium (cf. A., 1926, 422, 1051).

P. W. CLUTTERBUCK.

Conductivity of aqueous salt solutions containing calcium hydrogen carbonate. A. Nitschke (Biochem. Z., 1928, **192**, 128—131).—Considerably greater ionisation is detected by conductivity measurements in aqueous solutions containing calcium hydrogen carbonate than appears from Rona's expression (A., 1913, i, 544). For such solutions the mean equilibrium constant at 37° is 3030, a value agreeing fairly well with that obtained by the use of the Donnan theory, 2570 (see preceding abstract).

P. W. Clutterbuck.

Determination of the alkali reserve of the blood. S. P. Suner (XII Int. Cong. Physiol., 1926, 135—136; Chem. Zentr., 1927, ii, 305).—The blood (10 c.c.) is centrifuged for 10 min. with potassium oxalate (20 mg.), and 4 c.c of plasma mixed with 16 c.c. of distilled water. The p_H is determined electrometrically before and after the addition of 0·1 c.c. portions of 0·1*N*-hydrochloric acid. A. A. Eldridge.

Comparative buffering power of blood and body fluids. E. Gellhorn (Pflüger's Archiv, 1927, **216**, 253—266; Chem. Zentr., 1927, i, 2920—2921).—An examination of body fluids of echinoderms with respect to acid-neutralising and buffering power, and nitrogen content. A. A. Eldridge.

Copper in human blood-serum. O. Warburg (Klin. Woch., 1927, **6**, 1094—1095; Chem. Zentr., 1927, ii, 590).—Human blood serum contains loosely-combined copper in relatively large quantities ($1—2\times10^{-3}$ mg./c.c.), 0·2—0·4% of the total quantity of iron. The copper can be determined colorimetrically by means of ferrocyanide, or by measuring its catalytic effect on the oxidation of cysteine by atmospheric oxygen; by the latter method 10^{-5} mg. can be detected, and the effect due to copper can be readily differentiated from effects due to iron and manganese.

A. A. Eldridge.

Micro-determination of chlorine and iron in blood and other liquids. F. H. Smirk (Biochem. J., 1928, **22**, 201—207).—The determinations can be carried out by this method on 0·02—0·01 c.c. of the physiological fluid if the prescribed conditions are fulfilled. The principles of the methods are similar to those already described (*ibid*., 1926, **21**, 31; Fowweather, A., 1926, 443). S. S. Zilva.

Spreading into a unimolecular layer as a method for the determination of blood-fat. E. Gorter and F. Grendel (Biochem. Z., 1928, **192**, 431—456).—The usual Langmuir–Adam method is used for measurements of unimolecular layers of a variety of oils, sterols, phosphatides, and natural fats and is adapted for the determination of the total-blood-fat and of the fractions obtained after extraction with light petroleum. The total blood-fat may be determined with small quantities (0·1—0·2 c.c.) of blood with an accuracy of 1%, but the light petroleum extract from this amount of fat is too small to give a sufficiently large surface for measurement. The material extractable by light petroleum is therefore obtained by difference of the total fat and the fat remaining after light petroleum extraction.

P. W. Clutterbuck.

Reaction of blood in the determination of sex. Importance of manganese mixtures in a reaction for the determination of sex. W. W. Práwdicz-Neminski (Biochem. Z., 1928, **192**, 303—323).—A study of the Manoilov reaction for the determination of sex shows that the reagents alone, without addition of blood, can give the whole series of results described as "male," "female," etc., reactions. Variation of the concentration of hydrochloric acid from 9·52% to 0·1*N* gives all these reactions, the rôle of the acid being not limited to the change of p_H but being chiefly that of forming ozone and chlorine by reaction with permanganate. The type of reaction obtained in the presence of organic substances then depends on their oxidisability. P. W. Clutterbuck.

Influence of *X*-rays on certain blood constituents. A. Gigon and M. Lüdin (Schweiz. med. Woch., 1926, **56**, 814—816; Chem. Zentr., 1927, ii, 278).

Catalase value and catalase index of ox blood. T. Radeff (Berlin tierärztl. Woch., 1926, **42**, 781—782; Chem. Zentr., 1927, ii, 277).—The normal catalase value is about 8·54; in disease it is reduced without reduction of the catalase index (catalase value/erythrocyte value). A. A. Eldridge.

Action of arsenic on blood ferments. I. Parfentjev (Vestn. mikrobiol. epidemiol., 1926, **5**, 269—275; Chem. Zentr., 1927, ii, 446).—Amylase and peroxidase are not inhibited by arsenious oxide *in vitro*; catalase is markedly inactivated by 0·1%, but very dilute solutions stimulate the action of catalase and peroxidase. Only a high content is disadvantageous to lipase. In acute poisoning of rabbits *per os* there is no disturbance of fermentative processes.

A. A. Eldridge.

Action of arsenic and related elements. I. Significance of oxygen for arsine-hæmolysis. R. Labes (Arch. exp. Path. Pharm., 1928, **127**, 125—147).—Hæmolysis of a suspension of red blood-cells by arsine does not occur, or takes place very slowly, if oxygen is removed from the corpuscles by a current of an inert gas (hydrogen or nitrogen) or carbon monoxide, or by reduction with sodium sulphite. The addition of a culture of paramœcia (as a reducing agent) to the red cell suspension has a similar effect. Arsine-hæmolysis thus requires the presence of oxygen and this is supplied by the oxyhæmoglobin. The significance of these findings is discussed but no definite conclusions can be reached. Within the limits c_H 4×10^{-7} to $0{\cdot}25\times10^{-7}$ with phosphate buffers, c_H has no significant influence on arsine-hæmolysis, but high concentrations of phosphate tend to retard hæmolysis. A. Wormall.

Hæmolysis. Piettre and Chrétien (J. Pharm. Chim., 1927, [viii], **6**, 5—20).—The mechanism of hæmolysis is discussed from the authors' results on the hæmolytic power induced in sheep's serum by the injection of stroma solutions prepared by dissolving dried, pulverised stroma from various animals in alkali. The action of sodium chloride as a hæmolytic factor is rejected, except with reference to its action on the proteins present, whilst the existence of a sensitiser is postulated as a definite substance which forms a stable compound with the stroma-protein.

E. A. Lunt.

Influence of hydrogen-ion concentration on saponin hæmolysis. L. Kofler and Z. Lázár (Arch. Pharm., 1927, **265**, 610—623).—There is disagreement between Mond (A., 1926, 856) and earlier workers regarding the influence of hydrogen-ion concentration on hæmolysis by saponins, but this disagreement is now found to be only apparent. Actually, different saponins are differently affected, and they can be classed in two groups. In the first group the hæmolytic index is at its lowest when the medium has p_H 8—9 and rises on each side of this point, at first slowly, later quickly, until at p_H 5·6 or p_H 10·48 acid hæmolysis or alkaline hæmolysis, respectively, supervenes. To this group belong "saponin pur. albiss.," digitonin, smilacin, cyclamin, horse-chestnut saponin (Merck), the saponins from *Primula veris* and *P. eliator*, quillaia saponin, and *Gypsophila* saponin. In the second group the hæmolytic index is the lower the higher the figure for p_H, *i.e.*, there is practically no hæmolytic action until just before alkaline hæmolysis takes place, whereas on the acid side the hæmolytic index is very high. To this group belong "saponin-gereinigt" (Kahlbaum), senegrin, and sapindus saponin (two commercial preparations). The behaviour of this second class is probably to be accounted for on chemical grounds. In some of the above tests parallel experiments were made with products specially purified by electro-dialysis. In all the experiments cow's corpuscles were used; they were washed, and the suspensions were made up with Jarisch's phosphate buffer solution. The hæmolytic action of saponins is different according as washed or unwashed blood corpuscles are used; moreover, the effect of the serum present depends on the saponin used, thus, when digitonin acts on washed blood corpuscles it is about 11% more active than when it acts on unwashed corpuscles, whereas the difference when *Gypsophila* saponin (purified by electro-dialysis) is used is 452%. This effect of serum is attributed to the presence of cholesterol and other compounds, and to the buffering action on the already slightly acid saponin solution. Experiments showed that surface activity of saponin solutions and their hæmolytic action bore no relationship to one another.

W. A. Silvester.

Pancreas as a source of the fibrin ferment in blood. W. N. Boldyrev and A. W. Boldyrev (XII Int. Cong. Physiol., 1926, 22—23; Chem. Zentr., 1927, i, 3015).—Total or partial extirpation of the pancreas increases the coagulation time. Later the blood regains its power of coagulation.

A. A. Eldridge.

Anticoagulant action of peptone *in vitro*. J. O. W. Barratt (Biochem. J., 1928, **22**, 230—235).—Peptone acts on fibrinogen in citrated blood-plasma, diminishing its amount. It is without action on thrombin. S. S. Zilva.

Heparin. W. H. Howell (XII Int. Cong. Physiol., 1926, 80; Chem. Zentr., 1927, ii, 277).—Heparin, an anticoagulant prepared from liver, contains calcium and sulphate, but no protein, amino-acid, or phosphorus. It may be a conjugated glycuronic acid of glucosidic structure.

A. A. Eldridge.

Chemical changes in muscle. I. Methods of analysis. E. Boyland (Biochem. J., 1928, **22**, 236—244).—The minced muscle is extracted with cold alcohol. Glycogen is determined by a modified Pflüger's method in the alcohol-insoluble residue. After removing the alcohol from the filtrate, the fraction is cleared of lipins and protein by precipitation either with ammonium sulphate or with phosphotungstic acid. In the first procedure the solution is extracted with ether to remove the lactic acid and the sugars are determined by Hagedorn and Jensen's method (A., 1923, ii, 265) in the extracted solution after hydrolysis. In the second procedure the hexoses are removed from the solution by precipitation with copper sulphate and calcium hydroxide. For the determination of lactic acid a modified Clausen's method in which steam-distillation was combined with oxidation was employed. S. S. Zilva.

Combination of potassium in muscle. E. Raab (Pflüger's Archiv, 1927, **216**, 540—548; Chem. Zentr., 1927, ii, 593).—The results of Neuschloss (*ibid.*, **213**, 19) are not confirmed. In frog gastrocnemius, toad, and rabbit muscle all the potassium was diffusible with sodium chloride solution.

A. A. Eldridge.

Vasodilator constituents of tissue extracts. Isolation of histamine from muscle. W. V. Thorpe (Biochem. J., 1928, **22**, 94—101).—Fresh ox muscle was thoroughly extracted with 60% alcohol and after removing the alcohol, the fat-free aqueous extract was cleared with basic lead acetate, and the phosphotungstates were prepared. The latter were extracted with acetone, whereby the active substance was removed. On further fractionation by the Kossel–Kutscher method the histamine was found in the histidine fraction. After allowing the carnosine nitrate which formed the bulk of this fraction to crystallise from an alcoholic solution, the mother-liquor was dried with baryta and extracted with alcohol. After removal of alcohol and barium a crystalline precipitate was produced by the addition of picric acid. From this precipitate histamine dipicrate was isolated by fractional crystallisation. The amount of active substance obtained at the end of each stage in the purification was estimated by the action on the cat's blood-pressure. The distribution of the depressor substances in sterile extracts, in which hydrolytic changes were avoided, from a number of organs of horse and ox has also been determined. The whole of the depressor activity of the alcoholic extract of muscle is most probably due to histamine.

S. S. Zilva.

Microchemical studies on the nervous system. I. R. M. May (Bull. Soc. Chim. biol., 1927, **9**, 970—981).—See A., 1927, 986.

Metallic lakes of the oxazines (gallamin-blue, gallocyanine), and cœlestin-blue as nuclear stain substitutes for hæmatoxylin. F. Proescher and A. S. Arkush (Stain Tech., 1928, **3**, 28—38).—The dyes are dissolved in 5% aqueous ferric ammonium sulphate solution. The solutions are boiled for 2—3 min., cooled, and filtered. The iron lakes stain nuclei a deep blue or bluish-black in 3—5 min. No differentiation with acid is required. Cœlestin-blue gives the most stable solution and is recommended as a routine nuclear stain. The protoplasm remains practically colourless and counter-staining with acid dyes (ethyleosin, orange-G, fuchsin) gives results similar to a hæmatoxylin stain. Staining of fat with Sudan, scarlet-red, etc. does not interfere with nuclear staining by these dyes. They are superior to hæmatoxylin as stains for the central nervous system. The nature of the staining process is discussed.

H. W. Dudley.

Iodine content of thyroid in the Japanese fœtus, the new-born child, and at the age of puberty. T. Nosaka (Folia endocrinol. japon., 1926, 2, 1—17).

Adrenaline content of the suprarenals of various mammals. A. Leulier and P. Gojon (Compt. rend. Soc. Biol., 1927, 96, 547—548; Chem. Zentr., 1927, ii, 102).—The order is: rabbit (0·015%), sheep, pig, goat, cow, ox, horse, steer (0·246%). Keeping the tissue over sulphuric acid in a vacuum for 24 hrs. increases the adrenaline content. A. A. Eldridge.

Unsaponifiable matter from the stomach oil of *Scymnorhinus lichia*. E. D. Kamm (Biochem. J., 1928, 22, 77—79).—The unsaponifiable matter of the oil consists mainly (98%) of squalene, butyl alcohol (0·28%), and a residue (0·96%) which is chiefly selachyl alcohol. The bulk of the squalene was obtained by distilling the oil at 228—230°/2 mm. A much smaller yield of this compound was derived from the unsaponifiable fraction by distillation. Batyl alcohol crystallised on keeping from the fraction which distilled over from the unsaponifiable fraction at 190—225°/0·55 mm. The residue of the unsaponifiable fraction yielded batyl alcohol on hydrogenation. S. S. Zilva.

Biological significance of unsaponifiable matter of oils. III. Fish-liver oils. H. J. Channon (Biochem. J., 1928, 22, 51—59).—The liver oils of a number of fish were investigated. The oils of the *Selachii* differ from those of the *Teleostei* in that, in many cases, very large amounts of unsaponifiable matter occur in the former. In the liver oils of the *Selachii* the higher the percentage of unsaponifiable matter in a given oil, the lower is the percentage of sterol in that fraction. Squalene was not detected in the liver oils of any of the fish studied save in those from three members of the *Squalidæ* family. The origin of squalene is discussed. S. S. Zilva.

Lipin distribution in normal and abnormal liver. I. Ox liver. E. R. Theis (J. Biol. Chem., 1928, 76, 107—114).—Normal ox liver contains 4·6% of total lipins, of which 55% are phospholipins and 45% fats; figures are given for the distribution of the various fatty acids, indicating a high proportion of acids with 4 double linkings. In liver showing the signs of fatty degeneration, both the total amount and the iodine number of the phospholipin fraction are much decreased. C. R. Harington.

Composition of intraocular fluids. I. Ox and horse. E. Tron (Arch. Ophth., 1926, 117, 677—692; Chem. Zentr., 1927, ii, 586).

