BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

JUNE, 1929.

General, Physical, and Inorganic Chemistry.

Hartmann formula for calibration of spectral apparatus. F. Hoffmann (Physikal. Z., 1929, **30**, 238—239).—The Hartmann formula, $p=p_0+C/(\lambda-\lambda_0)^a$ ($\lambda_0=0{\cdot}2$, $a=1$, roughly), can be expressed differently with advantage, *e.g.*, $p\lambda=a+b\lambda+cp$; $p(\lambda-c)=a+b\lambda$ and $\lambda(p-b)=a+cp$ ($a=C-p_0\lambda_0$, $b=p_0$, $c=\lambda_0$). Similar equations can be obtained using ν instead of λ. The use of linear expressions as above is preferable for convenience and accuracy to the expression $\nu=\nu_0+ap+bp^2$ used by Russell and Shenstone (J. Opt. Soc. Amer., 1928, **16**, 298).

R. A. Morton.

Electrified spherical films and the Stark effect. L. Décombe (Compt. rend., 1929, **188**, 1094—1096).

Intensity and polarisation of forbidden lines. A. Rubinowicz (Z. Physik, 1929, **53**, 267—273).—Expressions are deduced for determining the intensity and polarisation of radiation due to forbidden transitions in a one-electron system with central symmetry.

E. B. Robertson.

Breadth of resonance lines and possibility of their displacement towards the red by repeated scattering. W. Orthmann and P. Pringsheim (Z. Physik, 1929, **53**, 367—379).—A theoretical discussion of the effect of absorption and multiple scattering in vapours on the form of resonance lines.

E. B. Robertson.

Spectrum emitted by a carbon plate under bombardment. A. A. Newbold (Phil. Mag., 1929, [vii], **7**, 706—719).—The electrostatic method developed by Richardson and Bazzoni (A., 1917, ii, 521) for the examination of radiations from gases and vapours and adopted by Lukirsky (A., 1924, ii, 215, 368) for the detection of soft *X*-rays is shown to be capable of use in precision measurements of the latter. It has been employed for the examination of the spectrum emitted by a carbon plate by electrons with energy up to 600 volts. Over the frequency range 5700—26,000 the spectrum obtained resembled closely that determined by Millikan and Bowen for gaseous carbon.

A. E. Mitchell.

Spectra of alkali metals excited by active nitrogen. J. Okubo and H. Hamada (Phil. Mag., 1929, [vii], **7**, 729—736).—Previous work (A., 1928, 210) has been extended to a study of the effects of the density of the vapours of sodium, potassium, and cæsium on their spectra excited by active nitrogen. With sodium it is found that as the temperature of the metal is raised the initial yellow glow becomes filled with a greenish-yellow core which with further rise in temperature becomes definitely green. In this core the first subordinate series is more enhanced than the principal series, whilst in the yellow glow this effect is reversed; also the intensities of the lines in the former series are greater than those of corresponding energy in the latter series. In the core the intensity maximum is displaced towards the higher member, whilst in the yellow glow the reverse is the case. The core exhibits the green band spectrum, due to sodium molecules, in the position between the $2p-4d$ and $2p-6d$ lines. Analogous effects were obtained with the other metals.

A. E. Mitchell.

Selective absorption by excited mercury vapour. E. P. Metcalfe and B. Venkatesachar (Nature, 1929, **123**, 761).—A statement of priority (cf. Ponte, A., 1928, 808). A. A. Eldridge.

Broadening of spectral lines. B. Trumpy (Z. Physik, **53**, 57—60).—Anomalies discovered in earlier work (A., 1927, 179, 997) on the broadening of the mercury line 2537 Å. at high partial pressures of foreign gases are discussed, and a theory of the interaction of impact and radiation as a cause of broadening is put forward as an explanation.

E. B. Robertson.

Patterns and Paschen–Back analogue in the Stark effect for neon. J. S. Foster and W. Rowles (Proc. Roy. Soc., 1929, **A**, **123**, 80—103).—An extension of Nyquist's work on neon (Physical Rev., 1917, **10**, 226). Using the modified Lo Surdo discharge tube and high-potential apparatus previously described (Foster, A., 1927, 179), an examination has been made of the Stark effect for 150 lines in the neon spectrum in high fields. The observed patterns for the individual arc lines are in no case more complex than, and in the majority of cases appear to be identical with, those reported in parhelium for lines associated with the same n, l values for the outer electron in initial and final states. A considerable number of diffuse and combination lines exhibit a simpler pattern, consisting apparently of but one parallel and one perpendicular component, and the displacement may be as great as that of the standard (0,1) component. In low fields, especially, the displacements are relatively large. The intensities, however, are somewhat different in that the perpendicular component is much the stronger. The displacements in fields above 100,000 volts/cm. are in fairly good agreement with the results of quantum mechanics. The displacements for the different members of a complex line are

such that the structure tends to fuse and form the normal Stark effect characteristic of the corresponding singlet line, in a manner analogous to the appearance of the Paschen–Back effect in high magnetic fields. This effect is not symmetrical with respect to the normal line group, and is partial in the sense that only the initial terms are appreciably affected. The interpretations of the Stark effect in neon recently given by Stark (" Handbuch der Physik," 1926, **23**, 146) and by Ishida (A., 1928, 1066) are discussed.
L. L. Bircumshaw.

Helium band spectrum. S. Imanishi (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, **10**, 193—209).—Continuing with improved methods the work of Dieke, Takamine, and Suga (A., 1928, 1295), the region 3000—7000 Å. was investigated and the results were tabulated. Two new parhelium bands $2S_0$—$7P_0$ and $2S_0$—$8P_0$ at 3366 and 3307 Å., and a new orthohelium band $2s_0$—$5p_1$ at 3181 Å. were found. Bands $2s_1$—$5p_1$ and $2s_1$—$5p_0$ of orthohelium (cf. Weizel and Füchtbauer, A., 1927, 909) are completed up to the first line in every branch. Extended observations on Curtis' band (cf. A., 1923, ii, 351) $2s_0$—$5p_0$ are made.
N. M. Bligh.

Excitation of helium lines. R. von Hirsch and R. Döpel (Ann. Physik, 1929, [v], **1**, 963—976).—The fading constant ("Abklingkonstante ") of the stronger, photographically active helium lines has been obtained. The apparatus and method of calculation are described. There is considerable difference in the constant for the different lines examined. The experiments were carried out with four cathodes of different forms in order to make allowances for distortion due to pressure. The constants for both the strongest lines (λ 4472 and λ 3889 Å.) are independent of the method of excitation.
A. J. Mee.

Energy of the helium atom in the ground state. E. A. Hylleraas (Physikal. Z., 1929, **30**, 249—250).—The older quantum theory failed to account for the ionisation potential of helium, Bohr's first model leading to 28·15 volts, a second model studied by Bohr and Kramers leading to 20·63 volts, whilst Lyman's spectroscopic data required 24·46 volts. The new quantum theory yields the value 24·35 volts (A., 1927, 808; 1928, 698) and the reality of the remaining small discrepancy has now been studied. Lyman's ground term can be expressed as $\lambda = -1{\cdot}45175$, the author's earlier work led to $\lambda = -1{\cdot}4496$, whereas considerations now shown in outline lead only to $\lambda = -1{\cdot}45162$. R. A. Morton.

Calculation of the energy of helium in the fundamental state and the lowest terms of orthohelium. E. A. Hylleraas (Z. Physik, 1929, **54**, 347—366).—Mathematical. J. W. Smith.

Properties of the terms of the helium molecule. G. H. Dieke (Nature, 1929, **113**, 716—717).

Spectrum of H_2. Bands analogous to the parhelium line spectrum. I. O. W. Richardson and P. M. Davidson (Proc. Roy. Soc., 1929, **A**, **123**, 54—80; cf. A., 1928, 345, 812).—A re-examination of the series of band systems previously described (*loc. cit.*) with the help of Gale, Monk, and Lee's tables has shown that the bands already published are only a small fragment of a much larger number of related bands. Instead of 6 progressions with a maximum of 4 members each there are now more than 50 progressions, several of them extending to 9 members, including most of the strength of the secondary spectrum from 3394 to 8902 Å. The irregular doublets previously described have now disappeared, the lines of all the bands being single. The final states of all these progressions belong to the electronic state 2^1S. There are no combinations between any of the lines of these bands and those of the α, β, γ, etc. bands, but, on the other hand, they seem to have the same final states as the B states of Dieke and Hopfield, and so will presumably combine with the lines of the Lyman bands. A detailed account is given of the properties of the system $3^1B \longrightarrow 2^1S$ (the strong Q band system, in which each band consists solely of one single Q form branch); and of the system $3^1C \longrightarrow 2^1S$ (the system with R very strong, P weak). The two systems are similar in that they have upper states with practically the same moment of inertia for large m, and the intensity distribution in corresponding bands of the system is very similar. Whilst no lines of the Q system show the Zeeman effect, every strong line of the system with R strong, P weak shows it.
L. L. Bircumshaw.

Stark effect in a violet region of the secondary spectrum of hydrogen. J. K. L. MacDonald (Proc. Roy. Soc., 1929, **A**, **123**, 103—107).—Observations have been made on the Stark effect for 20 lines in the violet region 3980—4080 Å. The lines on the violet side of the region investigated are displaced towards the violet, and those on the red side towards the red; there is a slight overlapping of the two groups. No close agreement is observed with previous investigations. Five of the normal lines examined have a very close structure which has not been reported before. L. L. Bircumshaw.

Relative intensities of Stark components in hydrogen. J. S. Foster and L. Chalk (Proc. Roy. Soc., 1929, **A**, **123**, 108—118; cf. A., 1926, i, 1070; 1927, 179).—Three modifications of the Lo Surdo discharge tube are described, suitable for measuring the relative intensities of Stark components and their relative advantages are discussed. Using a neutral glass wedge, direct and indirect determinations have been made of the intensities of the stronger components of H_α, H_β, H_γ, and H_δ. The results for H_α, H_β, and H_γ are found to agree, within the limits of experimental error, with Schrödinger's calculations. The measurements on H_δ are uncertain and the results for the p components of H_γ are not satisfactory. It is considered probable that the variation from Schrödinger is principally due to experimental difficulties. L. L. Bircumshaw.