Composition of human milk. G. D. Elsdon (Analyst, 1928, 53, 78—82).—Maximum, minimum, and average figures for total solids, solids-not-fat, and fat are recorded for 529 samples of human milk from 86 subjects. The proteins gradually diminished from 2·2% for 1 day to 1·23% for 50 days to 9 months, and the ash from 0·37% to 0·2%, whilst the fat increased. Average compositions based on recorded figures are taken as: 1—7 days, fat 3·0, protein 2·1, lactose 6·8, ash 0·3; 7—28 days, 3·5, 1·6, 6·8, and 0·25; 1—9 months, 3·5, 1·3, 6·9, and 0·22%. Mixed fat from samples taken early in lactation had iodine value 35·9, Reichert–Meissl–Wollny value, 3·4, Polenske value, 1·9, and Kirschner value 2·0.

D. G. Hewer.

Milk composition and energy. O. R. Overman and F. P. Sanmann (Illinois Sta. Rep., 1926, 91—92).—Formulæ are given for determining the energy value of milk. The true heats of combustion of butter fat, milk protein, and lactose probably lie between Anderson's and Abderhalden and Hammarsten's values. Chemical Abstracts.

Composition of milk of cows receiving cod-liver oil. E. C. V. Mattick (Biochem. J., 1928, 22, 144—149).—The addition of cod-liver oil to the diet of the cow changes the chemical composition of the milk. An increase in the percentage of total calcium and in the time of coagulation of the milk by rennet is particularly marked. This is not the case when arachis oil is added. S. S. Zilva.

Effect of heat on milk. IV. Iodine content. H. E. Magee and A. E. Glennie (Biochem. J., 1928, 22, 11—14).—Heat causes the disappearance by volatilisation of 20% or more, according to the duration of heating, of the total iodine of separated milk. In the case of boiled milk the evenness of the losses suggest that limit of loss produced by heat is nearly reached. The loss of iodine is due to volatilisation, since it does not occur after potassium hydroxide has been added to the milk. Of the iodine of cow's milk 83% is diffusible. This proportion is not disturbed by heating the milk. Milk-fat contains more iodine than an equal volume of separated milk. The iodine associated with the fat is most probably chemically bound with the unsaturated fats and is therefore not diffusible. S. S. Zilva.

Elimination of yellow vegetable colouring matters in human milk. H. Paffrath and A. Consten (Z. Kinderheilk., 1926, 42, 51—59; Chem. Zentr., 1927, ii, 110).—Carotin and xanthophyll were separately determined in human milk by a colorimetric method. The use of vegetables containing carotin or xanthophyll increases the amount of those substances, respectively, in the milk. Both are present when white vegetables are employed, and must in this case originate from animal foods.

A. A. Eldridge.

Nature of the protein surrounding fat globules of milk. R. W. Titus, H. H. Sommer, and E. B. Hart (J. Biol. Chem., 1928, 76, 237—250).—Determinations of nitrogen distribution, sulphur and phosphorus content, and optical rotation, and precipitin tests indicate that the protein of the envelopes of the fat globules of milk is probably caseinogen.

C. R. Harington.

Determination of constituents of bile after injection and absorption of sodium hydrogen carbonate. P. Carnot and Z. Gruzewska (Compt. rend. Soc. Biol., 1927, **96**, 912; Chem. Zentr., 1927, ii, 590—591).—The only changes are an increase in the carbon dioxide and a decrease in the pigment content. A. A. Eldridge.

Surface activity of bile-acids. I. N. A. Krajevski and N. Vedenski (Biochem. Z., 1927, **191**, 241—249).—Curves showing the variation of surface tension of aqueous solutions of sodium glycocholate and taurocholate with temperature and concentration are obtained. The surface tension of these solutions in relatively high concentration decreases linearly with temperature, the temperature coefficient and also the total surface energy (E) being smaller than for pure water. The surface tension of sodium glycocholate in small concentration ($0{\cdot}012M$) decreases with the temperature according to a typical curve. The surface activity (G) of the sodium salts of both acids in small concentration is very large and decreases rapidly with increase of concentration. The adsorption limit is attained very rapidly for both solutions (cf. A., 1927, 1104). P. W. Clutterbuck.

Colorimetric determination of bile salts in duodenal fluid. M. Chiray and L. Cuny (J. Pharm. Chim., 1928, [viii], 7, 97—106).—The method of Herzfeld and Haemmerli (A., 1925, i, 722) has been quantitatively studied and modified.

E. H. Sharples.

Nephelometric determination of trypsin and pepsin in gastric and intestinal juice. Stability of trypsin. P. Rona and H. Kleinmann (Klin. Woch., 1927, 6, 1174—1177; Chem. Zentr., 1927, ii, 721).—The authors' method depends on the addition of very dilute ferment solutions to very dilute serum-albumin or sodium caseinate solutions brought to a suitable acidity by the addition of acids or buffers. The reaction takes place at 37°; samples are taken at intervals, the ferment action being immediately stopped by heating or by changing the p_H. A suitable reagent is then added to the solutions to produce a stable, homogeneous opalescence which is proportional to the albumin content. The samples are compared nephelometrically with that taken before the addition of ferment, due allowance being made for change of concentration. A. A. Eldridge.

Buffering power of urine. S. P. Suner (XII Int. Cong. Physiol., 1926, 135; Chem. Zentr., 1927, ii, 279).—The buffering power of urine, which is much greater than that of blood, is a function almost exclusively of the phosphate content. The buffering curve, a straight line, is constant for an individual, but varies among individuals. A. A. Eldridge.

Relation between colloids, surface tension, and p_H of urine. S. P. Suner (XII Int. Cong. Physiol., 1926, 135; Chem. Zentr., 1927, ii, 279).—On acidification of normal urine, the fall in surface tension runs parallel with that of p_H; with urine from which colloids have been removed with animal charcoal, the surface tension is unchanged by progressive acidification. A. A. Eldridge.

Urine analysis. A. Jolles (Arch. Pharm., 1927, **265**, 717—720).—Piorkowski's paper (*ibid.*, 1926, **264**, 460) is commented upon. When thymol is used as a preservative there is a risk that erroneous results will be obtained in the Obermayer, Jaffé, or Salkowski tests. The violet colour due solely to the thymol is, however, easily distinguished as being such (cf. Jolles, Z. physiol. Chem., 1913, **87**, 310). Piorkowski recommends Spiegler's test for albumen, but this test sometimes gives a positive indication with normal urine, and sometimes fails to indicate albumin even when it is present, because there is a lack of sodium chloride in the urine. The author recommends a modified test, of which details are given, but suggests that reliance should not be placed on a single reagent. As confirmatory tests the ferrocyanide, acetic acid, sulphosalicylic acid, and Spiegler (as modified) are recommended; the last of these is the most sensitive.

W. A. Silvester.

Uric acid determination in urine as a test of kidney function. H. Lucke (Klin. Woch., 1927, 6, 1275; Chem. Zentr., 1927, ii, 1380).

Manganese in urine. R. F. McCrackan and E. Passamaneck (Arch. path. lab. med., 1926, 1, 585—589; Chem. Zentr., 1927, ii, 279).—By colorimetric determination in the ash of normal urine evaporated with nitric acid, 0·02 mg. [% ?] of manganese was found. A. A. Eldridge.

Determination of hippuric and phenaceturic acids in urine. E. J. Wayne (Biochem. J., 1928, **22**, 183—187).—The urine is boiled with sodium hydroxide and hydrogen peroxide to liberate the benzoic and phenylacetic acids. After neutralisation and treatment with bromine the solution is filtered, the filtrate acidified with sulphuric acid and extracted with ether. The ethereal extract is washed with an acidified saturated solution of sodium chloride, transferred to a special apparatus in which the solvent is evaporated and the acids are sublimed and trapped in a cotton-wool plug. The sublimed acids after being weighed are washed out with 90% alcohol and titrated. The titration serves as a check on the weight if the pure acids are present alone and with mixtures of benzoic and phenylacetic acids it serves to determine the relative amount of each. Duplicate experiments on the different samples of urine by this method giving 0·2—0·3 g. of sublimate were found to agree to within 0·07 g. Using a dog's urine of known hippuric acid content an average of 97% of added hippuric acid was recoverable as benzoic acid.

S. S. Zilva.

Determination of urobilinogen in urine and fæces. A. Adler (Deuts. Arch. klin. Med., 1927, **154**, 238—248; Chem. Zentr., 1927, i, 3213).—Isolation of urobilinogen is necessary for its accurate determination; a suitable extraction apparatus has been constructed. A. A. Eldridge.

Kahn's albumin-*A* reaction in serum. K. Posener and W. Behrens (Klin. Woch., 1927, 6, 853—854; Chem. Zentr., 1927, ii, 148).—A discussion of the diagnostic value of Kahn's reaction.

A. A. Eldridge.

Deposition of calcium and iron in the brain. E. C. Eaves (Brain, 1926, **49**, 307—332; Chem. Zentr., 1927, ii, 273).—Certain pathological conditions lead to an excessive storage of calcium and iron in the brain. A. A. Eldridge.

Lactic acid content of pathological discharges. R. Scheller (Münch. med. Woch., 1927, 73, 1879—1881; Chem. Zentr., 1927, i, 3100). A. A. Eldridge.

Analysis of urethral calculus. E. Lobstein (J. Pharm. Chim., 1927, [viii], 6, 156—159).—The calculus consisted principally of calcium phosphate and contained small amounts of ammonium magnesium phosphate, calcium carbonate, ammonium urate, and cystine. E. A. Lunt.

Activity of catalase in normal and neoplastic tissues. A. H. Roffo and B. Barbará (Bol. inst. med. exp., 1926, 2, 599—604; Chem. Zentr., 1927, ii, 446).—The catalase activity decreases in organs in the order liver, kidney, heart, lungs, spleen, and appears to be increased in the organs of cancerous animals. The oxidation–reduction relation is disturbed, the reduction phenomena being more marked in neoplasms. A. A. Eldridge.

Occurrence and detection of arginine in cystinuria. F. A. Hoppe-Seyler (Deut. Arch. klin. Med., 1927, 154, 97—106; Chem. Zentr., 1927, i, 3100).—Arginine was detected in the urine in cystinuria by precipitation with flavianic acid, decomposition of the precipitate with barium hydroxide, purification with phosphotungstic acid, and treatment of the filtrate with cupric carbonate, forming *d*-arginine-copper nitrate. A. A. Eldridge.

Glycolysis. I. Glycolysis in blood of normal (non-diabetic) dogs. B. Rohny (Biochem. Z., 1928, 192, 1—7).—Glycolysis in normal (oxalated) blood proceeds far more rapidly at 37° than at lower temperatures, but is inhibited at 56°. Glycolysis also takes place in serum, but is decreased or compensated for, especially in the first hour, by a parallel formation of sugar. Since the blood-sugar concentration is far greater in serum separated from clot than in serum in contact with clot, it is considered that clot contains a substance inhibiting increase of sugar concentration. P. W. Clutterbuck.

Glycolysis. II. Glycolysis in the blood of diabetic (depancreatised) dogs. Z. Aszódi (Biochem. Z., 1928, 192, 8—13).—The processes of formation of sugar and of glycolysis (cf. preceding abstract) occur similarly in the blood of both normal and diabetic (depancreatised) dogs and the glycolytic enzyme remains active in presence of oxalate, its activity increasing at temperatures up to 37° and being inhibited at 56°. P. W. Clutterbuck.

Quantitative variation of alloxuric substances in urine of diabetics in connexion with insulin therapy. G. Giorgi (Prob. nutriz., 1926, 3, 41—54; Chem. Zentr., 1927, ii, 279).—Administration of insulin causes an immediate increase in the excretion of alloxuric substances. A. A. Eldridge.

Behaviour of the blood-sugar in diabetes after administration of various carbohydrate carriers *per os*, with and without insulin. H. Mauerhofer (Z. klin. Med., 1927, 105, 641—660; Chem. Zentr., 1927, ii, 710).—Oatmeal appears to reduce glycosuria; the effect of barley is less marked and is followed by sugar excretion. A. A. Eldridge.

Action of nickel and cobalt salts on the hypoglycæmic effect of insulin on diabetics. M. Labbé, H. Roubeau, and F. Nepveux (Compt. rend., 1928, 186, 181—183).—Injections of nickel and cobalt chlorides into diabetic and normal human subjects have no effect on the blood-sugar, nor do these salts increase the effect of insulin in human diabetics as they do with dogs and rabbits (cf. A., 1926, 869). B. W. Anderson.

Iodine–starch test of body fluids. Deductions from tests of external secretion of pancreas in diabetes, in diseases of the gall-bladder and pancreas, and in a normal condition. A. Bassler (Arch. Int. Med., 1928, 41, 18—41).—Suggested modifications of the test proposed by the author (*ibid.*, 1925, 35, 162) for pancreatic activity are discussed. The results are given of the application of the test to many types of body-fluid and it is claimed that the test is valuable clinically. Emphasis is laid on the power of sugar and dextrin to combine with iodine and on the effect of this on the determination of diastase. W. O. Kermack.

Coefficient of dysdeaminisation. Relation between certain non-protein nitrogenous substances of the blood as evaluation of ureogenetic function. P. Cristol, A. Puech, and Trivas (Compt. rend. Soc. Biol., 1927, 96, 676—677; Chem. Zentr., 1927, i, 2749).—The "coefficient of dysdeaminisation" is the relation (polypeptide- + amino-acid-nitrogen)/(polypeptide- + amino-acid- + urea-nitrogen); its value (30—35%) is lowered in renal disease and raised in hepatic derangement. A. A. Eldridge.

Lactic acid in blood, particularly in hepatic disease. G. Noah (Klin. Woch., 1927, 6, 1465—1466; Chem. Zentr., 1927, ii, 1362).—The blood-lactic acid of rabbits is occasionally raised by the injection of a lethal quantity of phosphorus. In human liver disease the (fasting) value is normal, but high values were finally obtained in two cases of atrophy. Blood from a malignant tumour showed a high lactic acid and a low sugar value. A. A. Eldridge.

Technique and interpretation of the van den Bergh test [for bilirubin]. R. E. Steen (Irish J. Med. Sci., 1927, [vi], No. 21, 573—582).—A modified technique for the detection of hepatic bilirubin is described. Chemical Abstracts.

Iodine content of mussel shells [and its relation to] the goitre problem. II. E. Wilke-Dörfurt (Biochem. Z., 1928, 192, 73—82).—The amount of iodine in the shells of a large number of different kinds of these animals is tabulated and discussed in relation to their source and to the goitre problem (cf. A., 1927, 642). P. W. Clutterbuck.