Continuous spectrum of the hydrogen tube. D. Chalonge and M. Lambrey (Compt. rend., 1929, **188**, 1104—1106).—The intensity of the continuous spectrum obtained from the authors' hydrogen discharge tube (A., 1927, 489) increases very slowly with pressure (1·5—4 mm.) and passes through a maximum at 2—3 mm. It also increases slowly with decrease of wave-length (from 4400 Å.) and attains a maximum at 2200 A. Since the distribution of energy in the spectrum undergoes no appreciable modification with changing conditions of discharge and with different tubes it is suggested that such tubes might be useful as standards of intensity in the ultra-violet region.

J. Grant.

Fulcher bands of hydrogen. I. Sandeman (Proc. Roy. Soc. Edin., 1929, 49, [i], 48—64).—A co-ordination and extension of Richardson's arrangement (cf. A., 1926, 873; 1927, 1) and the measurements of Gale, Monk, and Lee (A., 1928, 1166). A number of combination relations are given for the lines of the Fulcher bands. These indicate three main branches in each band, R', Q, and P' branches, the Q branch being identical with that of Richardson. The R' and P' branches have a common initial level differing from that of the Q branch, whilst all three have a common final level. The arrangement yields term differences consistent throughout the bands, and in agreement with the new quantum mechanics.

N. M. Bligh.

Photometry of hydrogen and calcium lines in stellar spectra. (Miss) C. H. Payne and (Miss) E. T. R. Williams (Month. Not. Roy. Astron. Soc., 1929, 89, 526—538).

Hydrogen chromosphere. W. H. McCrea (Month. Not. Roy. Astron. Soc., 1929, 89, 483—497).—The pressure, density law, and means of support of hydrogen in the chromosphere are of a nature quite different from those of calcium. From the absolute measurement of H_γ the normal atoms are estimated to be present at the base of the chromosphere to the extent of 10^{12} atoms per c.c.; from observations on the continuous spectrum at the head of the Balmer series the ionised atoms in the same region are thought to be present at the rate of 2×10^{10} atoms per c.c. Ionisation in the chromosphere is discussed. It is shown that Ca^+ under the conditions usually assumed would probably be ionised to Ca^{++}, but that the excess of ionised hydrogen prevents this. The usual factors supposed to be effective in chromospheric equilibrium are not so in the case of hydrogen, and the possibility that they are effective in other stars is discussed (cf. this vol., 117). R. A. Morton.

3*d* trajectory in the ionised atoms P II, S II, S III, and Cl III. Cl III quadruplets. J. Gilles (Compt. rend., 1929, 188, 1158—1160).—The 3*d* trajectory falls between the 4*s* and 4*p* trajectories for the elements in the order phosphorus, sulphur, and chlorine. For Cl III the quadruplets $(a3d^4P-a4p^4S)$, $(a3d^4P-a4p^4P)$, and $(a3d^4P-a4p^4D)$ were established (cf. Bloch, A., 1927, 396), the term $3d^4P$ being inverted as in the cases of O II and S II. The term $3dD$ has a value of approximately 144,300. J. Grant.

Separation of the various spark spectra of antimony. R. Soulillou (Compt. rend., 1929, 188, 1103—1104).—The spark spectrum of pure antimony, comprising 300 lines between 3800 and 1900 Å., may be grouped into three classes due to Sb II, Sb III, and Sb IV corresponding with increasing intensities of excitation. The first group is made up of two sub-groups, but the two last are perfectly homogeneous (cf. Kimura and Nakamura, A., 1924, ii, 799). The spectra are accompanied by an independent, feeble continuous emission localised in the annular region near the bend of the tube. A number of lines, including some not previously observed, are tabulated with their intensities. J. Grant.

Arc spectrum of samarium. Measurements made at normal pressure between λ 2750 and 2200 X. S. Piña de Rubies (Compt. rend., 1929, 188, 1101—1102).—An extension of earlier work (this vol., 479). J. Grant.

Spectral relations between certain iso-electronic systems and sequences. I. Ca I, Sc II, Ti III, V IV, and Cr V. H. E. White (Physical Rev., 1929, [ii], 33, 538—546).—The spectra of V IV and Cr V should resemble closely the spectra of Ca I, Sc II, and Ti III, and extrapolations from known data for these have led to the identification of about 30 energy levels in both triply-ionised vanadium and quadruply-ionised chromium. The strongest lines in these spectra arise from combinations between ^3P, $^3D'$, ^3F, ^1P, $^1D'$, $^1F(3d4p)$ and ^3D, $^1D(3d4s)$ and ^1S, $^3P'$, ^1D, $^3F'$, $^1G(3d^2)$. The Moseley diagram and the irregular doublet law are used to determine the approximate positions of the various singlet and triplet levels and the location of the radiated frequencies. Landé's interval rule and, with one exception, Hund's rule are obeyed. The ionisation potentials of the 3*d* electrons of V IV and Cr V are determined, respectively, as 48·3 and 72·8 volts. N. M. Bligh.

Spark spectrum of nickel (Ni II). R. J. Lang (Physical Rev., 1929, [ii], 33, 547—548; cf. A., 1928, 679).—Twenty-six lines resulting from intercombinations between the lowest terms $d^9\,{}^2D_{2,3}$ and eleven more terms of the d^8p configuration b^4S', b^4P, b^4D'; c^2S', c^2P, c^2D'; b^2P, b^2D', b^2F; c^2F; b^2G' are tabulated and classified. These lines lie between 1537 and 1250 Å. (cf. Menzies, this vol., 226).

N. M. Bligh.

Variation in the intensities of mercury spectrum lines with pressure of the vapour. J. G. Frayne and C. G. Montgomery (Physical Rev., 1929, [ii], 33, 549—552).—The relative intensities of lines in the mercury spectrum in the direct-current arc and in the high-frequency discharge at low pressure were measured and tabulated for the wave-length range 7000—3000 Å. In the low-pressure discharge, there is an increase in intensity, relative to the triplet line 5460, of the singlet members, the sharp series showing the greatest increases; the relative intensity increases rapidly with ascending members of the series; combination singlets appear strong in the red. Five new lines in the sharp singlet series were observed.

N. M. Bligh.

Spark spectra of iodine. L. Bloch and E. Bloch (Ann. Physique, 1929, [x], 11, 141—166).—The iodine spectrum produced in the electrodeless oscillatory discharge has been studied from 7350 to 2220 Å. A large number of new lines, especially in the extreme red, have been measured for the first time. Four successive degrees of excitation are apparent, as compared with three for chlorine and bromine. The oscillatory discharge through iodine at low pressures is accompanied by a violet fluorescence resembling that exhibited by chlorine and bromine. H. F. Gillbe.

Arc spectrum of phosphorus. D. G. Dhavale (Nature, 1929, **123**, 799).—The presence of phosphorus in the sun is held to be established.
A. A. Eldridge.

Transition probabilities in the lithium atom. III. B. Trumpy (Z. Physik, 1929, **54**, 372—384; cf. A., 1927, 998; 1928, 1067).—Mathematical.
J. W. Smith.

Duplicity of the *D*-terms of sodium and potassium. A. Ferchmin and S. Frisch (Z. Physik, 1929, **53**, 326—330).—The potassium lines $2^2P_{3/2}-5^2D$, 5832 Å., and $2^2P_{3/2}-6^2D$, 5360 Å., have been examined with a Michelson echelon grating, and each has been found to possess a weaker satellite. The arrangement of the ^2D-terms is "inverted" (*i.e.*, the larger term has the smaller *j*-value); $\Delta 5^2D_{3/2,5/2}=0{\cdot}52$ cm.$^{-1}$; $\Delta 6^2D_{3/2,5/2}=0{\cdot}24$ cm.$^{-1}$ The sodium line $2^2P_{3/2}-4^2D$, 5688 Å., has been examined with the echelon grating and a large Lummer plate and found to be single; $\Delta 4^2D_{3/2,5/2}$ $0{\cdot}1 \ngtr$cm.$^{-1}$ E. B. Robertson.

Electrons that are "pulled out" from metals. E. H. Hall (Proc. Nat. Acad. Sci., 1929, **15**, 241—251).—Theoretical. In connexion with his theory of two classes of conduction electrons, the author investigates the minimum number of thermions, compared with the valency electrons or with the atoms, necessary to accord with his energy data and with the results of Millikan and Eyring (A., 1926, 219). The data of these and other authors are used, with the help of Oppenheimer's applications of wave mechanics to the phenomena. The values obtained for the number of thermions per c.c. range from $1{\cdot}8\times10^{15}$ to 8×10^{17}.
N. M. Bligh.

Mechanism of spark discharge. L. J. Neuman (Proc. Nat. Acad. Sci., 1929, **15**, 259—265).—The methods of distinguishing the possible mechanisms of a source of electrons at or near a cathode surface in a gas were made the basis of a critical experiment to decide which mechanism was the essential one in the spark discharge. A tube containing nickel electrodes and a sodium cathode in argon at various pressures was used, and voltage–pressure curves are given. The main conclusions reached are: in argon at low pressures the cathode material plays an important part, and the principal mechanism by which positive ions liberate electrons from the cathode depends on the velocity or impact energy of the positive ions with the cathode; as the pressure increases the predominating mechanisms of electron production change from those in which electrons are liberated from the cathode by the bombardment of swiftly-moving positive ions to those in which electrons are generated in the gas by collisions between swiftly-moving positive ions and neutral molecules.
N. M. Bligh.

Experiments with the electrolytic generator. V. M. Schulgin (Physikal. Z., 1929, **30**, 235—237).—Improvements in the electrolytic generator (*ibid.*, 1928, **29**, 724—726) are described. The high-frequency oscillations (of the Tesla type) which are generated arise apparently from hydrogen liberated at the platinum electrode.
R. A. Morton.