Possible increase of guanidine in blood in hypertension. R. H. Major and C. J. Weber (Arch. Int. Med., 1927, 40, 891—899).—By the use of a modification of the colorimetric method previously described by the authors (cf. Bull. Johns Hopkins

Hosp., 1927, **40**, 85) small increases in the amount of guanidine in the blood have been found in cases of arterial hypertension and larger increases in cases of uræmia. W. O. Kermack.

Amino-acid content of blood of children in health and in disease. S. H. Edgar (Biochem. J., 1928, **22**, 168—172).—The amino-acid nitrogen in fasting bloods is consistently lower than in non-fasting. The mean difference is 0·74 mg.-%. In rheumatism and chorea with or without carditis there is no change, in nephritis, on the other hand, and still more in renal and coeliac infantilism there is a lowering in the amino-acid nitrogen. S. S. Zilva.

Changes in catalase, lipase, and amylase content of blood of infants in digestive disturbances. M. Manicatide, A. Damboviceanu, and A. Rosianu (Compt. rend. Soc. Biol., 1927, **96**, 1243—1244; Chem. Zentr., 1927, ii, 707).—Infantile cholera and dyspepsia activate catalase, but do not affect lipase and amylase; athrepsia and dyspepsia with dystrophia reduce the activity of the lipase, the catalase and amylase remaining unaffected. During recovery the activity of the lipase and amylase is increased. A quinine-resistant lipase was found in the serum in infantile cholera. A. A. Eldridge.

Hydrogen-ion concentration of fæces of rachitic children. T. Redman (Biochem. J., 1928, **22**, 15—21).—There was no definite correlation between the different stages of rickets and the p_H values of the fæces of the patients under the conditions described. The p_H determinations were made by means of the quinhydrone electrode. S. S. Zilva.

Chlorides and inorganic constituents of serum and cerebrospinal fluid in meningitis. G. C. Linder and E. A. Carmichael (Biochem. J., 1928, **22**, 46—50).—The fall of chloride concentration in the cerebrospinal fluid in meningitis is dependent on a similar fall in the chloride concentration of the serum, the relative concentrations in the two remaining the same. The associated disturbances are an increase, sometimes large, of the hydrogen carbonate in both fluids and a small decrease in total base in the cerebrospinal fluid. Sometimes a greater depletion of base occurs in cerebrospinal fluid and in serum, and in such cases the hydrogen carbonate does not rise and may be low. S. S. Zilva.

Potassium and calcium in serum after ingestion of urea. R. E. Mark and E. Kohl-Egger (Zentr. inn. Med., 1927, **48**, 578—584; Chem. Zentr., 1927, ii, 710).—Normally the potassium content of dog's serum shows but slight changes after ingestion of urea, whilst the calcium value is raised and maintained for some time at a high level. In renal insufficiency the potassium content gradually rises and later falls, the calcium content exhibiting no marked change. A. A. Eldridge.

Cause of Andrewes' diazo-test for renal inefficiency. G. A. Harrison and R. J. Bromfield (Biochem. J., 1928, **22**, 43—45).—Andrewes' reaction (Lancet, 1924, i, 590) and Pauly's reaction are not identical. Histamine, tyramine, tyrosine, histidine, tryptophan, indole, and skatole do not give the former reaction. A cyclic amine such as histamine or tyramine cannot therefore be responsible for it (cf. Hewitt, A., 1925, i, 726). Evidence is produced that the substance in uræmic sera responsible for Andrewes' reaction is an indoxyl compound, presumably potassium indoxyl sulphate (indican) or possibly in part indoxyl glycuronate. S. S. Zilva.

Tuberculosis. I. Plasma proteins, cholesterol, and corpuscle volume. L. Eichelberger and K. L. McCluskey (Arch. Int. Med., 1927, **40**, 831—839).—As compared with normal the blood plasma of tuberculous patients shows an increase of fibrinogen and globulin and a decrease in albumin, the total protein being increased. The total cell volume is usually below normal, whilst the cholesterol content of the whole blood may be increased. An increasing or stationary hypercholesterolæmia indicates resistance to the disease. W. O. Kermack.

Glutathione content of organs of tuberculous guinea-pigs. P. Delore (Compt. rend. Soc. Biol., 1927, **96**, 974; Chem. Zentr., 1927, ii, 272).—The glutathione content of the organs of guinea-pigs is not constant, and is not definitely affected by experimental tuberculosis. As with dogs, the liver contains most and the lungs least glutathione. A. A. Eldridge.

Cystinuria in tuberculosis. R. Monceaux (Compt. rend. Soc. Biol., 1927, **96**, 323—324; Chem. Zentr., 1927, i, 3100).—The coefficient neutral/total sulphur is greatly increased in tuberculosis. Neutral sulphur appears in the urine as cystine; it is separated by clarification with lead acetate, removal of the lead with hydrogen sulphide, concentration, extraction with ammonia, concentration, and crystallisation. A. A. Eldridge.

Chlorine and sodium content of organs in uræmia. L. Blum and D. Broun (Compt. rend. Soc. Biol., 1927, **96**, 640—642; Chem. Zentr., 1927, i, 3014).—Uræmia is accompanied by chlorine retention; the sodium content is normal or increased with œdema, but reduced in absence of œdema. The brain and the musculature are particularly considered. A. A. Eldridge.

Basal metabolic rate of students in Sydney, N.S.W. E. M. Hindmarsh (Austral. J. Exp. Biol., 1927, **4**, 225—268).—The basal metabolic rate of 76 subjects has been determined by the gasometer method, by Benedict's oxygen absorption method, and by King's carbon dioxide output method. The methods gave respectively average reductions of 8·9, 9·6, and 6·0% for men and of 10·5, 10·9, and 7·3% for women, compared with the Du Bois standard values. It is suggested that these reductions are due to the more ready muscular relaxation of the students in the warm climate of Sydney. E. A. Lunt.

Regulation of metabolism. V. Hunger metabolism. Dependence of muscular glycogen deposition on the nervous system. VI. Neural regulation of glycogen deposition. E. Wertheimer (Pflüger's Archiv, 1927, **215**, 779—795, 796—803; Chem Zentr., 1927, i, 2570—2591).—Even in severe lack of glycogen, section of the ischiatic nerve or Achilles tendon is not accompanied by mobilisation of glycogen. Adrenaline acts directly on the liver, but through the nervous system on muscle. In severe hunger the fat deposition in the popliteal space after section of the ischiatic nerve is unchanged. Results with dogs, cats, rabbits, and guinea-pigs are compared. A. A. Eldridge.

Changes in blood and urine of starving puppies. G. W. Pucher (J. Biol. Chem., 1928, 76, 319—329).—New-born puppies were deprived of food and water, with the result that the body temperature fell, there was marked retention of carbamide and slight retention of chlorides in the blood, the oxygen and water content of the blood remained unchanged, and the blood-sugar fell to 30 mg.-% or less, without, however, the occurrence of hypoglycæmic convulsions. Puppies 6 weeks old showed similar, but much less marked reactions to starvation. No inanition fever, such as occurs in human infants and is associated with similar changes in the blood, was ever observed in these animals. C. R. Harington.

Pentose metabolism. II. Disposal of *l*-arabinose and of *d*-xylose in the rabbit. R. C. Corley (J. Biol. Chem., 1928, 76, 23—30).—Oral administration of *l*-arabinose, with or without dextrose, caused no change in the blood or urine; after intravenous injection, the excess of arabinose disappeared from the blood within 3 hrs. in the normal or insulin-treated rabbit, but was still marked after 4 hrs. in the rabbit suffering from tartrate nephritis. With oral doses of *d*-xylose up to 2 g. per kg. the maximum concentration attained in the blood and the rate of excretion in the urine was proportional to dosage; larger doses had no increased effect; simultaneous administration of dextrose, and, to a smaller extent, of lævulose, diminished the absorption of xylose. C. R. Harington.

Metabolism of lactose. III. Galactose tolerance in the rabbit. R. C. Corley (J. Biol. Chem., 1928, 76, 31—42).—Similar results were obtained with galactose to those already observed (cf. preceding abstract) with *d*-xylose. In presence of large amounts of dextrose, removal of galactose from the intestine can take place without corresponding increase in the blood; this process of removal is probably not bacterial. A dose of dextrose given subsequently to one of galactose reduced the concentration of the latter in the blood. C. R. Harington.

Effect of muscular work on endogenous tissue catabolism. H. H. Mitchell and J. H. Kruger (J. Biol. Chem., 1928, 76, 55—74).—The endogenous tissue catabolism of rats, as measured by the urinary excretion of creatinine, was not increased by muscular work when the diet contained much carbohydrate and little fat or much fat and little carbohydrate. It follows that, in the presence of sufficient non-nitrogenous food material to meet the energy requirements, tissue breakdown is not a necessary result of muscular work. C. R. Harington.

Chemical changes in the proteins of muscular tissue when passing into rigor. H. R. Hewer, H. Jairam, and S. B. Schryver (Biochem. J., 1928, 22, 142—143).—The experiments were carried out with the gastrocnemius and sartorius muscles of the frog. When the muscle was thrown into boiling 20% hydrochloric acid for hydrolysis immediately after excision it gave a single twitch when coming into contact with the hot vapour or liquid. Under these conditions about 30% of diamino-nitrogen was obtained. If the preliminary twitch was abolished by previous treatment of the animal with either urethane or β-eucaine the figure fell to 26—27%. If, on the other hand, the muscles were allowed to pass into rigor by remaining in a moist chamber for about 20 min. at 40° the diamino-nitrogen rose to 36%. This sank to about 30—31% when the muscles were allowed to pass out of rigor by keeping for several hours at 40°. The results are very analogous to the results obtained by the treatment of gelatin with acids (cf. Knaggs, A., 1923, i, 1143; Schryver and Buston, A., 1927, 785; Thornley, this vol., 81).
S. S. Zilva.

Dehydrogenation of succinic acid. A. Hahn and W. Haarmann (Z. Biol., 1928, 87, 107—114).—Fumaric acid is primarily formed when succinic acid is dehydrogenated by muscle tissue in a vacuum in the presence of methylene-blue and is then converted into malic acid by enzymic action. Other products are also formed in smaller amounts, presumably by dehydrogenation of malic acid, but these have not been identified. The criticism by Bach and Michlin (A., 1927, 591) of the theory of dehydrogenation of succinic acid in the muscle–methylene-blue experiments is not supported. A method for determining fumaric acid in the presence of malic and succinic acids is described. A. Wormall.

Cholesterol. III. Relation of the adrenal gland and the spleen to cholesterol metabolism. F. S. Randles and A. Knudson (J. Biol. Chem., 1928, 76, 89—93).—Removal of the spleen or of the adrenal glands has no effect on the cholesterol content of the blood of the rat. C. R. Harington.

Lipin metabolism and constitution. H. Much (Arch. Frauenk. Konstit., 1926, 12, 353—367; Chem. Zentr., 1927, ii, 595).—A discussion.
A. A. Eldridge.

Lipin metabolism and generative glands. R. Jaffé (Arch. Frauenk. Konstit., 1926, 12, 368—376; Chem. Zentr., 1927, ii, 282).—A survey.
A. A. Eldridge.

Fat metabolism. I. Influence of single foodstuffs on blood-lipins. C. W. McClure and M. E. Huntsinger (J. Biol. Chem., 1928, 76, 1—18).—The nitrogen and dextrose content of the blood were slightly diminished following ingestion of fat (oleic acid or olive oil); the cholesterol and fatty acid content was increased by all types of foodstuff. The iodine numbers of the cholesterol fraction showed a decrease after all types of food, suggesting qualitative variations in the sterols of the blood. The fatty acids of the blood were increased by all foods, whilst the lecithin-phosphorus was affected only by ingestion of oleic acid, which produced an increase. Changes in the iodine number accompanying increase in the fatty acid concentration after ingestion of oleic acid indicate that the increase is not due to the latter acid alone, and in general, the variations in blood-lipins observed in these experiments are ascribed to mobilisation of lipins from the tissues. C. R. Harington.

Oxidation of phenyl-fatty acids in the animal organism. H. S. Raper and E. J. Wayne (Biochem. J., 1928, **22**, 188—197).—Normal phenylpropionic, phenylbutyric, phenylvaleric, and phenylhexoic acids when administered to dogs yield amounts of benzoic and phenylacetic acids, as the case may be, which indicate that the fatty acid side-chain is oxidised quantitatively in accordance with the theory of β-oxidation. Under the same conditions phenylnonoic and phenyldecoic acids yield smaller amounts of benzoic and phenylacetic acid, respectively, than would be expected if quantitative β-oxidation of the side-chain takes place, which suggests that some other mode of oxidation occurs, in addition, with phenyl-fatty acids containing side-chains approaching in length those of the higher fatty acids. Cinnamic and phenyl*iso*crotonic acids yield the same amounts of benzoic and phenylacetic acids, respectively, as the corresponding saturated acids.

θ-*Phenylnonoic acid*, m. p. 29—30°, was prepared by esterification and reduction from *η-benzoyloctoic acid*, m. p. 74·5—75° (*semicarbazone*, m. p. 151·5—152°), obtained from azelaic acid. The methods for the preparation of the other acids are given.

S. S. Zilva.

Nutritive value of hydrogenated oils. S. Ueno, M. Yamashita, Y. Ota, and Z. Okumura (J. Soc. Chem. Ind. Japan, 1927, **30**, 378—385).—Olive oil, cotton-seed oil, cod-liver oil, peanut oil, soya-bean oil, sesame oil, and deodorised coconut oil were hydrogenated at 120° under conditions which would not destroy vitamin-*A*. In each case the hydrogenated oil gave a result superior to that of the original oil. This is attributed to the fact that the hardened oil consists chiefly of the glycerides of the saturated acids and of the oleic acid series, which are stable to light and air, and also that toxic substances are eliminated during purification and hydrogenation.

Y. Tomoda.

Nutritive value of fat. III. J. Ozaki (Biochem. Z., 1928, **192**, 428—430).—The nutritive value of a variety of natural fats is determined using rats by the method previously described (A., 1926, 1272; B., 1926, 930; this vol., 86), vitamin-*A* being added to each in order to prevent disturbances due to vitamin deficiency. The nutritive values of the fats examined decrease in the following order: butter, rapeseed oil, arachis oil, olive oil, liver fat, herring oil, cotton-seed oil, triolein, beef fat, lard, whale oil, and sardine oil. Liver fat does not appear to have a specially high nutritive value and its therapeutic importance must depend on its vitamin content.

P. W. Clutterbuck.

Digestion in the cockroach. III. Digestion of proteins and fats. V. B. Wigglesworth (Biochem. J., 1928, **22**, 150—161).—The proteolytic enzymes of the cockroach consist of a tryptase and a peptidase. Peptase is absent. The tryptase resembles pancreatic trypsin in the products of digestion, the relative production of "free acidity" and "formaldehyde acidity" during digestion, the effect of salts, and in acting on proteins only on the alkaline side of their isoelectric point. Its range of activity, however, extends further in the acid direction. The peptidase is present in the intestinal secretion. It has been partly separated from the tryptase by adsorption and it appears to have an optimal zone of activity about p_H 8·5. Lipase as present in a crude emulsion of the cockroach gut is usually but not constantly activated by sodium glycocholate, but is not activated by phosphates apart from their influence as buffers. Its optimal zone is around p_H 8·0. It is almost inactive at the normal reaction of the crop.

S. S. Zilva.

Digestibility of proteins of cotton seed. W. D. Gallup (J. Biol. Chem., 1928, **76**, 43—53).—The coefficient of digestibility (for the albino rat) of the proteins of cotton-seed meal is lower than that of the seeds themselves; the digestibility of both is reduced by autoclaving. Addition of gossypol to the diet in sub-lethal amounts had no effect on the digestibility of these proteins. C. R. Harington.

Value of whole potato in human nutrition. S. K. Kon and A. Klein (Biochem. J., 1928, **22**, 258—260).—An experiment is described in which two adults, a man and a woman, lived over a period of 167 days in nitrogen equilibrium and in good health on a diet in which the nitrogen was practically solely derived from the potato. The daily nitrogen intake was on the average 5·7 g. for the man and 3·8 g. for the woman. S. S. Zilva.

Nutritional value of tuberin, the globulin of potato. S. K. Kon (Biochem. J., 1928, **22**, 261—267).—Tuberin appears to be a complete protein from the dietetic point of view. Its biological value as measured at an 8% level of intake by Mitchell's method is 71. When fed to rats according to Osborne, Mendel, and Ferry's method a maximal gain of 2 g. body-weight per g. of protein ingested was found at a 7—8% level of intake. S. S. Zilva.

Relation of protein to mineral metabolism. S. Lauter (Verh. deuts. Ges. inn. Med., 1926, 330—331; Chem. Zentr., 1927, ii, 283).—With a diet rich in carbohydrate and fat and poor in mineral matter, there was an increase in alveolar carbon dioxide tension and blood alkali reserve, without change in nitrogen excretion, and a decrease in chlorine, sodium, and potassium. Administration of hydrogen chloride (oral) and sodium dihydrogen phosphate (intravenous) reduces the alveolar carbon dioxide tension, the blood alkali reserve, and the p_H of the blood, but there is a marked increase in the ammonia and nitrogen elimination. A. A. Eldridge.

Sodium chloride and protein content of the serum of pigs in feeding. T. Radeff (Arch. wiss. prakt. Tierheilk., 1926, **55**, 300—305; Chem. Zentr., 1927, ii, 278).—The sodium chloride content of fish meal fed to pigs does not affect the sodium chloride content of the serum. A. A. Eldridge.

Iron metabolism. II. Iron and hæmoglobin formation. III. Observations with animals kept in rarefied air. W. Lintzel (Z. Biol., 1928, **87**, 97—106, 137—144).—II. Young rats from the same litter have been fed on a practically iron-free diet consisting of egg-white, filtered lard, refined crystalline sucrose, specially treated rice, and vitamins (milk and orange juice), with and without the addition of iron in the form of ferric chloride or diluted ox-blood.

The total iron content of the animal and the hæmoglobin-iron were determined by a method described. The results show that the inorganic iron of the food can be utilised for the formation of hæmoglobin and to increase the total body-iron, whereas equivalent amounts of hæmoglobin-iron are without significant effect. It is calculated that one half to two thirds of the total hæmoglobin present has been synthesised from inorganic iron. The effect of inorganic iron in stimulating growth is confirmed, but the view that inorganic iron stimulates the bone-marrow is unnecessary.

III. Rats were kept for 1—5 weeks in rarefied air of pressure 280 mm. (corresponding with a height of 8000 metres) and fed on a mixed diet. The body-weight shows a decrease, whilst the absolute amount of hæmoglobin-iron increases up to 100%, the total iron increases to a less extent, and the weight of the heart (fresh and dry matter) also increases. After 3 weeks at the low pressure, acclimatisation is complete and no further increases in the iron values occur. Similar experiments with rats on an iron-free diet indicate that no appreciable increase (up to 20% only) in the hæmoglobin-iron occurs at the expense of the rest of the body-iron. A. WORMALL.

Sulphur metabolism. H. FLURIN (Progr. méd., 1926, **54**, 1706—1713; Chem. Zentr., 1927, ii, 282).—A critical discussion. A. A. ELDRIDGE.

Purine metabolism. V. Nuclear-plasmic ratio of frogs. R. TRUSZKOWSKI (Biochem. J., 1928, **22**, 198—200).—From monthly determinations over a period of more than a year it is concluded that the nuclear-plasmic ratio of *Rana esculenta* has a value of approximately double that of mammals. It is highest from May to January, the value falling slightly during the periods of winter sleep, hunger, and sexual activity which follow. The existence of specific reserve protein in the cytoplasm of the frog is not confirmed. S. S. ZILVA.

Uricæmia in its relation to nucleoprotein metabolism. I. Uricæmic equilibrium and the place of origin of endogenous uric acid. II. Action of the liver on degradation products of nucleoproteins. L. GAROT (J. physiol. path. gen., 1926, **24**, 525—540, 556—571; Chem. Zentr., 1927, ii, 283).—Supply of nucleoproteins effects a reduction of the uric acid value of the blood independently of the endogenous blood uric acid content. There is more uric acid in venous than in arterial blood. Liver function in respect of purine derivatives is discussed. A. A. ELDRIDGE.

I. Influence of administration of active iron oxide and of radiothorium on the formation of blood and on metabolism in normal rabbits, in regard to the urinary C : N quotient. II. Influence of radiothorium on the urinary C : N quotient. III. Influence of narcosis on the urinary C : N quotient (dysoxidisable carbon in urine after narcosis). A. A. GOLDBLOOM (Biochem. Z., 1928, **192**, 250—271, 272—297, 298—302).—I. Attempts to increase the red cell count of the blood of normal rabbits having failed, similar attempts are made using simultaneous administration of active iron oxide and radioactive substances. With daily peroral administration of 5 mg. of active iron oxide and 75 units of radiothorium per kg., the C : N ratio is, but the red cell count is not increased. Increasing the dose of radiothorium to 150 units or more led, however, to an increase in the number of red cells.

II. Daily peroral administration of radiothorium (22—240 units per kg.) causes a rise of urinary C : N ratio and a single intravenous injection of radiothorium (150—5000 units) causes in rabbits a gradual rise of the ratio.

III. The urinary C : N ratios in dogs before, during, and 1—4 days after narcosis by morphine, ether, ether and morphine, chloroform and morphine, or chloroform, morphine, and atropine are tabulated. Morphine, morphine with chloroform, and morphine, chloroform, and atropine did not affect the ratio, but ether and ether with morphine caused considerable increase, but only on the day of narcosis. P. W. CLUTTERBUCK.

Relation between (*a*) external hydrogen-ion concentration and (*b*) thallium salts and the rate of amphibian metamorphosis. J. BELEHRADEK, J. S. HUXLEY, and F. R. CURTIS (Biochem. J., 1927, **22**, 63—66).—The rate of metamorphosis induced by keeping frog tadpoles in weak thyroid extracts depends on the p_H of the medium, being, between p_H 6·8 and 8·0, greatest on the alkaline side and least on the acid side. This effect is not connected with variations of the internal p_H. In tadpoles treated with free iodine no definite effects of different external p_H could be detected. There is no antagonism between thallium and the metamorphosis-accelerating function of foreign thyroid or of the tadpoles' own thyroid under the conditions of this investigation. S. S. ZILVA.

Changes of the liver during diminished atmospheric pressure and during autolysis. A. LOEWY and J. LEIBOWITZ (Biochem. Z., 1928, **192**, 67—72).—The previous experiments (A., 1927, 792) on the distribution of phosphorus between the ether extract and residue of the normal liver and of the liver after a period under reduced pressure are repeated using rabbits, guinea-pigs, and rats, this time care being taken to use reagents free from phosphorus. The results with rats and rabbits are indecisive, but with guinea-pigs an increase of ether-soluble phosphorus (phosphatides) during diminished pressure from 5% to 15—36% of the total phosphorus is obtained, thus confirming the former result. Autolytic changes, although not totally excluded, do not account for these results. P. W. CLUTTERBUCK.

Production of hyperglycæmia by subcutaneous injections of arsenious oxide in the rabbit. F. P. UNDERHILL and A. DIMICK (J. Biol. Chem., 1928, **76**, 163—170).—Injection of sub-lethal amounts of arsenious oxide into rabbits produces marked hyperglycæmia, accompanied by disappearance of glycogen from the liver but by practically no glycosuria. C. R. HARINGTON.

Influence of arsenious acid on respiration and fermentation. II. K. DRESEL (Biochem. Z., 1928, **192**, 351—357).—In continuation of previous work

(A., 1927, 73) the effect of different concentrations of arsenious acid and the action of dextrose and metallic salts on the inhibition by arsenious acid of respiration and fermentation of yeast are investigated. Inhibition of fermentation by arsenious acid is always somewhat less than of respiration, but a concentration of 10^{-4} mol. considerably inhibits both. Increasing the concentration of dextrose decreases the inhibitory effect. Iron, manganese, cobalt, copper, zinc, and nickel sulphates all inhibit both respiration and fermentation of yeast. If respiration and fermentation are inhibited by 2×10^{-4} mol. of arsenious acid, addition of metallic salts then causes no change.

P. W. Clutterbuck.

Action of arsenious acid on the respiration model, especially on the oxidation of tartaric acid in presence of iron. K. Dresel (Biochem. Z., 1928, **192**, 358—368).—The influence of temperature on the oxidation of tartaric acid in presence of iron is investigated. The oxygen utilisation at 21° with concentrations of iron increasing from $M/4000$ to $M/1000$ after 60 min. is 0—14·9 mm.^{3} of oxygen, whereas at 37° it is 134 to >800 mm.^{3} The production of carbon dioxide is equal to the oxygen utilisation. Arsenious acid inhibits oxidation of tartaric acid at the ordinary temperature and at 37·5°, the greater the concentration of acid the greater the inhibition, and the inhibition increases with the time of reaction. Addition of iron counteracts the inhibition of oxidation by arsenious acid.

P. W. Clutterbuck.

Value of cholesterol determinations in blood in lead poisoning. E. Kühn (Zentr. Gewerbehyg., 1927, **14**, 117—129; Chem. Zentr., 1927, ii, 602).—In lead poisoning the cholesterol content of the total blood is frequently higher than that of the serum, whereas the reverse is normally the case. The frequency of the inversion, however, is not great enough to be regarded as specific for lead poisoning.

A. A. Eldridge.

Aromatic nitro- and amino-compounds as blood-poisons. W. Lipschitz (Zentr. Gewerbehyg., 1927, **14**, 11—14; Chem. Zentr., 1927, i, 2752).—In both cases the chief symptom is methæmoglobinæmia. Oxygen and quinine are antidotes.

A. A. Eldridge.

Influence of tetrahydro-β-naphthylamine on tissue oxidation and some of its partial processes. U. von Euler (Skand. Arch. Physiol., 1927, **51**, 129—135; Chem. Zentr., 1927, ii, 1365).—Decolorisation of methylene-blue in finely-minced muscle (rabbit, frog, and guinea-pig) takes place more rapidly in presence of 10^{-10} to 10^{-4} (max. 10^{-6}) parts of tetrahydro-β-naphthylamine, and more slowly in presence of 10^{-3} parts. Washed muscle reacts only in presence of succinate as donator.

A. A. Eldridge.

Influence of parasympathetic poisons on blood-sugar concentration. I. S. Láng and M. Vas. II. S. Láng and L. Rigo (Biochem. Z., 1928, **192**, 137—143, 172—175).—I. The action of pilocarpine, physostigmine, muscarine, choline, and atropine on blood-sugar concentration is investigated. Substances which stimulate the parasympathetic system in small doses decrease, and in large doses increase, the blood-sugar concentration, whilst medium doses show a diphasic effect, at first increasing and then decreasing. Atropine behaves similarly, but choline in large doses tends to decrease rather than to increase the blood-sugar. The results cannot be explained in terms of variation in the water content of the blood.

II. Arecoline, acetylcholine, and scopolamine in small doses decrease and in large doses increase the blood-sugar concentration, whilst atropine inhibits the blood-sugar lowering effect of pilocarpine.

P. W. Clutterbuck.

Pharmacological determination of atropine. J. de D. Fernandez (Arch. exp. Path. Pharm., 1928, **127**, 197—203).—The isolated heart of the grass- or water-frog, brought to a standstill by acetylcholine, has been used to determine the strength of atropine solutions. The time required for the latter to abolish the standstill is noted and compared with the effect of suitable standard atropine solutions. If the atropine solution is not too strong, the atropine can be washed out of the heart completely by Ringer solution and several successive determinations can be made on the same heart.

A. Wormall.

Detection and determination of atropine in the smoke of *Stramonium* cigarettes. J. de D. Fernandez (Arch. exp. Path. Pharm., 1928, **127**, 204—211).—The smoke from cigarettes prepared from *Stramonium* leaves was drawn through acidified distilled water and the solution purified. The presence of atropine in these solutions was demonstrated by the chemical tests of Vitali and of Arnold, and pharmacologically by the effect on cat's-eyes and by the relaxation of isolated ox bronchial muscle contracted by pilocarpine. The determination of atropine was made by the frog's heart method (cf. preceding abstract) and by the antagonistic effect on the lowering of the blood-pressure of the cat by acetylcholine. The purified smoke solution from 1 g. of leaves, which contain about 3 mg. of alkaloid per g., contains 0·1 mg. of atropine, but this is a minimum figure, since much alkaloid is destroyed during purification. A. Wormall.

Detection of caffeine, morphine, and barbituric acid derivatives in the brain [following intravenous injection]. Problem of sleep. II. E. Keeser and I. Keeser (Arch. exp. Path. Pharm., 1928, **127**, 230—235).—Caffeine, after the injection of 0·1—100 mg. per kg. into the ear vein of a rabbit, can be detected by a sublimation method (cf. A., 1927, 1110) in all the parts of the brain examined when the animal is killed ½—5 hrs. after the injection. After the injection of morphine (0·005—0·12 g. per kg.), morphine can be detected similarly in relatively large amounts in the diencephalon and also in the great hemispheres; in no case did the mid-brain, the pons, medulla oblongata, or the cerebellum give positive results. Injection of barbituric acid derivatives (veronal, luminal, or diallylbarbituric acid) in amounts of 40—70 mg. per kg. led to a recovery of the narcotic in the diencephalon, principally in the thalamus, whilst the results were negative with the great hemispheres, mid-brain, medulla oblongata, pons, and cerebellum. These results are discussed in relation to the problem of sleep. A. Wormall.