Thermionic emission through double layers. W. Georgeson (Proc. Camb. Phil. Soc., 1929, **25**, 175—185).—Theoretical.

Measurement of excitation and ionisation potentials by the diffusion method. W. Gliwitzky (Ann. Physik, 1929, [v], **1**, 701—720; cf. Bartels and Gliwitzky, A., 1928, 452).—The measurements on argon have been confirmed and extended and a helium–neon mixture has been studied. Full details of the new technique are given.
R. A. Morton.

Regularity of the total photo-electric emission. R. Suhrmann (Z. Physik, 1929, **54**, 99—107).—The total photo-electric emission observed when platinum foil is irradiated with black-body radiation from a source at different temperatures has been found to be in good agreement with theoretically deduced values.
J. W. Smith.

High values of *e*/*m* obtained with a Thomson vacuum tube. S. Ray (Z. Elektrochem., 1929, **35**, 209—210).—A discussion of variable values of the charge on an electron obtained from measurements with the Thomson tube.
H. T. S. Britton.

Exponential yield of positive ions in argon. (Miss) K. B. Blodgett (Proc. Nat. Acad. Sci., 1929, **15**, 230—234).—An electric discharge was passed through an argon-filled tube and the current carried by electrons and by positive ions was measured. Graphs are given of the current–voltage for various temperatures, the arc current, electron current against voltage for three pressures, and for three temperatures. A mechanism to account for the observed relationships is suggested.
N. M. Bligh.

Mobility distribution and rate of formation of negative ions in air. J. L. Hamshere (Proc. Camb. Phil. Soc., 1929, **25**, 205—218).—A modification of the alternating-field method of measuring ionic mobility in a gas gives an experimental curve showing upper and lower limits for the mobility. From this a distribution curve is derived which has a calculable resolving power. The mobility of negative ions in dry air shows a continuous distribution between the limits 2·15 and 1·45, with a peak value about 1·8. At low pressures the current is resolved into ions and free electrons. From the relative numbers reaching the electrometer it is found that the electron makes an average of $9{\cdot}4\times10^4$ collisions before capture, independent of field strength and pressure, and therefore independent of the electron speed over a velocity range 2×10^5 to 7×10^5 cm./sec.
N. M. Bligh.

Secondary electron emission from solid metal surfaces. C. F. Sharman (Proc. Camb. Phil. Soc., 1929, **25**, 237—254; cf. A., 1927, 287).—The mechanism of electron reflexion and the calculation of the total secondary effect are considered theoretically, and secondary emission is shown to be a complicated phenomenon involving many monatomic layers. The experimental study of slow δ-ray or true secondary emission from copper is described, and energy-distribution curves are given. An inverse square distribution law is applied, and tested experimentally by a retarding-potential method. The energy distribution of the total electronic emission can be represented by two curves, one for the electrons originally in the metal, and falling considerably below the inverse square distribution at high energies, and the other for the primary electrons reflected from the surface. N. M. Bligh.

Motion of ions in constant fields. L. Page (Physical Rev., 1929, [ii], 33, 553—558).—Theoretical. It is shown that the effect of a constant electrical or gravitational force on ions passing through a constant magnetic field is to cause the circular or helical ion paths to advance in a direction at right angles to both the force and the field with a constant velocity. Ion paths relative to a rotating earth are discussed on the assumption that the earth's field is purely magnetic relative to the inertial system of the centre of the earth. N. M. Bligh.

Angular scattering of electrons in helium, neon, hydrogen, and nitrogen. G. P. Harnwell (Physical Rev., 1929, [ii], 33, 559—571; cf. A., 1928, 1169).—The angular distribution of electrons of various energies scattered by the gases was investigated qualitatively. It was found that those electrons which were scattered elastically were in general deflected through only a few degrees. Those which had sustained an exciting collision were scattered through slightly larger angles. Evidence of electrons which had undergone two inelastic collisions was obtained, and these were distributed through still larger angles. A general tendency for slower electrons to be scattered through larger angles was observed. N. M. Bligh.

Dependence of electron emission from metals on field strengths and temperatures. R. A. Millikan and C. C. Lauritsen (Physical Rev., 1929, [ii], 33, 598—604).—A combined field-current and thermionic equation has been deduced, and field currents have been shown to be independent of temperature up to about 1100° Abs., when the energy of thermal agitation begins to assist the fields appreciably in causing the escape of electrons from metals. These results have been questioned by de Bruyne (cf. this vol., 3; also Fowler and Nordheim, A., 1928, 681). Further support for the original views is given. N. M. Bligh.

Rate of formation of negative ions by electron attachment. A. M. Cravath (Physical Rev., 1929, [ii], 33, 605—613).—A new method is described by which the fraction of the collisions between electrons and molecules which result in the attachment of the electron to form a negative ion has been measured in air and oxygen as a function of the average electron energy, the gas pressure, and the moisture content. In oxygen this fraction increased with either increase or decrease of average electron energy about a minimum of 0·9 volt, and in air increased for energies below this value. It increased rapidly with pressure at low constant energy, and was of the same order of magnitude in moisture as in oxygen, but in mixtures of these two was much larger than in either alone. Evidence of the detachment of electrons from negative ions in oxygen at very high fields was found. N. M. Bligh.

Test of the theoretical explanation of secondary electron emissions. H. Daene and G. Schmerwitz (Z. Physik, 1929, 53, 404—421).—Klemperer and Joffé have given an explanation of the Wehnelt phenomenon of secondary electron emission which cannot be confirmed by the authors. A new one, based on the assumption of a potential layer arising from the striking of primary electrons, is deduced. Distribution curves for secondary electrons emitted from glass and platinum are given. G. E. Wentworth.

Reactions in ionised gases from the point of view of Faraday's law. S. S. Joshi (Trans. Faraday Soc., 1929, 25, 143—147).—If univalent electrolytes are considered to be electrochemical analogues of ionised gases, then Faraday's ratio M/F may be obtained from the data for the decomposition of nitrous oxide by a silent electric discharge (cf. this vol., 521). The large values of M/F are explained in terms of the theory of the kinetics of a chemical change in the silent discharge previously advanced (Elliott, Joshi, and Lunt, A., 1927, 630). Assuming collisions between nitrous oxide molecules and electrons only (*i.e.*, in the initial stages of the decomposition), it is calculated that $1{\cdot}9\times10^3$ mols. are decomposed per electron. J. Grant.

Refraction of light waves by electrons. S. K. Mitra and H. Rakshit (Nature, 1929, 123, 796—797).

Electron deflexion by metallic films. E. Rupp (Ann. Physik, 1929, [v], 1, 773—800).—Electrical measuring arrangements have been devised for studying the deflexion phenomena which occur when electrons pass through thin sheets of foil, in this case of metals possessing cubic lattices. From the refractive indices for electron waves the inner lattice potentials of silver and nickel are found to be near 12 and 17 volts, respectively. The spatial and localised velocity distribution of the deflected electrons reveals a selective effect in certain directions, which leads to a definition of deflected electrons as those electrons which, after traversing the metallic foil, undergo deflexion in a selective angular range without suffering appreciable loss in velocity. All other electrons are regarded as scattered. The application of the refractive index for electron waves to the problem is discussed and it is pointed out that the foil is a conglomerate of small crystals and not a strictly plane parallel plate. Date are recorded for nickel, aluminium, silver, and chromium. R. A. Morton.

Electron reflexion and deflexion at unicrystalline surfaces. E. Rupp (Ann. Physik, 1929, [v], 1, 801—814).—When fairly slow electrons pass through metal foil deviations occur from the de Broglie relation $\lambda=h/mv$ which are accounted for by the introduction of a refractive index $\mu>1$. The physical basis for this term is the existence of a positive inner lattice potential E_0 corresponding with the relation $\mu=(V+E_0/V)^{\frac{1}{2}}$, V being the electron velocity in volts. The reflexion of electrons from unicrystalline nickel, copper, silver, gold, aluminium, and lead (metals with cubic face-centred lattices) has been studied. Volatilisation from tungsten enabled most of the crystals to be oriented with the 111 plane parallel to the surface under investigation. It is found that the refractive index for electron waves is greater than 1 for all metals, that it decreases towards unity with increasing velocity, and that for a given velocity it is constant for a given metallic lattice.

E_0 varies between 11 and 17 volts. The values obtained by this and other methods are compared, and correlated with Sommerfeld's theory of metallic conduction. R. A. Morton.

Application of electron diffraction to the investigation of gas adsorption. L. H. Germer (Z. Physik, 1929, **54**, 408—421).—Under suitable experimental conditions diffraction diagrams of four very different types can be obtained from the electron diffraction from a single crystal of nickel. Of these, one records the space lattice of the metal, the second the structure of the surface layer of the metal, a third that of a monatomic adsorbed gas film, and the fourth that of a thicker gas film. Hence it is claimed that this method affords a rapid new method of studying gas adsorption and crystal structure. J. W. Smith.

Electron reflexion from cobalt, and electron waves. M. N. Davis (Nature, 1929, **123**, 680—681).—The secondary emission on bombardment of the metal by electrons of known velocity has been resolved into its velocity components. A. A. Eldridge.

Temperatures of positive ions in a uniformly ionised gas. J. M. Dewey (Nature, 1929, **123**, 681).—By the use of data on the width of lines emitted from the negative glow of the helium arc, and assuming that the positive ions acquire energy solely from the energy of random motion of the electrons whilst they lose energy by collision with the molecules of neutral helium at a rate which may be calculated from kinetic theory, the temperature of positive helium ions is calculated from the electron temperature and the pressure of the gas in a field-free space. A. A. Eldridge.

Selenium and cathode rays. C. E. S. Phillips (Nature, 1929, **123**, 681—682).—When a cell, prepared by condensing the vapour of heated selenium on a gold grid, was exposed to cathode rays, a rapid diminution of resistance, which could be widely varied by deviating the rays with a magnet, occurred. The effect is not attributed to the production of *X*-rays in the selenium. A. A. Eldridge.

Elastic collisions of electrons with helium. N. F. Mott (Nature, 1929, **113**, 717).—The scattering predicted by the wave mechanics has been worked out by a method involving two separate approximations. A. A. Eldridge.