System catalase—anticatalase in blood and various animal organs under different physiological and pathological conditions. E. D. Gagarina and W. D. Jankowsky (Compt. rend. Soc. Biol., 1927, 97, 481—482; Chem. Zentr., 1927, ii, 1353).—With animals poisoned by morphine there is an increase of catalase in all organs, especially the liver and muscle, but a considerable decrease in the blood catalase. The anticatalase content of all organs except muscle and lungs is reduced. With arsenic poisoning there is an increase of catalase and anticatalase in organs and a decrease in the blood; with alcohol poisoning there is a reduction of catalase and anticatalase in the liver and blood, and a small increase in the other organs. A. A. Eldridge.

Alkaloid ferrocyanides. M. Gadreau.—See this vol., 314.

Chemical constitution and toxicity. E. Walker (Biochem. J., 1928, 22, 292—305).—The toxicity was measured against the unicellular organism *Colpidium colpoda* and also against *Glaucoma scintillans*. Most of the compounds investigated were arsenic derivatives, but some antimony, bismuth, and mercury compounds have also been examined. Aromatic arsenic compounds are more toxic than the aliphatic derivatives, the tervalent derivatives than the quinquevalent derivatives, the secondary derivatives than the primary and tertiary derivatives, and the primary derivatives than the tertiary derivatives. The most toxic arsenic compounds are the tervalent secondary derivatives and within this class compounds of the diphenylarsine type are the most toxic. There are indications that antimony compounds are more toxic than the corresponding arsenic compounds. Organisms which have ceased all movement under the influence of arsenic can be revived at once and continue to live for periods up to 2 hrs. by the addition of a suitable sulphydryl compound. Unicellular organisms afford only a measure of general protoplasmic toxicity. S. S. Zilva.

***In vitro* tests of the toxicity of certain drugs for hydatid scolices.** I. C. Ross (Austral. J. Exp. Biol., 1927, 4, 283—288).—The action of acriflavine, trypan-blue, potassium antimony tartrate, and emetine on hydatid scolices has been examined *in vitro*. A 1 in 1000 solution of acriflavine proved fatal in 3 hrs. and a 1 in 10,000 solution in 8 hrs.; a 1 in 1000 solution of the tartrate killed all scolices in 6 hrs. Emetine and trypan-blue proved relatively ineffective, a large proportion of scolices remaining active after 14 hrs. with a 1 in 1000 solution of the former, and after 16 hrs. with a 1 in 200 solution of the latter. E. A. Lunt.

Acid penetration into living tissues. N. W. Taylor (J. Gen. Physiol., 1928, 11, 207—219).—Evidence is obtained that acid penetration through a membrane occurs either in the form of the undissociated molecule or by the simultaneous passage of hydrogen ion and an anion, and that the sourest acids are those which penetrate most rapidly. Measurements have been made of the threshold concentrations for sourness of nine acids, and the relative concentration gradients of the undissociated acids across the cell membrane have been calculated for a series of acids having equal sourness. It is considered that a comparison of the data obtained, and the relative concentration gradients calculated from acid penetration experiments of other workers, with the results of adsorption experiments on charcoal, indicates that the acids are taken up by the tissues by adsorption processes. Polar groups (OH, Cl, and Br) reduce markedly the ability of organic acids to penetrate living tissues. The influence of the optical character of the acid on penetration is briefly discussed. A. Wormall.

Cell physiology. V. Antagonism of cations in their actions on the protoplasm of *Amœba dubia*. P. Reznikoff (J. Gen. Physiol., 1928, 11, 221—232).—By means of immersion and injection experiments (cf. Chambers and Reznikoff, A., 1926, 759) the antagonistic effects of the chlorides of calcium, lithium, sodium, and potassium for amœbæ have been determined. Lithium chloride has a much greater dispersing effect on the plasmalemma and liquefies the internal protoplasm even more markedly than sodium chloride. Both calcium and magnesium antagonise sodium in its action on the plasmalemma much better than they antagonise potassium, whilst the reverse occurs with the internal protoplasm. The antagonistic effect is greater with magnesium than with calcium against sodium in the immersion experiments and against potassium in the injection experiments. With higher and toxic concentrations of the salts, the combined solutions of antagonising salts are more rapidly toxic than either alone. The antagonistic action of these salts with the internal protoplasm differs from that with the surface membrane, and there appears to be no relationship between the degree of antagonising power and the solidifying or dispersing effect on protoplasm of each salt individually. A. Wormall.

Penetration of methylene-blue into living cells. M. M. Brooks (Proc. Nat. Acad. Sci., 1927, 13, 821—823).—The influence of p_H in the range 5·4—9·0 on the rate of penetration of methylene-blue into the living cells of *Valonia* has been investigated. At 25° penetration is so rapid that no variation can be detected; at 22·5° the rate of penetration increases with increasing p_H. Spectrophotometric analyses indicate that this dye is absorbed as such and undergoes subsequent oxidation in the cell to trimethylthionine. E. A. Lunt.

Affinity of different types of enzyme for their substrates. J. B. S. Haldane (Nature, 1928, 121, 207).—The enzymes can be classified into three groups according to the values of the dissociation constants of the enzyme-substrate compounds: (*a*) of low affinity, including the hydrolytic enzymes acting on crystalloidal substrates, yeast carboxylase, and liver catalase, (*b*) of medium affinity, consisting of the enzymes which hydrolyse colloidal substrates, (*c*) of high affinity, consisting of the only oxidising-reducing enzymes other than catalase so far studied (plant peroxidase, milk xanthine-oxidase, yeast oxygenase). A. A. Eldridge.

Structure and enzyme reactions. III. System polysaccharide–amylase–protein. S. J. Przylecki and H. Niedzwiecka (Biochem. J., 1928, **22**, 34—42; cf. Przylecki and others, A., 1927, 1113).—Ten g. of powdered caseinogen adsorbs 20% of starch from 50 c.c. of 1% solution of the latter. Alcohols reduce adsorption by 13—15%. Coagulated egg-white adsorbs from 30 to 40% of the starch under the above conditions and in this also the adsorption is reduced by the presence of alcohols by 20%. The action of the alcohols in both cases is elutive. Seventy to 95% of pancreatic amylase is adsorbed by coagulated egg-white. Alcohols affect the adsorption of the enzyme only to a small extent. Liver coagulum also adsorbs amylase. Although the enzyme cannot be removed from the residue by washing, the latter retains the activity for several months. Alcohols also do not remove the enzyme from this residue. Similar results of irreversible adsorption were obtained by treating amylase with carbohydrate-free liver coagulum. Glycogen causes a negligible elution of amylase from egg-white or from liver coagulum. The presence of coagulated egg-white or liver coagulum retards the velocity of the enzymic hydrolysis of starch in proportion to the degree of adsorption. The addition of alcohols to such systems leads to an acceleration of reaction proportional to the degree of elution of adsorbed polysaccharide. In the presence of fresh egg-white the reaction is scarcely retarded and the addition of small quantities of alcohols has no accelerating effect on the velocity of hydrolysis. The velocity of reaction in the system polysaccharide–amylase–protein gel is therefore regulated entirely by the concentration of unadsorbed substrate. S. S. Zilva.

Diastase. IV. Extractable and non-extractable α-diastase content of different kinds of cereals. V. Synievski (Biochem. Z., 1928, **182**, 457—462).—The α-diastase and nitrogen contents of samples of oats, wheat, rye, and barley are tabulated. The number of diastatic units per mg. of nitrogen decreases in the following order: wheat, barley, rye, oats. About one third of the diastase of wheat and barley, four fifths of that of rye, and the whole of that of oats can be extracted by water. The proportionality between the number of α-diastase units and the nitrogenous material rendered extractable by the action of papain is only slight. Agreement is approximate for barley and wheat but deviation is considerable with rye and oats (cf. A., 1925, i, 469; 1926, 93). P. W. Clutterbuck.

Conversion of α- into β-diastase. F. Polak and A. Tychovski (Biochem. Z., 1928, **192**, 463—478).—The optimal p_H for α-diastase is 5·10 and for β-diastase 4·30. A normal barley extract (20 g. of barley and 100 c.c. of distilled water) has a p_H of 6·30, its β-diastase action being increased 17 times by displacement of the p_H to 4·30. An extract of barley after treatment of the grain with papain contains, at the optimal p_H, twice the amount of β-diastase as an ordinary aqueous extract. It is concluded that by changes of p_H conversion of α- into β-diastase occurs. P. W. Clutterbuck.

Enzymic decomposition of α- and β-glycerophosphoric acids. P. Karrer and R. Freuler (Festschr. A. Tschirch, 1926, 421—424; Chem. Zentr., 1927, i, 3064).—A comparison of the behaviour of synthetic racemic sodium α- and β-glycerophosphates towards glycerophosphatase. The hydrolysis is equally rapid in the two cases, and follows the same course; it proceeds best in strongly acid solution. A. A. Eldridge.

Biochemical synthesis of glycerides. Reversibility of enzymic action of the cytoplasm of the castor-bean. A. Morel and L. Velluz (Compt. rend., 1928, **186**, 43—46).—The active portion of the castor-bean is the cytoplasm, which, when activated by 0·1*N*-acetic acid in presence of olive oil by a special process, washed, dried, and pulverised, is capable of causing both hydrolysis of olive oil and the reverse process of esterification. B. W. Anderson.

Synthetic action of bacterial lipases. N. van der Walle (Zentr. Bakt., 1927, II, **70**, 369—373; Chem. Zentr., 1927, ii, 583).—*Bacillus pyocyaneus* esterifies oleic acid with propyl, *iso*butyl, amyl, hexyl, or octyl alcohol, methylnonylcarbinol, or glycerol, but not with methyl, ethyl or benzyl alcohol or ethylene glycol. Acetic acid was not esterified with methyl, ethyl or amyl alcohol or glycerol, nor butyric acid with glycerol. *Staphylococcus aureus* powder esterifies oleic acid with glycerol, but not with amyl alcohol. *B. prodigiosus* esterifies oleic acid with glycerol. *B. coli* ferment powder does not affect mixtures of oleic acid with *iso*butyl alcohol, amyl alcohol, or glycerol. The ferment powder from *B. dysenteriæ* (*a*) Shiga-Kruse and (*b*) Flexner was inactive for mixtures of oleic acid and amyl alcohol or glycerol. The synthesis is never quantitative. Possibly the unsaturated character of oleic acid is concerned with its reactivity. A. A. Eldridge.

Action of bile on the tributyrinolytic power of blood-serum. L. Avellone (Riv. pat. sperim., 1926, **1**, 395—399; Chem. Zentr., 1927, ii, 278).—In presence of bile, serum-lipase appears not to be inhibited by quinine. A. A. Eldridge.

Effect of rennin on caseinogen. II. Properties of casein. V. Pertzoff (J. Gen. Physiol., 1928, **11**, 239—253).—Purified casein preparations, obtained by the action of rennin on caseinogen (cf. A., 1927, 895), dissolve in combination with base to the extent of 1450 g. per mol. of sodium hydroxide at 21—37°, compared with a combining weight of 2100 g. for caseinogen under the same conditions; a comparison of the titration curves of the two proteins confirms the view that casein is a stronger acid than caseinogen. Casein is not a product formed by partial hydrolysis or by denaturation of caseinogen, nor is it identical with caseinogen modified by excess of alkali. A casein preparation which gave an abnormal base-combining capacity (1700 g. per mol. of sodium hydroxide) does not appear to be a mixture of casein and caseinogen, and no appreciable alteration in the combining capacity occurred on digestion with rennin. A. Wormall.

Peptic digestion of coagulated egg-white. E. G. Young and I. G. Macdonald (Trans. Roy.

Soc. Canada, 1927, [iii], 21, V, 385—393).—Coagulation of egg-white by heating at 100° for 2—30 min. does not affect the rate at which it is digested *in vitro* by pepsin. W. O. Kermack.

Xanthine oxidase. X. Action of light. F. Bernheim and M. Dixon (Biochem. J., 1928, 22, 113—124).—The reduction of methylene-blue by the xanthine oxidase system is markedly accelerated by light but only if traces of oxygen are present. Previous exposure of the oxidase solution or the methylene-blue to light in the presence of oxygen for short periods produces an acceleration of the reaction. Exposure for longer periods produces a destruction of the enzyme. Neither effect occurs on irradiation in the absence of oxygen. These phenomena are due to the formation of an active oxidising agent, probably hydrogen peroxide, by the action of light since the presence of $10^{-6}M$-hydrogen peroxide in general more than doubles the activity of the enzyme whilst a very definite acceleration is produced by $10^{-8}M$. In higher concentrations the peroxide destroys the enzyme. The nature of the effect produced by a peroxide solution of given strength and by methylene-blue which has been exposed to light and oxygen depends on the amount of oxidase present. The accelerating action of added hydrogen peroxide on the enzyme also takes place when aldehyde is substituted for hypoxanthine and nitrate for methylene-blue. In presence of peroxidase the peroxide formed during the aërobic irradiation of methylene-blue solutions is able to carry out secondary oxidations of nitrites. This oxidation does not occur in the absence of either peroxidase, oxygen, or light. S. S. Zilva.

Reduction of nitrates in animal tissues. F. Bernheim and M. Dixon (Biochem. J., 1928, 22, 125—134).—The livers of all the animals studied but only the muscle of the rat and the guinea-pig reduced nitrate. Hydrogen donators did not increase the reduction of nitrate by washed muscle. The dehydrases of muscle are incapable of reducing nitrate. The properties of the nitrate-reducing system in muscle are described. The system appears to be enzymic and completely disappears on addition of $0\cdot002M$-cyanide. In the liver the nitrate-reduction is due to (*a*) a system having the same properties as that in muscle and (*b*) the aldehyde (xanthine) oxidase probably identical with that in milk. The two systems can be separated. No hydrogen donator other than the substrates of the oxidase has been found which will increase the reduction of nitrate in liver. S. S. Zilva.

Melanin formation. H. Schmalfuss (Naturwiss., 1927, 15, 453—457; Chem. Zentr., 1927, ii, 713).—Most melanins are formed by a fermentative process, whereby a chromogen (*e.g.*, 3 : 4-dihydroxyphenylalanine), a suitable gas (*e.g.*, oxygen), and a suitable ferment are necessary. The formation of melanin under various conditions was examined. It is inhibited by sulphur dioxide, hydrogen sulphide, hydrogen cyanide, chlorine, bromine, and ammonia, and by a hydrogen-ion concentration greater than 5×10^{-5}. Light has no effect. The ferment is destroyed by heat, but a heat-resistant material produces melanin at high temperatures. A. A. Eldridge.

Crystalline urease. II. J. B. Sumner and D. B. Hand (J. Biol. Chem., 1928, 76, 149—162; cf. A., 1926, 1061, 1176).—Inactivation of crystalline urease by dilution of its aqueous solution may be prevented by using 2% gum arabic as a diluent. A modification of the author's method for obtaining crystalline urease is described which may be applied to Jack beans of low enzymic content. The typical crystalline preparations described have never been obtained free from urease; urease is but slightly adsorbed on the crystalline proteins of the Jack bean; the enzymic activity of the preparations rises on re-crystallisation; the identity of the preparation with the enzyme itself is therefore regarded as established. C. R. Harington.