Mass-spectrum of lead from bröggerite. C. N. Fenner and C. S. Piggot (Nature, 1929, **123**, 793).—The composition and age of the bröggerite from which Aston's sample of lead tetramethyl (this vol., 370) was prepared are discussed. The proportion of Pb^{208} is computed to be 2·64%. The uranium–thorium equivalence factor (0·38) may require correction. A. A. Eldridge.

Groupings of radioactive atoms. H. Jedrzejovski (Compt. rend., 1929, **188**, 1043—1045).—Chamié's method (A., 1928, 810) has been used for the study of the distribution of radioactive matter in activated sources. Direct activation in radon and activation in a vacuum by the α-recoil of radium-*B* (from radium-*A*) or by the β-recoil of radium-*C* (from radium-*B*) gave characteristic groupings analogous to those obtained by Chamié. Images from sources prepared by distillation of radium-*B*+*C* in a vacuum or at atmospheric pressure, however, were quite different, and indicate that the destruction of the groupings by distillation is due to the removal in succession of the outer atoms. These groupings are unchanged after 15 min. at 350°, but once they are destroyed they do not tend to form again rapidly. J. Grant.

Grouping of the atoms of radioactive elements. (Mlle.) C. Chamié (J. Phys. Radium, 1929, [vi], **10**, 44—48; cf. A., 1928, 810).—The radioactive mixture is put into close contact with a photographic plate, so that the α-particles have their whole path in the gelatin. A number of "star" effects is then obtained, each of which indicates the position of a radioactive group. If the plate is covered with mercury which has absorbed a little radioactive material, the same grouping effect is always found on development, no matter what method has been employed to activate the mercury. From this it is concluded that these radioactive groups existed in the original mixture and had been absorbed unchanged by the mercury. The groups will remain unchanged for weeks in mercury. To investigate the presence of these groups in radioactive gas mixtures, the gas was streamed against a photographic plate and the same effect was obtained, showing the presence of complexes. In a similar way the presence of groups in liquids has been demonstrated. It is concluded that these groups contain many atoms, and their origin and properties are discussed. J. L. Buchan.

Conditions of formation of groups of radioactive atoms. H. Herszfinkiel and H. Jedrzejovski (Compt. rend., 1929, **188**, 1167—1169; cf. A., 1928, 215).—Radioactive deposits produced by distillation on to a thin mica surface show groupings only in the presence of impurities, the smallest trace of which suffices to act as a nucleus for their formation. Thus, the groupings were more sharply defined when a drop of hydrochloric acid was placed on the mica before distillation, or was used to wash it after distillation, than when distilled water was used. It was shown that solutions free from groupings will activate filter-paper by direct adsorption and that groups present on a mica surface do not penetrate it under the influence of radioactive recoil. J. Grant.

β[-Particle] recoil. L. Wertenstein (Compt. rend., 1929, **188**, 1045—1047).—Radioactive sources prepared by direct activation in radon or by means of the α-recoil of radium-*B* (from radium-*A*) give recoil products containing radium-*B* and -*C*, whilst a source prepared by distillation in a vacuum from a platinum surface of the collected deposit gives pure radium-*C* (cf. preceding abstract). The yield of recoil product is not influenced by the method of preparation, but decreases rapidly with time and as a result of preheating the source at 250°. It is dependent on the emitting and receiving surfaces, a maximum yield of 20% being obtained with a clean aluminium source and bismuth receiver after a few minutes' exposure; it is unchanged if the receiver is cooled in liquid air. J. Grant.

Mode of action of the electron counter of Geiger and Müller. H. Kniepkamp (Physikal. Z., 1929, 30, 237—238).—Experiments with treated and untreated wire (cf. Geiger and Müller, this vol., 114) show that under the correct electrical conditions plain wire is effective. The condition of the surface of the anode wire cannot be more than a secondary factor in the operation of the counter. R. A. Morton.

Energy relations in artificial disintegration. (Sir) E. Rutherford and J. Chadwick (Proc. Camb. Phil. Soc., 1929, 25, 186—192).—When certain elements are disintegrated by α-particle bombardment protons are liberated and the α-particle is assumed to be captured by the nucleus. The energy changes of this type of reaction are investigated theoretically with the help of data for the maximum ranges of the protons obtained by experiments on aluminium. Support is obtained for the view that nuclei of the same element do not have identical masses. N. M. Bligh.

Distribution of range of the α-particles from radium-*C*′ and thorium-*C*′. N. Feather and R. R. Nimmo (Proc. Camb. Phil. Soc., 1929, 25, 198—204; cf. this vol., 371).—The particles of abnormally short range were investigated from measurements of tracks formed in an expansion chamber for 2134 and 729 α-particles from thorium-*C*′ and radium-*C*′, respectively, and range-distribution curves were obtained. The origin of marked differences in the proportion of short-range particles in each is discussed. Estimates of the linear straggling coefficients relative to the absorption of the two groups of particles in air are made. N. M. Bligh.

Number of high-velocity β-rays. H. M. Cave (Proc. Camb. Phil. Soc., 1929, 25, 222—224; cf. Yovanovitch and D'Espine, A., 1927, 915).—A simple determination was made of the average number of high-velocity β-particles per disintegration from radium-$B+C$, and it is concluded that the number of such particles is certainly less than 1 per 500 and probably less than 1 per 1000 disintegrations. N. M. Bligh.

Evaluation of the α-radiation of the active deposit of actinium by measurement of its β-radiation. Nahmias (Compt. rend., 1929, 188, 1165—1167).—The absolute value of the α-radiation from actinium-*C* may be determined from the ratio of the ionisation current produced by the β-radiation to that due to the α-radiation remaining after the former has become feeble. Ionisation from the effect of β-rays during the measurement of the α-radiation amounts to 0·013 of the current due to the latter, and is determined by the use of an aluminium screen 0·06 mm. thick to cut off all the α-radiation. J. Grant.

Determination of radium content from the γ-radiation. W. A. Sokolov (Z. Physik, 1929, 54, 385—398).—For determination of radium content the method of γ-radiation measurement is much more accurate than that of the α-radiation and moreover for this purpose the material requires no chemical treatment such as is necessary for emanation measurement. A new form of γ-ray electroscope is described, using the same principle as that of Dorsay (J. Opt. Soc. Amer., 1922, 6, 633), the chief improvements made being in making the space for the material to be investigated much larger and the substitution of a forked electrode for the cylinder used by Dorsay. By this means it has been found possible to measure radium contents as low as 2 parts in 10^{10} of radium-containing minerals. J. W. Smith.

Atomic disintegration. W. Bothe and H. Franz (Z. Physik, 53, 1929, 313—316).—The essential differences between results obtained by these authors and Kirsch and Pettersson (this vol., 234) are stated. No correlation seems possible. G. E. Wentworth.

Cosmic radiation and radioactive disintegration. N. Dobronravov, P. Lukirsky, and V. Pavlov (Nature, 1929, 123, 760).—Experiments with two nearly equal quantities of radon, the exact ratio of the activities of which had been determined, did not reveal any action of cosmic rays on the speed of disintegration, although the possibility of such action, *e.g.*, in causing the disintegration of the first member of the radioactive family, is not thereby excluded. A. A. Eldridge.

Nature of penetrating radiation. W. Bothe and W. Kolhörster (Nature, 1929, 123, 638, and Naturwiss., 1929, 17, 271—273).—It is concluded from experimental evidence that the penetrating radiation is not of γ- but of corpuscular type. A. A. Eldridge.

Theory of quantum jumps. J. Ullmo (J. Phys. Radium, 1929, [vi], 10, 15—31).—Mathematical.

Foundation of Nernst's hypothesis of formation of radioactive elements on the basis of wave-mechanics. J. Kudar (Z. Physik, 1929, 53, 166—167).—Mathematical note.

Diagram of quantum states and the formation of the elements in the periodic system. O. M. Corbino (Nuovo Cim., 1928, 5, lvii—lxiv; Chem. Zentr., 1929, i, 185).—*n*-Values from 1 to 7 (K—Q) are plotted as abscissæ against the corresponding states $k=0$ to $k=3$ (s, p, d, f) as ordinates; the states are divided into groups corresponding with different *k*-values. A. A. Eldridge.

Distribution of charge and current in an atom consisting of many electrons obeying Dirac's equations. D. R. Hartree (Proc. Camb. Phil. Soc., 1929, 25, 225—236).—An approximation for the many-electron atom is applied to electrons obeying Schrödinger's wave equation and also to those obeying Dirac's equation, in order to divide the electron groups into half groups for which the distribution of charge is spherically symmetrical. An investigation is made as to whether the direction of the spin axis of the electron can ever be specified, and it is concluded that this can be done only for states for which the magnetic quantum number m has its extreme value $\pm j$. N. M. Bligh.

Theory of columnar ionisation. II. G. Jaffé (Ann. Physik, 1929, [v], 1, 977—1008; cf. A., 1913, ii, 658).—Mainly mathematical. The theory of ionisation in columns advanced in the earlier paper is extended and developed and a formula is derived for the increase in ionisation density. A comparison is made with experimental results. A. J. Mee.

Theoretical expression for the life of the atom in the metastable state. M. Saha and D. S. Kothari (Naturwiss., 1929, **17**, 271).—Classical theories lead to the expression $T=3mc^3/8\pi^2e^2\nu^2$ for the life of the excited atom in the metastable state, (Abklingungszeit), and for $\nu=10^4c$ the value is of the order 10^{-8} sec. A rough expression for the life of the atom in the metastable state is given by $T=3c^5m^2/\pi^2e^2h\nu^3$, and taking $\nu=10^4c$, T is $1{\cdot}5\times10^{-1}$ sec., in agreement with experimental values found by Kannenstine and Hertz. R. A. Morton.

Estimates of the ages of the Whin Sill and the Cleveland Dyke by the helium method. V. S. Dubey and A. Holmes (Nature, 1929, **123**, 794—795).—Values, respectively, of 182 and 26×10^6 years are obtained. A. A. Eldridge.

Quantum mechanics of many-electron systems. P. A. M. Dirac (Proc. Roy. Soc., 1929, **A**, **123**, 714—733).—The methods and results of group theory are translated into the language of quantum mechanics so as to obtain a treatment of the "exchange" (Austausch) phenomena of electrons. The general theory is given of systems containing a number of similar particles, showing the existence of sets of states such that a transition can never take place from a state in one set to a state in another. The theory is then applied to the case when the particles are electrons, taking into consideration the spin of the electrons and Pauli's exclusion principle, and a proof is obtained of the fundamental theorem of multiplet structure, that for each stationary state of the atom there is one definite numerical value for s, the magnitude of the total spin vector. The perturbation theory is applied to an approximate calculation of the energy level of the states, the result being expressible by a simple formula, showing that, in the first approximation, the exchange interaction due to the equivalence of the electrons may be replaced by a coupling between their spins, the energy of this coupling for each pair of electrons being equal to the scalar product of their spin vectors multiplied by a numerical coefficient given by the exchange energy. In this way a justification is obtained for the assumptions of the old orbit theory.

L. L. Bircumshaw.

Discussion on the structure of atomic nuclei. (Proc. Roy. Soc., 1929, **A**, **123**, 373—390).—(Sir) E. Rutherford. The progress which has been made in the last fifteen years is reviewed. Three methods of attacking the problem are discussed: (1) the proof of the isotopic constitution of the ordinary elements and the accurate determination of the masses of the individual isotopes; (2) the artificial disintegration of the elements by bombardment with α-particles, and (3) the study of the wave-lengths of the penetrating γ-rays which have their origin in the disintegration of the radioactive nucleus. Earlier work on isotopes showed that the masses of the elements are approximately expressed by whole numbers (oxygen=16), but the main interest now lies in the departures from the whole-number rule. The second method of attack shows definitely that the actual structure of the nucleus can be altered by the application of external agencies, whilst the third gives evidence of the modes of vibration of the particles constituting the nucleus. In a study of the scattering effects of α-particles of elements from copper (at. no. 29) to uranium (at. no. 92) it is found that the scattering is normal—*i.e.*, assuming the inverse square law the number of α-particles scattered through an angle of about 135° varies as $1/E^2$, where E is the energy of the α-particles. From this it is concluded that the radius of the copper nucleus is less than the closest distance of approach (about 10^{-12} cm.), whilst for uranium this distance is about 3×10^{-12} cm. The scattering of the lighter elements is quite abnormal and a detailed study of these deviations leads to the conclusion that the close approach of an α-particle to the nucleus causes a polarisation of the charged constituents of the latter. This gives rise to an attractive force which varies as the 5th power of the distance from the centre of the nucleus. Calculations on this basis agree fairly well with the experimental observations on aluminium. The nuclei cannot be regarded as point forces, but have a certain structure and volume, and the latter may in some cases be flat ellipsoid rather than spherical. Scattering experiments show that a swift α-particle cannot penetrate deeply into the nucleus of uranium, whilst other considerations indicate that this should occur. An explanation of this difference can be obtained by applying the ideas of wave mechanics, but this makes the radius of the uranium nucleus very small (about 7×10^{-13} cm.), and in this small nuclear volume 238 protons and 146 electrons must be accommodated. A picture is presented of the gradual building up of atomic nuclei in which the latter are composed of α-particles, protons, and electrons which, owing to the distortional forces, attract each other strongly. A highly concentrated and firmly bound nucleus results, accompanied by the emission of energy and this binding is closest for atomic mass 120, where the loss of mass due to packing is a maximum. The nucleus consists, therefore, of a very tightly-packed structure at the centre, becoming less dense as the outside is approached, and is a system surrounded by a potential barrier which normally prevents α-particles from escaping. This view explains why atoms heavier than uranium cannot exist permanently.

F. W. Aston. The packing fractions of the elements are discussed, and the essential differences between the light atoms of odd atomic number (hydrogen, lithium, beryllium) and those of even atomic number (helium, carbon, oxygen) are emphasised.

J. Chadwick. Experiments on artificial disintegration by α-particles reveal the fact that protons liberated from the odd-numbered elements have greater maximum energies than those from even-numbered, and if the disintegration consists of the capture of an α-particle and the emission of a proton, then an element of odd number will be changed into one of even number, and *vice versa*. This suggests, in agreement with other evidence, that the even elements are more stable than the odd.

C. D. Ellis. The nature and origin of the γ-rays occurring in radioactive disintegrations are discussed.

These rays are more frequently associated with the β-ray type of disintegration and appear to be homogeneous to at least 1 part in 1000 parts. Experiments in progress on the intensities of the photo-electric groups emitted from lead when exposed to γ-radiation from a radioactive source provide some evidence of a curious coupling between the nucleus and the electronic system.

G. Gamow. A theory is suggested which treats an assembly of α-particles—*e.g.*, the α-particles constituting a nucleus—with attractive forces between them, which vary rapidly with the distance, as a small drop of water with the particles held together by surface tension. From the equation connecting the energy of the α-particles with the surface tension of the imaginary water drop and the quantum condition of ordinary quantum mechanics, a relation is obtained between the " drop energy " and the number of α-particles contained in the drop (*i.e.*, the at. wt. of the nucleus). The shape of the curve for this relation agrees well with Aston's curve showing the defect of mass. On the basis of wave mechanics this model can be treated by Hartree's method of self-consistent field.

R. H. Fowler. The nucleus is pictured as a tiny enclosure surrounded by a potential hill and enclosing an α-particle (represented by a standing wave), of which the energy is less than the potential energy at the top of the barrier. On the classical theory it will stay inside for ever, but on the quantum theory there is a finite chance that the wave can leak out through the thin wall. Its chance of doing this will be greater, the greater is the energy of the α-particle, the thinner the barrier it has to go through, and the smaller the height of this barrier. A virtue of this theory is that it gives the Geiger–Nuttall law of α-ray disintegration independently of the details of nuclear structure.

O. W. Richardson. Spectroscopic evidence is submitted in favour of the rotation of the nuclei.

L. L. Bircumshaw.

Synthesis of elements. G. I. Pokrovski (Z. Physik, 1929, **54**, 123—132).—Mathematical. The energy and frequency of the radiation which would be produced by combination of a single proton with an atomic nucleus are calculated. The period of vibration of this radiation is shown to be equal to a whole number of chronons. The frequencies calculated for particular cases agree with the observations of Millikan and Cameron (A., 1928, 1303) on high-frequency radiation. J. W. Smith.

Ordinary matter and radiant energy as different phases of one and the same fundamental state. W. Anderson (Z. Physik, 1929, **54**, 433—444).—Mathematical. J. W. Smith.

Quantum theory of the atomic nucleus. T. Sexl (Z. Physik, 1929, **54**, 445—448).—Mathematical.

J. W. Smith.

Chromium echelette gratings on optical flats for infra-red investigations. R. W. Wood (Phil. Mag., 1929, [vii], **7**, 742—744).—The preparation of chromium echelette gratings is described. The method of ruling is as described previously (*ibid.*, 1910, [vi], **20**, 886), except that a suitably-cut diamond replaces the carborundum crystal. The grating is ruled on optically flat copper and after the ruling the surface is electroplated with chromium, the deposition of which is without effect on the distribution of the light. Gratings of this description up to 4 in. diameter have been made and can be supplied to laboratories requiring them. They can be ruled for concentration at any desired wave-length and with any desired spacing. Concave gratings of this type of 1 and 2 m. radius have been made. A. E. Mitchell.

σ-Type doubling and electron spin in the spectra of diatomic molecules. J. H. Van Vleck (Physical Rev., 1929, [ii], **33**, 467—506).—The two rotational effects considered together with their inter-relation are the distortion and the σ-type doubling of spectral lines due to removal of the degeneracy associated with the energy equality of left- and right-handed axial rotations in stationary molecules. The methods of matrix and wave mechanics are used. A summary and comparison with Mulliken's experimental data (cf. following abstract) are given. N. M. Bligh.

Electronic states and band spectrum structure in diatomic molecules. VIII. Some empirical relations in σ-type doubling. R. S. Mulliken (Physical Rev., 1929, [ii], **33**, 507—511; cf A., 1928, 1166).—Some empirical relations are summarised, and the magnitudes of the doublet intervals are considered. The observed relations agree with the work of Van Vleck (cf. preceding abstract), which shows definitely that the ^3P levels involved in the second positive nitrogen bands are both normal and not inverted.

N. M. Bligh.

Structure of multiplet *S*-states in diatomic molecules. I. H. A. Kramers (Z. Physik, 1929, **53**, 422—428).—A theoretical explanation of the characteristic multiplicity of normal ^3S-states in the O_2 molecule. E. B. Robertson.

Structure of multiplet *S*-terms in diatomic molecules. II. H. A. Kramers (Z. Physik, 1929, **53**, 429—438).—Mathematical. E. B. Robertson.

Two-quantum excited states of the hydrogen molecule. E. C. Kemble and C. Zener (Physical Rev., 1929, [ii], **33**, 512—537).—An extension of the work of Heitler and London and of Sugiura (cf. A., 1927, 923; 1928, 345) on the interactions of normal hydrogen atoms by the method of wave mechanics, to cases of certain excited states of the H_2 molecule which dissociate adiabatically into a normal H atom and a two-quantum excited H atom. The application of the results to the qualitative prediction of the nature of the different excited states of the molecule and to London's theory of non-polar valency is considered. The principles of selection for transitions between the various types of electronic state are formulated and compared with the rules of Kronig (cf. A., 1928, 456). A first-order perturbation theory computation of the potential energy curves for the *P* states shows that two of them have the form requisite for the formation of stable molecules, and may be identified respectively with the *C*-state upper level for Werner bands, and the 2^3P-state reported by Richardson (cf. A., 1927, 495). N. M. Bligh.