Effects of phloridzin and other substances on fermentations by yeast. W. J. Dann and J. H. Quastel (Biochem. J., 1928, 22, 245—257).—Phloridzin shows a much higher retarding action on the normal rate of zymin fermentation of dextrose than salicin, æsculin, or amygdalin, especially when relatively small quantities of the substances are used; 10^{-4} g.-mol. of phloridzin effects a 31% retardation and 10^{-3} g.-mol. a 59% retardation of the rate of fermentation due to zymin. Phloretin shows a similar but somewhat less vigorous action than phloridzin. The rate of fermentation after addition of phloridzin is linear. Of the polyhydric phenols, phloroglucinol is the most effective in retarding the rate of fermentation of dextrose by zymin. The retarding action of phloridzin is not exhibited in the zymin fermentation of pyruvic acid or in the fermentations of dextrose and pyruvic acid by living yeast. Allyl alcohol and acrylic acid retard fermentation of dextrose by zymin and living yeast, the retardation increasing with time. Neither allylamine nor allylacetic acid has such an action. The rate of the evolution of carbon dioxide was measured by Tryhorn and Jessop's apparatus. S. S. Zilva.

Isolation of a second sterol from yeast-fat. I. Smedley-Maclean (Biochem. J., 1928, 22, 22—26).—A sterol, *zymosterol*, $C_{27}H_{42}O$, m. p. 108—109° $[\alpha]_{5461}$ in ether, $+34\cdot1°$ (*acetate*, m. p. 112—113°) present in yeast is described. It can be separated from the less soluble ergosterol of the crude sterol fraction by recrystallisation from alcohol, ether, and acetone. The iodine value suggests the probable presence of three ethenoid linkings. It can be brominated. Specimens of zymosterol in a dilution in alcohol of 1 in 20,000 showed no selective absorption in the ultra-violet region. In lower dilutions the absorption bands characteristic of ergosterol in this region are visible. Like ergesterol it is precipitated by digitonin. S. S. Zilva.

Formation of fats by micro-organisms. G. Seliber (Mon. Sci. Inst. Lesgaft, Leningrad, 1926, 1—101).

Diffusion products of bacterial cells as influenced by the presence of various electrolytes. H. J. Shaughnessy and C. F. A. Winslow (J. Bact., 1927, 14, 69—99). Chemical Abstracts.

Soluble specific substances of Friedländer's bacillus. III. Types *A* and *C*. W. F. Goebel and O. T. Avery (J. Exp. Med., 1927, **46**, 601—607; cf. A., 1927, 1114).—The carbohydrate obtained from type *A* has α_D −100 to −105°, acid equivalent 430—445, C, 43·98, H, 6·00%, and gives 64—68% of reducing sugars (as dextrose) and a sugar acid on hydrolysis. The carbohydrate obtained from type *C* has α_D +100°, acid equivalent 680, yields about 75% of reducing sugar (chiefly dextrose) and a sugar acid.

Chemical Abstracts.

Nitrogen fixation by *Azotobacter chroococcum*. S. Ranganathan and R. V. Norris (J. Indian Inst. Sci., 1927, **10A**, 79—96).—An examination of the carbon metabolism of *A. chroococcum* is described. The decreased activity of cultures of the organism with age was more marked in mineral salts-mannitol-agar than in soil extract-mannitol-agar media. The amount of nitrogen fixed increases as the amount of sugar fermented. More than half of the total fixation of nitrogen occurs in the first few days of the fermentation. No definite relationship exists between the amount of nitrogen fixed and the concentration of sugar in the media. The acceleration of nitrogen fixation by phosphates is not accompanied by any reduction in the amount of sugar decomposed. During the fermentation of dextrose by *Azotobacter*, carbon dioxide, ethyl alcohol, aldehyde, and formic, acetic, lactic, and tartaric acids are formed. Ammonia is probably the first product of nitrogen fixation and is probably elaborated into complex substances through the intermediate stage of mono- and di-amino-acids. Cells contain about 30% of protein matter and considerable amounts of fat and phosphatides.

A. G. Pollard.

Certain cell constituents of acid-fast [bacteria] and their antigenic character. I. A. Korff-Petersen and W. Liese (Z. Immunitätsforsch., 1927, **51**, 87—114; Chem. Zentr., 1927, ii, 583—584).

A. A. Eldridge.

Reaction between toxin and antitoxin and the significance for the immune action of serum. S. Schmidt (Dansk Tidsskr. Farm., 1928, **2**, 25—40).—The rate of flocculation of toxin by antidiphtheritic sera of different individuals is very variable. The variations in the flocculability, however, show no relationship to the antitoxin titre and often a serum feeble in antitoxic power flocculates more rapidly than a serum rich in antitoxin. In general, a satisfactory agreement is found between the velocity of neutralisation and that of flocculation. Heating at 60° for 1 hr. sometimes destroys the flocculating power, but the neutralisation affinity between toxin and antitoxin is not affected. Salts have a marked influence on the rate of flocculation and also retard or prevent the formation of the toxin–antitoxin complex. The influence of sodium iodide on the latter process is very marked and suitable amounts may produce at least partial dissociation of the toxin–antitoxin complex, even when this is in the form of a precipitate. The instability of the complex supports the conception of Arrhenius and Madsen that there is a reversible reaction, toxin+antitoxin $\rightleftharpoons$ toxin–antitoxin complex.

A. Wormall.

"Kombucha." I and II. S. Hermann (Biochem. Z., 1928, **192**, 176—187, 188—199).—"Kombucha" is allied to fungi and contains besides *Bacterium xylinum* and *B. xylinoides* a previously unknown bacillus, *B. gluconicum*, which converts dextrose quantitatively to gluconic acid. Sucrose, on account of the presence of yeasts, is also quickly decomposed and from the invert-sugar large amounts of gluconic acid are obtained, whilst the alcohol formed by fermentation is oxidised to acetic acid. It is suggested that the therapeutic action of "Kombucha" is related to the presence of *B. gluconicum*.

P. W. Clutterbuck.

Decomposition of organic substances in the sea. J. Kořínek (Biochem. Z., 1928, **192**, 230—237).—Organic material in the neighbourhood of the coast is decomposed by sea-water bacteria, the fresh-water bacteria, swept down into the sea, taking no important part. In the mixing of sea- and fresh-water, that type of bacteria develops for which the salt concentration is optimal. Most soil bacteria have their optimum in fresh-water; the more sea-water added, the more is their growth inhibited. Sea- and fresh-water mixed in different proportions do not show proportional differences in p_H because of the difference in the type of bacteria finding their optimal conditions in the different mixtures. In general, the bacterial flora of brackish and sea-water causes greater acidification of a fluid containing dextrose than the flora of fresh-water. Sea-water appears to rid itself of fresh-water bacteria chiefly by their agglutination.

P. W. Clutterbuck.

Factors causing variable results with flagella stains. W. H. Wright (Stain Tech., 1928, **3**, 14—27).—A summary of the methods of staining flagella is given and the effects of varying such conditions as the reaction of the mordant and the temperature at which the staining is performed are discussed.

H. W. Dudley.

Preparation of agar culture media. A. R. Grace (Austral. J. Exp. Biol., 1927, **4**, 269—270).—A method is described for the preparation of clear agar jelly in which the dry agar is tied into a gauze bag suspended in the water in an Erlenmeyer flask in which the jelly is to be made. The flask is autoclaved for 25 min. at 120°, the bag raised out of the water, and the agar allowed to drain out of the bag for 10 min. at 110°, again in the autoclave. E. A. Lunt.

Respiration and glycolysis of the skin and the influence of hormones. E. Klopstock (Dermatol. Woch., 1926, **83**, 1468—1471; Chem. Zentr., 1927, i, 3015). A. A. Eldridge.

[Action of various substances on the composition of the blood.] II. Thyroid gland. III. Tyramine. F. Rothschild and M. Jacobsohn. **IV. Adrenaline. V. Atropine. VI. Choline.** M. Jacobsohn and F. Rothschild (Z. klin. Med., 1927, **105**, 403—405, 406—409, 410—413, 414—416, 417—419; Chem. Zentr., 1927, ii, 105—106).—After administration of "thyreophorin" (0·3—1·0 g.) the blood-cholesterol and -calcium (usually) are increased, the residual nitrogen, potassium, and organic phosphorus decreased, and the sugar and organic phosphorus unchanged. In patients with marked exophthalmic goitre injection of tyramine tartrate (0·5 mg.) reduces the blood-sugar, cholesterol, organic phosphorus and calcium, and increases the potassium and residual nitrogen, whereas with animals different results were obtained. Adrenaline raises the blood-sugar, calcium, and cholesterol, and diminishes the potassium and phosphorus. Atropine (with animals) increases the sugar and inorganic phosphorus and decreases the cholesterol and organic phosphorus. Choline causes a fall in sugar, cholesterol, and inorganic phosphorus, and a rise in organic phosphorus. A. A. Eldridge.

Effect of thyroid substance, adrenaline, and insulin on the lactacidogen content of muscle and the phosphoric acid of organs. Y. Terada (Folia endocrinol. japon., 1926, 2, 13—15, 302—331).—Injection of adrenaline or ingestion of thyroid substance reduces the lactacidogen content of the femoral quadriceps of the rabbit; insulin increases it. The total phosphorus of the blood, heart, and kidneys is increased, and that of the liver reduced, by adrenaline, thyroid, thyroidectomy, or insulin; muscle-phosphorus is increased by the last and diminished by the first three. Chemical Abstracts.

Effect of adrenaline on oxidation processes. A. Bornstein (Arch. exp. Path. Pharm., 1927, **127**, 63—68).—Addition of adrenaline to oxygenated defibrinated goose-blood does not influence the oxygen consumption. Similarly, no increase in oxygen usage of a surviving leg of the dog perfused with dog-blood or calf-blood occurs when adrenaline is injected intravenously. Intraperitoneal injection of adrenaline causes a marked increase in the oxygen usage of normal dogs, but not in that of curarised dogs. This increased oxidation in the normal animal is not primary, but is attributed to the increased tension, excitability, and tremor of the muscles. A. Wormall.

Influence of adrenaline on acetone excretion in disease. S. Hirschhorn and L. Pollak (Z. klin. Med., 1927, **105**, 371—402; Chem. Zentr., 1927, ii, 102).—Acetonuria in normal metabolism is markedly increased by the subcutaneous injection of adrenaline (1 mg.); in diabetes the reaction is not constant. A. A. Eldridge.

Insulin. III. Action of insulin on the formation of lactic acid in the liver. U. Sammartino (Arch. Farm. sperim., 1927, **44**, 11—21).—In rabbits to which insulin is administered, the amount of lactic acid collecting in the liver amounts to 50·06 mg. per 100 g. of liver, which is similar to the quantity found in the same animals subjected to Bernard's puncture (A., 1924, i, 446). T. H. Pope.

Determination of dextrose insulin equivalents. K. L. E. Lamers (XII Int. Cong. Physiol., 1926, 94; Chem. Zentr., 1927, ii, 103).—For the determination of the dextrose equivalent of insulin, the sugar must be administered subcutaneously. Part of the sugar actually undergoes combustion, and part may be converted into acid products. A. A. Eldridge.

Decomposition of dextrose in toxic insulin action. F. Fischler (Münch. med. Woch., 1927, **74**, 680—682; Chem. Zentr., 1927, i, 3097).—In toxic insulin action there is an abnormal decomposition of dextrose with increased formation of methylglyoxal, to which the toxic effect is due. Traces of an iodoform-forming substance can be recovered from the blood and muscles of animals poisoned with insulin. A. A. Eldridge.

Action of insulin. III. Action on the gaseous exchange of the tortoise. B. von Issekutz and F. Végh (Biochem. Z., 1928, **192**, 383—389).—The gaseous exchange of the tortoise is greatly increased by insulin, but the R.Q. is unchanged (cf. A., 1927, 594). P. W. Clutterbuck.

Influence of insulin and dextrose on the oxygen consumption of surviving frog's spinal cord. H. J. Wolf (Pflüger's Archiv, 1927, **216**, 322—336; Chem. Zentr., 1927, ii, 103).—Addition of insulin, not too long after the death of the animal, to the frog's spinal cord suspended in dextrose solution can effect a considerable increase in the oxygen consumption. Insulin alone scarcely affects the respiration of the spinal cord. Dextrose alone increases the oxygen consumption only when the cord is injured or the animal diseased. A. A. Eldridge.

Effect of insulin on the morphological and chemical condition of the blood. A. Schmidt and R. Saatčian (Zhur. eksp. biol. med., 1926, 4, 353—379).—The blood solids are increased; the light petroleum extract, the inorganic phosphorus, and the serum-calcium are diminished. Convulsions cause an increase in serum-calcium and inorganic phosphorus. It is suggested that insulin promotes the formation of lactacidogen, which undergoes fission during convulsions; the phosphorus is swept into the blood. Chemical Abstracts.

Action of insulin on the lipins of the blood. I. Oku (Folia endocrinol. japon., 1926, 2, 279—301).—The lipæmia caused by olive oil, lard, and cod-liver oil is attributable chiefly to the fatty acids. Alimentary lipæmia is suppressed by insulin. Chemical Abstracts.

Uric acid metabolism and insulin. L. Kurti and G. Györgyi (Klin. Woch., 1927, **6**, 1426—1428; Chem. Zentr., 1927, ii, 1362).—Administration of insulin, in small doses, to persons with otherwise normal uric acid excretion produces delay in the excretion of exogenous uric acid. On long-continued administration of insulin a limitation of purine supply is indicated. A. A. Eldridge.

Liver glycogen after partial pancreatectomy in the guinea-pig. B. Splatt (Austral. J. Exp. Biol., 1927, 4, 213—219).—The continued daily injections of pituitrin or of insulin into guinea-pigs effects a diminution of the glycogen content of the liver. In the latter case this effect is somewhat compensated by partial pancreatectomy. A diminution in the case of insulin, and a slight increase in the case of pituitrin, in the residual adrenaline of the suprarenals follows the injection of these substances into guinea-pigs in which a portion of the pancreas has been removed. E. A. Lunt.

Pituitrin and blood-lipins. G. Blix and C. A. Ohlin (Skand. Arch. Physiol., 1927, **51**, 167—174; Chem. Zentr., 1927, ii, 1361).—Subcutaneous administration of pituitrin to rabbits and dogs does not affect the blood-cholesterol; neutral fat is diminished, but the phosphatide-fatty acid fraction is considerably reduced (max. 3—9 hrs.). A. A. Eldridge.

Relation of the parathyroid hormone to the calcium content of the blood and to blood coagulation. L. M. Zimmermann (Klin. Woch., 1927, 6, 726—730; Chem. Zentr., 1927, i, 3202).—The increased calcium content of the blood produced by Collip's parathyroid extract has no influence on the coagulation time. A. A. Eldridge.

Placental hormone ("feminin"). E. Glimm and F. Wadehn (Klin. Woch., 1927, 6, 999—1000; Chem. Zentr., 1927, ii, 273—274).—The crude extract of the placenta is treated with cold acetone in neutral and alkaline solution to separate it from phosphatides and part of the fatty acids; the residue after evaporation of the acetone is extracted with methyl alcohol, and the residue on evaporation is dissolved in ether and shaken with water. On evaporation of the ether there remains a brown oil which is poured into much light petroleum from which there falls a brownish precipitate containing 0·25—0·5 of the amount of hormone present. The solution of this substance in dilute ammonia solution is freed from resin by shaking with ether. A more active preparation can be obtained from the hormone remaining in the light petroleum. The hormone is attacked by atmospheric oxygen. A. A. Eldridge.

Detection of thyroxine in hyperthyroidised mammals. B. Zawadowsky and G. Asimov (Pflüger's Archiv, 1927, 216, 65—81; Chem. Zentr., 1927, i, 2918).—Thyroxine was detected in hyperthyroidised guinea-pigs by the use of axolotls. The hormone accumulates in the liver; in the blood it appears chiefly in the serum. Hens destroy the hormone more slowly, and detection is easier. Acceleration of the metamorphosis of axolotls is a more convenient and certain test than the acceleration of metamorphosis and deceleration of growth of tadpoles. A. A. Eldridge.

Vitamins of orange juice. S. G. Willimott (Biochem. J., 1928, 22, 67—76).—The juice of the navel orange contains sufficient vitamin-*A* in 5 c.c. for growth and well-being of the rat; 10 c.c. of Valencia orange juice are adequate for the vitamin-*B* requirements of the rat. Vitamin-*D* is not present in the navel orange juice. Analyses of the juices are tabulated. S. S. Zilva.

Vitamin-*A* deficiency and urolithiasis. E. C. van Leersum (J. Biol. Chem., 1928, 76, 137—142).—The observation of Osborne and Mendel (J. Amer. Med. Ass., 1917, 69, 32) regarding the frequency of occurrence of calcium phosphate calculi in rats on a diet deficient in vitamin-*A* is confirmed. It is suggested that the cause may be keratinisation of the epithelial cells of the renal tubules, analogous to the xerophthalmia known to be associated with deficiency of vitamin-*A*. C. R. Harington.

Antineuritic yeast concentrates. III. Curative pigeon test: a critique. H. W. Kinnersley, R. A. Peters, and V. Reader (Biochem. J., 1928, 22, 276—291).—The conditions necessary for obtaining good quantitative results with the curative test on pigeons are enumerated. A summary of the methods of feeding pigeons is given. S. S. Zilva.

Vitamin-*B* required during lactation. H. M. Evans and G. O. Barr (J. Biol. Chem., 1928, 76, 263—272).—For satisfactory rearing of the young, the vitamin-*B* intake of the lactating rat must be increased to about 5 times the usual amount; the essential part of the extra requirement is the antineuritic fraction of vitamin-*B*. C. R. Harington.

Effect of diastase on polyneuritis developed on diets rich in starch. L. Randoin and R. Lecoq (J. Pharm. Chim., 1927, [viii], 6, 340—346).—The effect of the addition of diastase to diets rich in starch and free from vitamin-*B* has been found, in the pigeon, to accelerate slightly the rate of development of polyneuritis. This effect is attributed to the increased digestibility of the carbohydrate of the diet. Partial cooking of the diet is shown to have the same effect. The sources of starch used were separated rice and potato starch. Addition of diastase to a diet rich in barley flour appears to retard the development of the polyneuritis. E. A. Lunt.

Examination of yeast-fat for the presence of vitamins-*A* and -*D* before irradiation and of vitamin-*D* after irradiation. E. M. Hume, H. H. Smith, and I. Smedley-Maclean (Biochem. J., 1928, 22, 27—33).—A sample of total fat derived from pressed brewer's yeast showed no activity for vitamin-*A* when administered in daily doses of 0·18 g. Daily doses of 0·14 g. of a sample of acetone-soluble fat prepared from yeast which had been incubated in a carbohydrate–phosphate solution were found to promote neither growth nor the formation of bone in rats on diet deficient in the fat-soluble vitamins (cf. Luce and Smedley-Maclean, A., 1925, i, 483). The same two kinds of yeast-fat together with a sample of fat prepared from yeast after a preliminary boiling with normal acid were irradiated with the mercury vapour quartz lamp and very small doses of these were fed to rats on a diet deficient in the fat-soluble vitamins. The best results were obtained with the fat derived from incubated yeast which promoted growth and bone formation in daily doses of 0·005 mg. S. S. Zilva.

Determination of vitamin-*D*. H. Jephcott and A. L. Bacharach (Biochem. J., 1928, 22, 60—62).—The lowering of the fæcal p_H of rats on a rachitic diet by the administration of vitamin-*D* is a function of the amount administered. S. S. Zilva.

Determination of vitamin-*D*. E. Poulsson and H. Lövenskiold (Biochem. J., 1928, 22, 135—141).—The rats are kept on a Steenbock and Black or similar diet (A., 1925, i, 1020) and after a preparatory period of 25 days a skiagram of the left knee-joint is taken and the animals are weighed. The antirachitic substance to be tested is then given for 6 days, at the end of which time another skiagram is taken and the rats are again weighed. The minimum protective dose is taken as a unit and is expressed by the number of such units per g. of active substance. S. S. Zilva.

Antirachitic substances. VII. Purified cholesterol. C. E. Bills, E. M. Honeywell, and

W. A. MacNair (J. Biol. Chem., 1928, **76**, 251—262). —Provitamin-*D* is not entirely removed from cholesterol by bromination or treatment with charcoal but is reduced to about 3% of the original amount. A concentrated solution of cholesterol so treated shows the three characteristic absorption bands of ergosterol, together with two further bands at 315 and 304 $\mu\mu$; the latter bands may represent some substance other than ergosterol which can be activated by ultra-violet light. In addition to the previously recorded absorption bands of ergosterol, there has been observed a fourth band, common to it and to cholesterol, at 260 $\mu\mu$. C. R. Harington.

Sterols and antirachitic vitamin. A. Windaus and A. Hess (Nachr. Ges. Wiss. Göttingen, 1926, 175—184; Chem. Zentr., 1927, i, 2921—2922).—A discussion of the influence of irradiated foods on experimental rickets, of the properties of ergosterol, and of the differences between the provitamin and cholesterol. A. A. Eldridge.

Is the antirachitic vitamin of cod-liver oil an irradiated ergosterol? A. Adam (Klin. Woch., 1927, **6**, 1289; Chem. Zentr., 1927, ii, 1365).—Alcoholic extracts of cod-liver oil vitamin were prepared at various hydrogen-ion concentrations; with increasing p_H the extracts become darker, whereas at p_H 3—5 they are only faintly yellow. Fluorescence phenomena are different. The absorption spectra of the acid extracts closely correspond with those of irradiated ergosterol. The acid extracts have strong, and the alkaline extracts weak, antirachitic properties. Irradiation of the extract with the quartz lamp in presence of air affects the spectrum in the direction of greater permeability; hence the vitamin can be decomposed by irradiation. The whole of the substance precipitable by digitonin, including the vitamin, can be absorbed on animal charcoal. The spectrum of insulin is similar to that of an irradiated ergosterol. A. A. Eldridge.

Optical detection of a vitamin. R. Pohl (Naturwiss., 1927, **15**, 433—438; Chem. Zentr., 1927, ii, 711).—A lecture.

Influence of the cow's diet on the fat-soluble vitamins of winter milk. II. J. Golding and S. S. Zilva (Biochem. J., 1928, **22**, 173—182; cf. Golding and others, A., 1927, 79).—A winter ration for cows containing silage and hay is described which produced an antirachitic butter of moderate potency. The daily addition of 2 oz. of cod-liver oil to this ration did not significantly depress the percentage of milk-fat nor did it raise the vitamin-*D* of the butter to any appreciable extent. Higher doses of cod-liver oil depressed the percentage of milk-fat and raised the antirachitic potency of the butter. S. S. Zilva.

Relative food values of brown (from "entire" wheat grain) and white (from endosperm of grain) wheaten flour, and their comparative potency for prevention of xerophthalmia in guinea-pigs. E. J. Sheehy (Proc. Roy. Irish Acad., 1927, **37**, 415—425).—Guinea-pigs fed on mangels (20 g.), white flour *ad. lib.*, and 0·4 g. hydrogenated soya-bean oil decline in weight and contract xerophthalmia in 3—7 weeks. The xerophthalmia, but not the decline in weight, is cured when cod-liver oil is substituted for hydrogenated oil. When brown flour made from the entire wheat grain is substituted for white flour, xerophthalmia occurs much more rarely, although the animals decline in weight. If the diet is restricted, brown flour appears to be preferable as a food to white flour. W. O. Kermack.

Effect of irradiation and cod-liver oil on calcium balance in the human adult. M. C. Hart, D. Tourtellotte, and F. W. Heyl (J. Biol. Chem., 1928, **76**, 143—148).—Both irradiation and administration of cod-liver oil were without effect on the calcium balance of a human adult on a diet deficient in calcium. C. R. Harington.

Paralysis in sucklings of mothers deprived of vitamin-*E*. H. M. Evans and G. O. Burr (J. Biol. Chem., 1928, **76**, 273—297).—In the absence of a sufficiency of vitamin-*E* in the diet of the lactating rat, a large proportion of the young exhibit paralysis at the weaning period; this paralysis is specifically the result of deficiency of vitamin-*E*, since it occurs when all other vitamins and food constituents are administered in liberal amounts, and it is not associated with any deficiency in growth. C. R. Harington.

Rat technique for demonstrating interfering effect of cereals on bone calcification. H. N. Green and E. Mellanby (Biochem. J., 1928, **22**, 102—112).—A diet containing inactivated caseinogen, sodium chloride, "marmite," lemon juice, and dried cabbage was used. On such diet the rats grow. This and the ratio of ash of the bones to the difference between the weights of the fat-extracted dry bone and ash determined after a definite period (cf. Chick and others, A., 1927, 176) were used as criteria.

By this method the anti-calcifying action of cereals in rats was demonstrated (cf. Mellanby, Brit. Med. J., 1922, ii, 849; Med. Res. Counc. Report, series No. 93, 1925; J. Physiol., 1926, **61**, Proc., xxiv). The intensity of rickets was made worse by increasing the cereal intake whilst the other dietetic ingredients were kept constant. Oatmeal and wholemeal flour brought about the worst calcifications of the bones, whilst barley meal and white flour were associated with the best calcified bones. Germ of wheat and maize had a rachitic action. Cod-liver oil or cereal exposed to ultra-violet light neutralised the rickets-producing effect of these substances. The raising of the calcium carbonate or calcium phosphate content of the diet minimised the action of the cereals. The anti-calcifying action of cereals is destroyed by boiling with hydrochloric acid. S. S. Zilva.

[Formation of oxygen from carbon dioxide by protein–chlorophyll solutions.] M. Eisler and L. Portheim (Biochem. Z., 1928, **192**, 132—136). —The authors' original results (A., 1923, i, 424) are maintained in reply to the criticisms of Dolk and van Veen (A., 1927, 703). P. W. Clutterbuck.

Seasonal changes in conifer leaves, with reference to enzymes and starch formation. J. Doyle and P. Clinch (Proc. Roy. Irish Acad., 1927, **37**, 373—414).—The disappearance of starch from conifer leaves during the winter is associated with various tissue changes and in particular with a decrease in the activity of certain carbohydrate-splitting enzymes. W. O. KERMACK.

Seasonal variations in the carbohydrate content of pine and fir stems. E. GÄUMANN (Ber. deut. bot. Ges., 1927, **45**, 591—597).—Carbohydrate determinations by the König and Becker hexosan method were made on young and old pine and fir wood throughout the year. In young pine wood there were two periods of maximum carbohydrate content—in April and October—and a minimum period in February. Similar variations occurred in young fir wood. In both cases the spring maximum corresponded with a maximum in the water-soluble matter; but no autumn maximum in the water-soluble content was observed. In old wood variations in both carbohydrate and water-soluble matter contents were much smaller. Curves expressing the former were characterised by one minimum point occurring in March for the pine and in November for firs. The periodicity of the above values can be generally correlated with periods of maximum growth and assimilation. A. G. POLLARD.

Growth of grapes. II. Relationship between sugar and acid in the juice. III. Effect of environment on growth constants. P. R. v. d. R. COPEMAN (Trans. Roy. Soc. S. Africa, 1927, **14**, 389—393, 395—403; cf. A., 1927, 908).—II. The acid content of grapes decreases during ripening, whilst the sugar content increases. A mathematical expression of the relation is deduced and compared with the results of observation.

III. The constants occurring in the equations expressing the change in various factors during the growth of grapes are influenced by the locality in which the grapes are grown as well as by the variety of grape employed. W. O. KERMACK.

Effect of metallic salts on plant growth. M. CARETTE (J. Pharm. Chim., 1927, [viii], **6**, 151—156).—The effect of soaking seeds in potassium nitrate solution before planting has an excitatory rather than a nutritional value, and although it increases the rate of growth in the earlier stages it does not necessarily produce a high yield. E. A. LUNT.

Differential effect of the ions of three-salt solutions on growth of potato plants in sand culture. F. G. GREGORY (Proc. Roy. Soc., 1928, **B**, **102**, 311—327).—The work of Johnson (Maryland Agric. Exp. Stat. Bull., 1924, 270) is critically examined and discussed and the results are submitted to new statistical analysis. For a given relative ionic concentration, cations have a greater growth-producing effect than the anions examined. The effect of cations is in the order calcium (greatest), magnesium, potassium. Of the anions nitrate has a positive effect, sulphate is indifferent, and phosphate a negative effect. Based on these calculated values, it is shown that predicted yields for the solutions used by Johnson are more closely in agreement with the mean experimental results than are the results of duplicate experiments. A. G. POLLARD.

General presence of sodium in plants. G. BERTRAND and (MME.) M. ROSENBLATT (Compt. rend., 1928, **186**, 200—202).—The triple sodium magnesium uranyl acetate (cf. A., 1927, 1046) has been used in determining the sodium content of some 20 plants in which sodium has not hitherto been detected. The amounts of sodium found in the dry matter range from 0·0015% in wheat grain to 0·4112% in oat stems. The ratio K/Na ranges from 729 in potatoes to 2·05 in pea stems. B. W. ANDERSON.