Band systems of the hydrogen molecule. R. Mecke and W. Finkelnburg (Naturwiss., 1929, 17, 255—256).—Analysis of the many-lined spectrum of hydrogen discloses the predominance of singlet and triplet systems. In addition to 550 lines already classified, 725 lines are now shown to belong to 60 bands with 179 branches of a new triplet system ascribed to the hydrogen molecule. The bands consist of three intense Q-like branches ($\Delta m=0$) and two weaker branches ($\Delta m=\pm 2$). The 2^3S end term is common to all the new bands. Relevant terms and molecular constants are given. Since the more intense lines of the spectrum have now been rigidly classified, the rôle of H_2^+ and H_3 in the many-lined spectrum must be subordinate compared with that of H_2 molecules. R. A. Morton.

Absorption band spectrum of chlorine. A. Elliott (Proc. Roy. Soc., 1929, A, 123, 629—644).—An analysis has been made of the rotation structure of the three chlorine bands $2\longrightarrow 17$, $2\longrightarrow 18$, and $2\longrightarrow 19$, using an absorption tube 1·6 m. long containing chlorine at 1 atm. A feature of the bands is the close similarity of the P and R branches and the remarkable way in which they run side by side. No Q branches are found. The values obtained for the molecular constants indicate that the normal chlorine molecule expands considerably on the absorption of a quantum of radiation. Taking Kuhn's assignment of quantum numbers for the initial state (in absorption) with the addition of one half unit (cf. A., 1926, 1192), the quantum numbers for the excited state are calculated from the magnitude of the isotopic separation of the band origins. These are found to be rather high, as the first band observed in the progression in which $n''=1$ has the value $n'=12$. The lines comprising the bands due to the molecule $Cl^{35}Cl^{35}$ show an alternation in intensity, the ratio of strong to weak lines being about 1·42 : 1. This effect is not, however, present in the non-symmetrical molecule $Cl^{35}Cl^{37}$. This is in accordance with the theory of Hund (A., 1927, 495), which states that alternation in intensity of band lines is to be expected only when the nuclear masses are equal. The molecules $Cl^{35}Cl^{35}$ and $Cl^{35}Cl^{37}$ have different moments of inertia but equal internuclear distances, and must be identical except in respect of nuclear mass. The mean intensity of the lines in each band is approximately proportional to the number of molecules present of the kind required to produce the band.

L. L. Bircumshaw.

Constitution of oxygen. H. D. Babcock (Nature, 1929, 123, 761).—The A' band of oxygen has been augmented from 26 to 73 lines, of which about half belong to the alternate system of doublets which are to be expected from the molecule $O^{16}O^{18}$. The relative abundance of the molecules $O^{16}O^{16}$ and $O^{16}O^{18}$ is approx. 1250 : 1 (cf. Giauque and Johnston, this vol., 369; Aston, this vol., 484).

A. A. Eldridge.

Absorption of ultra-violet radiation by ozone. A. Läuchli (Z. Physik, 1929, 53, 92—94).—The absorption coefficients of ozone for light of wave-lengths between 2378 and 3341 Å. have been measured. The ozone was determined by a differential method similar to Warburg's, and the intensity of the light determined by means of a photo-electric cell with thermionic valve amplification. The effect of scattered light on the absorption coefficient was investigated, and found to be greatest for the lines 2482 and 2652 Å. and negligible for the resonance line 2537 Å. For the wave-length range 2800—3350 Å., which is of importance in atmospheric absorption, the absorption coefficient is given by an empirical formula.

E. B. Robertson.

Ozone absorption during the long Arctic night. S. Rosseland (Nature, 1929, 123, 761).

Active nitrogen. P. K. Kichlu and S. Basu (Nature, 1929, 113, 715—716).—Active nitrogen is molecular nitrogen in a metastable condition; its life can be varied by the regulation of pressure, increasing continuously and regularly with decrease of pressure. Infra-red lines of nitrogen belonging to the electronic configurations $2L_2M_1 \longleftarrow 2L_2M_2$ have been produced by exciting nitrogen and active nitrogen with an uncondensed discharge under identical conditions; no change in the relative intensity of lines was observed, whence no appreciable density of atoms is present. A. A. Eldridge.

Active nitrogen. (Lord) Rayleigh (Nature, 1929, 113, 716).—A reply to Kichlu and Basu (preceding abstract). A. A. Eldridge.

Infra-red radiations of active nitrogen. P. K. Kichlu and D. P. Acharya (Proc. Roy. Soc., 1929, A, 123, 168—171).—The band spectrum of active nitrogen has been photographed in the infra-red, and it is shown that the bands extending from 7500 to 8900 Å. consist of an extension of the first positive group of nitrogen occurring in the yellow, green, and red regions. The fact that no trace is found of the group of lines of atomic nitrogen at 8200 Å. indicates that the analogy between active nitrogen and active hydrogen is not complete (cf. Sponer, A., 1926, 8).

L. L. Bircumshaw.

Active nitrogen. II. Influence of surface on the afterglows in nitrogen and oxygen. III. Mutual effect of nitrogen and oxygen on their respective afterglows. B. Lewis (J. Amer. Chem. Soc., 1929, 51, 654—665, 665—674).—II. The introduction of oxygen into nitrogen immediately after the latter has been subjected to high-tension discharge does not produce an afterglow. The nature of the surface of the containing vessel seems to be a determining factor governing the visibility of the afterglow in nitrogen and in oxygen. Thus nitrogen, pure or containing a trace of oxygen, at very low pressure shows prolonged afterglow when treated in an ordinary vessel, but with continued baking of the vessel the glow progressively disappears. Similar results were found for pure oxygen. Afterglow which has been removed in this manner may be restored by adding sufficient water vapour to cover the surface of the vessel. The phenomena are the same in a paraffin-covered vessel as in an ordinary glass vessel. Heat decreases the duration and intensity of the afterglow in an uncleaned vessel, and *vice-versa* (reversed temperature effect). The oxygen afterglow, which decays abruptly, appears to be quenched at liquid air temperatures, whereas the nitrogen afterglow is intensified.

III. Curves are given representing the duration of the afterglow as a function of pressure for a series of nitrogen and oxygen mixtures. Normal oxygen molecules have a marked quenching action on the nitrogen afterglow, but normal nitrogen molecules do not affect the oxygen afterglow. The kinetic aspect of the phenomena is discussed. S. K. Tweedy.

Spectral absorption of lithium hydride and the molecular constants of LiH. G. Nakamura (Z. physikal. Chem., 1929, **B**, **3**, 80—82).—An analysis of the absorption spectrum of lithium hydride is given. The band system consists of a number of bands fading towards the red. Each band is made up of a simple *P*- and a simple *R*-line, and is similar to the ultra-violet bands of BeH^+. The moments of inertia of the lithium hydride molecule in the normal state are calculated. A. J. Mee.

Titanium oxide bands in the orange, red, and infra-red region. F. Lowater (Nature, 1929, **123**, 644).—Bands in the region 5600—8000 Å. have been analysed into a singlet system in the orange, due to the electronic transition ^1P—^1S, and a triplet system in the red and infra-red due to the transition ^3S—^3P. A. A. Eldridge.

Effect of adsorbed ions on the light absorption of heavy metal halides. K. Fajans and G. Karagunis (Naturwiss., 1929, **17**, 274).—When Ag^+ and Tl^+ ions are adsorbed by colloidal silver bromide or Pb^{++} ions by lead iodide, the strongly anion-deforming cations bring about an increased extinction detectable on the long-wave descending portion of the absorption curve. Silver iodide, so highly dispersed that scattered radiation plays a minor part, permits the measurement of intensities on both sides of the absorption maximum at 420 μμ. Adsorption of Ag^+ in this case causes the intensity of the whole band to be increased markedly without appreciable shift of the wave-length of maximum absorption. The adsorption of Ag^+ on the silver iodide lattice increases either the number of atoms in the particular state or the number of quantum transitions, of which the band forms a measure. The transition is probably involved in the photo-electric conductivity and the photo-decomposition of the silver halide. The sequence: $Ag_nI_n \longrightarrow [Ag_nI_n]Ag^+ \longrightarrow Ag_2I^+$ is in accord with observation since Ag_2I^+ shows negligible absorption in the visible and there is no ultra-violet maximum until 245·5 μμ is reached. R. A. Morton.

Absorption spectrum of liquid benzene. J. W. Ellis (Physical Rev., 1929, [ii], **33**, 625—626).—A criticism of the work of Barnes and Fulweiler (cf. A., 1928, 1306). N. M. Bligh.

Absorption spectrum of liquid benzene. J. Barnes (Physical Rev., 1929, [ii], **33**, 627).—A reply to Ellis (cf. preceding abstract). N. M. Bligh.

Structure and activation of the molecules of aliphatic aldehydes. III. Absorption spectra of solutions. S. A. Schou (J. Chim. phys., 1929, **26**, 69—90; cf. this vol., 236).—Measurements have been made of the absorption spectra of formaldehyde vapour and of solutions in hexane. The maxima for these two states are at 2935 and 2940 Å., respectively, showing that formaldehyde in the unimolecular state absorbs in the same region as acetaldehyde and propaldehyde. In aqueous formaldehyde solution there is less than 1 mol. of H·CHO for 1200 mols. of the hydrated or polymerised form. The absorption spectra of acetaldehyde in aqueous and in hexane solution indicate that the enolic form can exist under conditions where the aldehyde is polymerised, *e.g.*, in alkaline solution or when the polymerisation is catalysed by an acid. Measurements have also been made of the absorption of propaldehyde and of chloral in aqueous and in hexane solution. O. J. Walker.

Intensity of the *K*-lines of the *X*-ray spectrum in relation to atomic number. H. T. Meyer (Wiss. Veröff. Siemens-Konzern, 1929, **7**, [2], 108—162).—Methods for determining the intensities of *X*-ray lines recorded photographically are described, together with refinements and corrections. The relative intensities of the *K*-lines in the spectra of the elements from indium (49) to titanium (22), with the exceptions of masurium and krypton, have been determined. Taking $K\alpha_1$ as 100, α_2 varies from 46·0 to 54·9, β_1 from 15·8 to 26·1, and β_2 from 0·15 to 4·22. On the whole, the ratio $\alpha_1 : \alpha_2$ agrees very well with the theoretical value 2 : 1, whilst $\alpha_1 : \beta_1 = 4 : 1$, a result without known theoretical basis. The relatively small deviations from the 2 : 1 and 4 : 1 ratios are to a great extent smoothed out by plotting $\alpha_2 Z/\alpha_1 A$ against atomic number, *A* being the atomic weight, and *Z* the atomic number. No such effect is observed for the ratio $\beta_2 : \alpha_1$. From gadolinium onwards the ratio β_2/α_1 increases with increasing atomic number, indium being anomalous. When $(\alpha_2 - \beta_1)/\alpha_1$ and $(\alpha_2 - \beta_1)Z/\alpha_1 A$ are plotted against atomic number, a gradual decrease is recorded from vanadium to bromine, whilst from rubidium to indium practically constant values are obtained. The ratio β'/β_1 has been determined for manganese and the ratio α_3/α_1 for manganese, chromium, and vanadium. R. A. Morton.

Intensity of scattered light, and its dependence on temperature. C. Landsberg and M. Leonowitsch (Z. Physik, 1929, **53**, 439—448).—The intensities of the lines in the spectrum of light scattered by quartz have been investigated by means of a photographic photometer, and the intensity of the strongest red satellite is found to be about 40% of that of the principal line. On raising the temperature, the intensity of the red satellites remains practically constant, that of the principal line increases as the absolute temperature, and that of the violet satellites increases even more quickly. E. B. Robertson.

Theory of sensitised fluorescence. A. Carelli (Z. Physik, 1929, **53**, 210—215).—On Schrödinger's theory, an explanation is given of the preference for the resonance state in the conversion of energy of excitation in collisions of the second kind, as observed in the sensitised fluorescence of metal vapour mixtures. E. B. Robertson.

***X*-Ray luminescence of mercury vapour.** S. Mrozovski (Z. Physik, 1929, **54**, 422—426).—Careful spectroscopic investigation of the *X*-ray luminescence of mercury vapour leads to the conclusion that it is not the direct *X*-ray fluorescence which plays the major rôle in this case, but that the visible and ultra-violet spectrum is excited by the slow-moving photo-electrons. J. W. Smith.

Phosphorescence and photochemical activity of some organic and inorganic substances after ultra-violet irradiation. F. Kirchhof (Physikal. Z., 1929, 30, 240—241).—A faintly green paper after ultra-violet irradiation was found to darken a photographic plate. The effect is not purely chemical (*i.e.*, the irradiation is essential), nor is it due to the slight phosphorescence which arises when the ash is tested separately. Photoactivity is observed with fluorene and zinc salts of organic sulphonic acids, but there is no necessary connexion between photoactivity and visible phosphorescence (using an ultra-violet analysis cabinet). R. A. Morton.

Phosphorescence of beryllium sulphide and a luminescent-analytical arrangement particularly for feebly phosphorescent preparations. E. Tiede and F. Goldschmidt (Ber., 1929, 62, [*B*], 758—762).—Beryllium oxide is converted by ignition with sugar charcoal in a current of chlorine or hydrogen chloride into beryllium chloride, which, after repeated sublimation, is heated in a stream of hydrogen sulphide. The pale grey, apparently amorphous beryllium sulphide thus prepared, which contains traces of chloride, is non-phosphorescent but yields weak phosphors after suitable treatment with bismuth or antimony. Beryllium sulphide, prepared from the pure metal and sulphur vapour in a current of hydrogen at 1000—1300°, without addition of excitant or flux, exhibits a feeble but distinct blue phosphorescence. The effect may be enhanced by addition of sodium chloride. It is attributed to the presence of iron in minute amount, but the effect is not increased by known addition of further amounts of the metal.

The analytical arrangement consists of a metal arc (iron, copper, or nickel) as source of the light which is passed through a black glass filter and uviol glass lens. The range of the light is 400—300 μμ. Intense illumination of very small surfaces is thus achieved and the arrangement is particularly suitable for minute objects. H. Wren.

Cause of the phosphorescence of calcium tungstate. A. Schleede and T. Tsao (Ber., 1929, 62, [*B*], 763—768).—Technical tungstic acid or ammonium tungstate is purified by alternate treatment with concentrated hydrochloric acid (or aqua regia) and sodium hydroxide or ammonia and converted by calcium chloride into calcium tungstate which is ignited at 1000°. The Röntgen-fluorescence of the preparation is about equal to that of the best technical specimens, whilst phosphorescence is sometimes present, sometimes absent. The latter property is inhibited by addition of calcium molybdate, but the fluorescence is sensibly diminished. Similar preparations are obtained from ammonium tungstate and calcium chloride in very dilute solution. Calcium tungstate, prepared from repeatedly crystallised sodium tungstate and calcium chloride, still exhibited phosphorescence but a non-phosphorescent material resulted when re-crystallised ammonium tungstate was used as initial material. Röntgenographic examination of the residues obtained from the mother-liquors from the ammonium tungstate disclosed the presence of arsenic and molybdenum. The addition of ammonium arsenate to ammonium tungstate previous to precipitation with calcium chloride leads to preparations with good fluorescence but marked phosphorescence; similar results are induced by ammonium antimonate. Ammonium molybdate does not induce phosphorescence. H. Wren.

Optical relationship between alkali halide phosphors and complex salt solutions. H. Fromherz and W. Menschick (Z. physikal. Chem., 1929, B, 3, 1—40, and Naturwiss., 1929, 17, 274—275).—Recent work on forces in crystals and in solutions of electrolytes leads to the supposition that the phosphors obtained by the addition of a trace of a heavy metal salt to an alkali halide, and the solutions of heavy metal salts in concentrated solutions of alkali halides, owe their origin to the same cause, viz., the formation of complex ions. The crystalline phosphors have sharp absorption bands in the ultra-violet. It was hoped to show that the solutions of heavy metal salts in alkali halide solutions have similar absorption bands. For this purpose the crystalline phosphors described by Smakula (A., 1927, 1125) were investigated, viz., alkali halide and silver halide, and alkali halide and copper halide. The extinction curves of the following pure solutions were obtained: sodium chloride, sodium bromide, potassium chloride, potassium bromide, potassium iodide, sodium perchlorate, silver perchlorate, cupric perchlorate, cupric chloride, and cupric bromide. The spectral absorption of the following complex solutions were also investigated: sodium chloride+silver chloride, potassium chloride+silver chloride, sodium bromide+silver bromide, potassium bromide+silver bromide, potassium iodide+silver iodide, silver perchlorate+silver iodide, potassium chloride+cupric chloride, potassium bromide+cupric bromide, potassium chloride+cuprous chloride, potassium bromide+cuprous bromide. By graphically subtracting the extinction curves, those of the pure complexes were obtained, and the curves for the crystals and the solutions were compared. The absorption bands of the pure alkali halide solutions are displaced towards the red by about 30 mμ in comparison with those of the crystalline compounds. The bands obtained with complex alkali halide solutions of silver and cupric salts agree in form, position, and sharpness with those of the corresponding crystals. The bands are displaced by only 6—10 mμ towards the red. From the ratio of the size of the absorption bands in the crystals and in the complex solutions it is shown that only 0·2—2% of the heavy metal salt is in the crystal lattice itself in an optically active form. The results show that association of atomic ions to form complex ions is the cause of the characteristic absorption bands and optical excitability of crystalline phosphors.

A. J. Mee.

Theory of Raman effect. L. Fernandes (Atti R. Accad. Lincei, 1929, [vi], 9, 407—409).

Raman effect and nagative absorption. B. Rossi (Atti R. Accad. Lincei, 1929, [vi], 9, 319—324).—Mathematical.

Raman effect in atomic hydrogen. B. Podolsky (Nature, 1929, **123**, 761).—A theoretical note.
A. A. Eldridge.

Raman effect in diatomic gases. F. Rasetti (Proc. Nat. Acad. Sci., 1929, **15**, 234—237; cf. Ramdas, A., 1928, 1307).—With the object of testing certain deductions on the Raman effect (A., 1928, 685, 1075) made from the new quantum mechanics, experiments were conducted on the effect for oxygen, nitrogen, and carbon monoxide. The results were found to be in accordance with the quantum theory of dispersion.
N. M. Bligh.

Raman effect in gases. I. Hydrogen chloride and ammonia. R. W. Wood (Phil. Mag., 1929, [vii], 7, 744—749).—Apparatus has been developed for the examination of the spectra of scattered light in gases and has been employed to measure the effects in hydrogen chloride. The mercury line 4046 Å. excites a modified line at 4581·8 Å. The frequency difference between the exciting line and the modified line corresponds with a wave-length of 3·466 μ in the infra-red. This is almost exactly the wave-length of the centre of the gap between the branches of the absorption band found by Imes. It is therefore identified as a *Q* branch not observed in absorption. A number of nearly equidistant bands close to the mercury line 4358 Å. are found to correspond fairly closely with alternate bands in rotation bands observed by Czerny. For ammonia the band at 3 μ was identified, but no trace of the strong NH_3 bands at 6·1 or 10·5 μ.
A. E. Mitchell.

Selection rules in the Raman effect. F. Rasetti (Nature, 1929, **123**, 757—759).—Experimental support is afforded for the selection rule whereby in order that a shift corresponding with the transition $i \longrightarrow k$ may be observed, it is necessary that both states *i* and *k* combine at least with a third state *l*. The Raman scattering becomes intense when the energy, $h\nu$, of the impinging quantum is near to $E_l - E_i$; if $E_l - E_i = h\nu$, fluorescence is observed. Using the mercury line 2536 Å., in oxygen and nitrogen there appear on both sides of the line a number of equally spaced lines, evidently due to rotational transitions. The spacing is considered theoretically, and for nitrogen the observed and calculated values are tabulated. The moment of inertia of the N_2 molecule is computed to be $13{\cdot}8 \pm 0{\cdot}1 \times 10^{-40}$ g. cm.^{2} It appears that in the normal state of N_2, only even rotational states are present, or these have a higher statistical weight than the odd ones. An explanation of the fact that the Raman lines corresponding with vibrational transitions in nitrogen and oxygen show no rotational structure is offered. The Raman spectrum of gaseous hydrogen has also been observed. Data for carbon dioxide support Eucken's model.
A. A. Eldridge.