Occurrence and significance of manganese in plants. D. H. WESTER (Festschr. A. Tschirch, 1926, 321—325; Chem. Zentr., 1927, i, 2914).—Fertiliser experiments show manganese to be of great importance in plant physiology. The active portions of *Lupinus luteus* are richest in manganese, which has a favourable influence on the content of active constituents of *Prunus laurocerasus*, *Brassica nigra*, and *Papaver somniferum*. A. A. ELDRIDGE.

Minimum toxicity of a mixture of two salts with respect to plants. L. MAUME and J. DULAC (Compt. rend., 1927, **184**, 1081—1083).—The root-growth of wheat in cultures containing standard dilute solutions of sodium or potassium chloride mixed in varying proportions with similar solutions of calcium or magnesium chloride has shown that the minimum toxic effect is produced when the two salts are present in such proportions that their ionisation coefficients are equal. B. W. ANDERSON.

Analysis of plant tissues. C. O. APPLEMAN, W. E. LOOMIS, T. G. PHILLIPS, W. E. TOTTINGHAM, and J. J. WILLAMAN (Plant Physiol., 1926, **1**, 397—402).—Recommendations by a committee of the American Society of Plant Technologists.

CHEMICAL ABSTRACTS.

Physical structure of pine lignin. W. FUCHS (Biochem. Z., 1928, **192**, 165—166).—Willstätter's lignin is doubly refracting and in the polarising microscope shows indistinct crystalline aggregates (cf. A., 1927, 546, 650). P. W. CLUTTERBUCK.

Evidence for phosphatides in the external surface of plant protoplast. F. C. STEWARD (Biochem. J., 1928, **22**, 268—275).—Leaching experiments with various parenchymatous tissues produced no evidence that phosphatides are present in the surface layer of the protoplasm or that they diffuse from living tissues into distilled water. S. S. ZILVA.

***Curcuma magna* rhizome.** R. GUTTENBERG (Z. ges. exp. Med., 1927, **54**, 642—652; Chem. Zentr., 1927, ii, 599).—Extraction of the rhizome with alcohol and ether yields a terpene, *curcumene*, $C_{15}H_{24}$, b. p. 140—142°/12 mm., d^{20} 0·90, α_D^{16} −10·5°; the compound is emetic, and has a slightly irritant action on the skin. It is partly excreted by the dog and rabbit conjugated with glycuronic acid. The extract also yields an irritant resin, and the alcohol extract a glucoside; the osazone of the sugar has m. p. 179—180°.

A. A. ELDRIDGE.

Chemistry of kirondro fruit. I and II. Y. VOLMAR and B. SAMDAHL (J. Pharm. Chim., 1927, [viii], **6**, 295—299, 346—353).—A bitter principle, to which the name *kirondrin* has been given, has been isolated from the seeds of the kirondro (*Perriera Madagascariensis*). By crystallisation from a mixture of alcohol and ether it has been separated into two fractions, α-*kirondrin* (m. p. 220—221°) and β-*kirondrin* (m. p. 237—240°) which are probably optical isomerides. To α-kirondrin the formula $C_{24}H_{27}O_{10}$ is assigned; it gives the general reactions for alkaloids, reduces silver nitrate and Fehling's solution in the cold, gives no phenylhydrazone even after hydrolysis, and exhibits an intense yellow fluorescence. It is thought to possess a lactonic structure, to be a derivative of anthracene, and to contain several aldehydo-groups, and no ethylenic linkings or phenolic groups. E. A. LUNT.

Seeds of *Nerium oleander*, L. H. MATTHES and P. SCHÜTZ (Festschr. A. Tschirch, 1926, 162—173; Chem. Zentr., 1927, i, 2753—2754).—The seed contains water 8·01, fat 17·43, nitrogen 2·8, crude protein 17·5, ash 3·76%. The seed oil has d^{15} 0·9355, n_D^{25} 1·4721, n_D^{40} 1·4669, acid value 2·5, saponification value 206·8, Reichert–Meissl value 16·30, Polensko value 0·40, iodine value (Hübl) 105·2 (2 hrs.), 108·6 (18 hrs.), acetyl value 12·5, Hehner value 92·09 (Hehner fatty acids n_D 1·4595), unsaponifiable matter 2·12%. The seta oil has d^{15} 0·9253, n_D^{70} 1·4550, saponification value 182·4, iodine value (Hübl) 91·4 (2 hrs.), unsaponifiable matter 8%. The solid fatty acids (iodine value 3·6) appeared to be a mixture of palmitic and stearic acids. The unsaponifiable matter contains a sitosterol, m. p. 137·5°. A. A. ELDRIDGE.

Occurrence of coumarin in indigenous plants. A. VON LINGELSHEIM (Festschr. A. Tschirch, 1926, 149—154; Chem. Zentr., 1927, i, 2914).—Coumarin is present in *Prunus avium*, *P. fructicosa*, and *P. fructicosa-Cerasus*. A. A. ELDRIDGE.

Non-alkaloidal constituents of ipecacuanha. O. KELLER (Festschr. A. Tschirch, 1926, 85—98; Chem. Zentr., 1927, i, 2916).—"Ipecacuanhic acid" is a glucotannoid or glucosidal tannin of weakly acid character. In addition to small quantities of fat and resin, an acid saponin, malic and citric acids are present. A. A. ELDRIDGE.

Extraction of asperuloside from *Galium verum*, L. Presence of the glucoside in *Rubiaceæ*. H. HÉRISSEY (Bull. Soc. Chim. biol., 1927, 9, 953—956, and J. Pharm. Chim., 1927, [viii], 6, 497—501).—See A., 1927, 1116.

Preparation of sinigrin. H. HÉRISSEY and R. BOIVIN (J. Pharm. Chim., 1927, [viii], 6, 337—339).—See this vol., 207.

Chemical nature of the glucoside of *Alliaria officinalis*. H. HÉRISSEY and R. BOIVIN (J. Pharm. Chim., 1927, [viii], 6, 385—387).—See this vol., 208.

Constituents of *Artemisia brevifolia*, Wallich. ANON. (Pharm. J., 1927, 119, 688).—The following substances have been isolated from *A. brevifolia*: *l*-camphor, m. p. 177°, $[\alpha]_D$ −44° (monobromide, m. p. 76°); an essential oil (terpene), b. p. 110—180°, *d* 0·950, and a white, crystalline *substance*, m. p. 80°, present to the extent of 0·01%, for which the name *brevifolin* is suggested. This substance gives an intense blue colour with concentrated nitric acid, is optically inactive, and is unaffected by light. E. H. SHARPLES.

Separation of tannins and anthocyanidins occurring in the same organs of plants. Isolation of a new anthocyanidin from the red leaves of *Acer platanoides*. S. IONESCO (Compt. rend. Soc. Biol., 1927, 96, 1020—1022, 1022—1023; Chem. Zentr., 1927, ii, 267).—Tannins may be separated from anthocyanidins by taking advantage of their solubility in ether. The anthocyanidin from the red leaves of *Acer platanoides* is named *aceridin* and is similar to pelargonidin except as regards solubility in water and acids. Substances can be extracted from organs by solvents in which the pure compounds are not soluble, owing to the existence of complexes or to adsorption phenomena. A. A. ELDRIDGE.

Red and blue colouring matters of flowers and fruits. A. E. TSAKALOTOS (Festschr. A. Tschirch, 1926, 291—298; Chem. Zentr., 1927, i, 2915).—The red and blue colouring matters of flowers are accompanied by chlorophyll and yellow colouring matters. A spectro-analytical examination of a solution of the anthocyanin zone indicates no sharp distinction of the anthocyans. The colouring matter of fresh, but not dried, whortleberries on capillarity separation yields a mixture of two components; a similar difference was observed with *Sambucus nigra*. Two distinct zones can also be observed with alkanet. A. A. ELDRIDGE.

Freezing as a method of preserving plant tissue for the determination of nitrogenous fractions. G. T. NIGHTINGALE, W. R. ROBBINS, and L. G. SCHERMERHORN (N.J. Agric. Exp. Sta. Bull., 1927, 448, 1—16).—Methods for the determination of nitrogen fractions are described which give results unaffected by freezing. CHEMICAL ABSTRACTS.

Colloidal albumin content of living plant cells. T. BOKORNY (Kolloid-Z., 1928, 44, 166—173).—An account of matter mainly already published on the aggregation of the cell contents of living plants. E. S. HEDGES.

Carbamide in fungi. N. N. IVANOV (Biochem. Z., 1928, 192, 36—40).—Reply to the criticisms of Kiesel (Ergeb. Biol., 1927). P. W. CLUTTERBUCK.

Formation of diastase by *Aspergillus niger*. G. L. FUNKE (Rec. trav. bot. neerl., 1926, 23, 200—244; Chem. Zentr., 1927, ii, 706).—Reducing sugars when sterilised in neutral solution become brown by the action of alkali from the glass, but in presence of acid phosphate there is no change. The brown material inhibits the growth of *Aspergillus* and retards the production of amylase; the production of amylase in lævulose solution, however, is increased Dextrose and starch promote, whereas lævulose, mannose, lactose, and inulin hinder amylase formation. Galactose as such does not reduce amylase formation, but the metabolic products of mannose do so. Glycerol has no effect. A. A. ELDRIDGE.

Rancidity of coconut oil produced by mould action. W. N. STOKOE (Biochem. J., 1928, 22, 80—93).—*Penicillium palitans* was grown on a gelatin medium containing deodorised coconut oil. The melted medium and growths were then distilled in a current of nitrogen. The residue, the aqueous and the oily distillates were examined. The odoriferous oily distillate was shown to contain methyl amyl, methyl heptyl, and methyl nonyl ketones. The methyl amyl ketone occurs in the greatest quantity and is responsible for the characteristic odour of the rancid oil. There were also present secondary alcohols corresponding with the ketones, ethyl alcohol, esters of the secondary alcohols and ethyl alcohol with caprylic acid and free fatty acids. The selective action of *P. palitans* and *Oidium lactis* was also studied on pure fatty acids, secondary alcohols, methyl ketones, keto-esters, and keto-esters in presence of beef-fat. The poisoning capacity of the fatty acids towards *Penicillium* increases with the mol. wt. up to *n*-octoic acid and then decreases. Only acids up to lauric acids are absorbed. The fatty acids with the exception of butyric acid and perhaps the lower acids are more poisonous to *O. lactis* than to *Penicillium*. *Oidium lactis* does not induce ketonic fission of the keto-acid. The fatty acids from coconut oil were oxidised with hydrogen peroxide by Dakin's method, but the formation of secondary alcohols as intermediate products could not be demonstrated. S. S. Zilva.

Significance of the red crystals appearing, on treatment with cresol-blue, in the cells of certain algæ. G. Manganot (Compt. rend., 1928, **186**, 93—95).—Iodides react with cresol-blue to form red crystals of oxonium iodide. This reaction is sensitive enough to enable the distribution of iodides in the vacuoles of algæ to be accurately determined.

B. W. Anderson.

Ergot. A. Damonte (Giorn. Farm. Chim., 1927, 76, 127—131; Chem. Zentr., 1927, ii, 150).—"Stabilisation" of ergot by means of alcohol under pressure is useless. Water extracts only part of the alkaloids, and the yield is scarcely increased when acidified water is used. A. A. Eldridge.

[Non-]effect of *X*-rays on decomposition of starch. E. Schneider (Strahlentherapie, 1926, 23, 326—335; Chem. Zentr., 1927, i, 3065).—Decomposition of starch was not observed.

A. A. Eldridge.

Occurrence of barium and probably strontium in arable earths. G. Bertrand and L. Silberstein (Compt. rend., 1928, **186**, 335—338).—The presence of barium in six samples of soils obtained from widely differing sources has been proved by spectroscopic examination of the alkali carbonate fusion products. In two cases the presence of strontium was observed. It is possible that all arable earths contain barium sulphate, and the occurrence of strontium is probably more common than has been shown. H. Burton.

Automatic gas analysis for respiration experiments. M. Kleiber and A. Wirth (Biochem. Z., 1928, **192**, 241—249).—An apparatus for automatic gas analysis in respiration experiments is described in which the result is registered photographically as a difference of pressure, arising after absorption of one constituent, between measuring and compensating pipettes, the accuracy of the method being claimed to be practically as good as in the Haldane method.

P. W. Clutterbuck.

Simple spectro-colorimeter. H. F. Holden (Austral. J. Exp. Biol., 1927, 4, 221—224).—This instrument is designed to obviate the use of the spectro-photometer in the determination of substances which themselves or in their derivatives show well-defined absorption bands in the visible spectrum, *e.g.*, for globin or for hæmoglobin. The apparatus consists of a colorimeter the illuminated cups of which provide a light source for a direct-vision spectroscope. The unknown and the standard solutions of the same substance are adjusted in the colorimeter until the intensities of their chief absorption band appear by means of the spectroscope to be equal.

E. A. Lunt.

Surface tension of physiological solutions. Difficulties of measurement and interpretation. J. M. Johlin (J. Gen. Physiol., 1928, **11**, 301—308).—Surface-tension values obtained by the ring method are not trustworthy when absolute values are required even with pure liquids, and with semi-colloids the changes in surface tension following the formation of a new interface are not consistently reproduced. The changes in the surface tension of gelatin solutions—a decrease sometimes followed by a rise as determined by the capillary rise method (cf. A., 1925, ii, 388)—show similar irregularities with the ring method, and the results indicate the impossibility of obtaining consistent results with solutions of this type. With solutions of semi-colloids, equilibrium values are not readily obtained and the rate of change of surface tension with time differs with similar solutions and occasionally with different samples of the same solution. A. Wormall.

Nephelometric determination of chlorine and silver. T. von Heidlberg (Biochem. Z., 1928, **192**, 238—240).—Nephelometric methods are described for the determination of silver and chlorine in small amounts. The limits of the method are about 0·005 mg. of silver nitrate when the error is about 3—5%. Above 0·1 mg., silver chloride precipitates.

P. W. Clutterbuck.

Electrolytic determination of arsenic in biological material. A. E. Osterberg (J. Biol. Chem., 1928, 76, 19—22).—A modification of the apparatus of Fink (A., 1927, 600) is described in which the whole sample may be placed in the cathode chamber, the reduction of the arsenic being thus facilitated.

C. R. Harington.

Micro-colorimetry. I. Molybdic acid–stannous chloride reagent. Determination of phosphate and calcium in pus, blood-plasma, and cerebrospinal fluid. T. Kuttner and H. R. Cohen (J. Biol. Chem., 1927, **75**, 517—531).—Substitution of stannous chloride for the quinol or other reducing agent employed by Briggs (A., 1922, ii, 718) and previous workers, yields a reagent which gives a more rapidly developing and intense colour with phosphates. With the aid of a micro-colorimeter the method allows of the determination of phosphates and of calcium (after incineration of the material and precipitation of calcium as tertiary phosphate) in 0·1—0·2 c.c. of the above biological materials.

C. R. Harington.