Raman effect in quartz. M. Czerny (Z. Physik, 1929, **53**, 317—325).—The infra-red absorption of quartz, for wave-lengths greater than 30 μ, has been investigated with a grating spectrometer. Of the absorption maxima expected from the Raman effect, those occurring at 38 and 78 μ have been found, but the one expected to occur at 48 μ appears to be absent. The result is discussed with reference to the great differences between the relative intensities of Raman lines and of the corresponding infra-red absorption bands.
E. B. Robertson.

Secondary radiations in light diffused by calcspar. J. Cabannes (Compt. rend., 1929, **188**, 1041—1043; cf. Daure, this vol., 240).—The depolarisations of the two principal secondary lines of calcite have been studied. Each line may be considered to be emitted by a number of "virtual oscillators," the mean square of the electric displacement of which may then be calculated with respect to three axes at right angles. Contrary to Raman's theory, the radiation 280 cm.$^{-1}$ appears to be derived from oscillators which vibrate in an incoherent manner, the amplitude being the same whatever their orientation with respect to the exciting vibration. The displacement of the oscillators of the line 1083 cm.$^{-1}$ (which may be derived from vibrations of the carbon atoms of the carbonate ions) is always parallel to the incident vibration whether this is parallel or perpendicular to the ternary axis.
J. Grant.

Photo-electric emission from phototropic mercury compounds. S. V. R. Rao and H. E. Watson (J. Indian Inst. Sci., 1929, **12A**, 17—29).—The photo-electric emission from twelve phototropic mercury compounds (cf. this vol., 660) has been measured by a thermionic valve method (Toy and others, A., 1927, 293). In the dark the emission is zero or negligible. On exposure to the light of a mercury-vapour lamp the emission increases to a maximum after 250—300 sec. and then remains steady without signs of photo-electric fatigue even after exposures up to 80 min. duration. At 2 mm. pressure a maximum current of 82×10^{-11} amp. was recorded for the substance $HgI_2,2HgS$. The photosensitiveness falls on heating or on keeping in the dark almost to that of the freshly-prepared compounds. The emission of darkened compounds is constant, whether the darkening was caused by visible or ultra-violet light. Some indication was found that for related compounds the photo-electric and phototropic properties run parallel.
F. G. Tryhorn.

Electric moments of molecules and methods of determining them. G. B. Bonino and P. Cella (Gazzetta, 1929, **59**, 79—105).—A discussion of the importance of electrical molecular moments and a critical review of methods which have been used in determining them from measurements of specific inductive capacity. An oscillating valve circuit which has been found by the authors to be satisfactory is described and results are given of measurements of the dielectric constants of carbon tetrachloride and tetrachloroethylene at various temperatures, using benzene as a reference liquid in each case. The values of the constants for the internal molecular fields of these molecules calculated from the above measurements by the authors differ considerably from the classical values. These discrepancies are discussed in relation to Debye's theory.
F. G. Tryhorn.

Molecular structure and dipole moment. W. Hückel (Z. physikal. Chem., 1929, **B**, **2**, 451—457).—In order to explain the dipole moment possessed by symmetrical organic compounds of the type $C\alpha_4$ it has been assumed that the carbon atom has a pyramidal structure instead of a tetrahedral one. This structure is discussed, and it is shown that the occurrence of dipole moments in these compounds is not in contradiction with classical stereochemistry.

A. J. MEE.

Non-polar combination and atomic refraction. II. R. SAMUEL (Z. Physik, 53, 1929, 380—403).—In the calculation of molecular refraction of an organic molecule two different refractive equivalents are chosen, instead of the usual value, as the radical functions positively or negatively in the molecule. Many unexplained anomalies disappear. Among these are exaltation, depression, or the necessity of different values for the atomic refraction of the nitrogen atom in amines and other compounds. By this method some conclusions on the function of the radical in non-polar molecules are reached.

G. E. WENTWORTH.

Measurement of the dielectric constants of liquids, with a determination of the dielectric constant of benzene. L. HARTSHORN and D. A. OLIVER (Proc. Roy. Soc., 1929, A, 123, 664—685).—In view of the large discrepancies in the values obtained by different observers for the dielectric constant of any one liquid, the various methods of measurement have been studied and all are found to involve errors. A highly accurate method has been worked out, by means of which the dielectric constant of a given liquid can be determined with a probable error of 1 part in 10,000 parts. It is shown that the test condenser must possess a capacity of at least 100 $\mu\mu F$, must be as rigid as possible, and must be completely enclosed in a conducting screen; the air gap between the plates must have a minimum value of 1 mm., the plate systems must be insulated from the screen, and it must be possible to disconnect the plate systems from the leads at points inside the screen without appreciably changing the position of the leads. Data are given for the absolute determination of the dielectric constant of a sample of commercial benzene (A.R. grade) with such a condenser, which needs about 500 c.c. of liquid to fill it. Measurements were then made to show that if one liquid is standardised absolutely, and comparisons are made between it and a second liquid by a method requiring only a small quantity of the second liquid, the value so obtained is identical with that found by the direct use of the absolute method. Finally, the dielectric constant of highly purified benzene was found by the comparison method to be $2{\cdot}282_{5\pm5}$ at 20° (vacuum=1). Moisture appears to be the only impurity of importance in dielectric constant measurements.

L. L. BIRCUMSHAW.

Measurement of weakly elliptically polarised light in the ultra-violet. G. SZIVESSY and C. MUNSTER (Z. Physik, 1929, 53, 13—51).—A method is described for determining the constants of the vibration path of weakly elliptically polarised ultraviolet light. The azimuth of the path can be estimated to within the fraction of a minute, and an eccentricity of 0·005 to an accuracy of about 1%.

E. B. ROBERTSON.

Paramagnetism and the structure of combined atoms. B. CABRERA (Anal. Fís. Quím., 1929, 27, 73—107).—The mechanics of the atom, as modified by combination with other atoms, is discussed from the point of view of magnetic behaviour. Langevin's formula leads to values of the magnetic moment which confirm the existence of the magneton of Weiss, a conception which leads to a new hypothesis governing the configuration of combined atoms and responsible also for chemical valency. Sidgwick's theory of the formation of new electronic shells in the nuclear atom of a complex molecule has many difficulties from the magnetic point of view. H. F. GILLBE.

Diamagnetic anomaly (observed) of gases. A. GLASER (Ann. Physik, 1929, [v], 1, 814—820).—Certain diamagnetic molecular gases exhibit an anomaly in the pressure–susceptibility curve. Oxygen, which is paramagnetic, does not show the effect. Investigation of the behaviour of argon and neon discloses that under conditions favourable to the observation of the diamagnetic anomaly (*e.g.*, in carbon dioxide or nitrogen) neither of the rare gases shows any departure from the linear relationship. This result is ascribed to the atomic character of the gases. Control experiments provide no support for the view that traces of moisture are responsible for the anomaly.

R. A. MORTON.

Atomic dynamics of ferromagnetic substances. R. SWINNE (Wiss. Veröff. Siemens-Konzern, 1929, 7, [2], 85—99).—Ferromagnetism occurs only in crystals with a non-polar lattice. The idea of a "bound outer electron," distinct from the electron of the valency linking, is discussed in relation to the electronic structure of metals in the transition series of the periodic table. The work of Heitler, London, and Heisenberg is considered in relation to ferromagnetism (cf. A., 1928, 344, 589, 1077, 1300).

R. A. MORTON.

Diamagnetism of some binary halogen compounds. R. HOCART (Compt. rend., 1929, 188, 1151—1153).—Determinations of the magnetisation coefficients of hydrogen chloride and of a number of metallic chlorides in the solid state and in solution have been carried out by the ascension and translation pendulum methods with accuracies of at least 0·1 and 0·3%, respectively. The diamagnetism of the ions in solution is not strictly additive.

J. GRANT.

Diamagnetism of the azoxyanisole crystal and Larmor's precession. G. FOËX (Compt. rend., 1929, 188, 1154—1156).—The mean coefficient of magnetisation of monoclinic *p*-azoxyanisole is $-5{\cdot}69\times10^{-7}$. The value found for δ (0·283) indicates that Larmor's theorem of the precession of an electron around the field does not apply, but is compatible with the existence of partial precession. The orientation of the orbits in fixed circuits, however, is in agreement with Pascal's laws of additivity, and if the molecules are completely oriented the values of the principal coefficients are a measure of the molecular disymmetry. Molecular orientation is more complete in the crystal than in the nematic substance in an intense field. J. GRANT.

Magnetic moment of the lithium atom. D. A. JACKSON (Z. Physik, 1929, 53, 458).—Polemical against Taylor (this vol., 491).

Magnetic moment of the lithium atom. O. Stern (Z. Physik, 1929, 54, 158).—Polemical; cf. Taylor (this vol., 491); Jackson (preceding).
J. W. Smith.

Spectroscopic confirmation of the quantum-mechanical theory of homopolar linking. W. Heitler and G. Herzberg (Z. Physik, 1929, 53, 52—56).—Evidence from band spectra is discussed which indicates that certain atoms, such as carbon, become capable, on excitation, of entering into firmer chemical combination. This is in accordance with the quantum-mechanical theory of homopolar chemical linking, according to which, in many cases, an atom must be excited in order to exert its full valency. Thus, the quadrivalent carbon atom arises out of the normal bivalent atom by excitation of about 1·6 volts (^5S state).
E. B. Robertson.

Configuration of quadrivalent atoms. T. M. Lowry (Proc. Camb. Phil. Soc., 1929, 25, 219—221).—The problem of the configuration of *cis-* and *trans*-forms of radicals or molecules of the type MA_4 has been solved by the *X*-ray analysis of crystals of both types and the results are supported by the change in the crystallographic system of the two series.
N. M. Bligh.

Constitution of the boron hydrides. E. Wiberg (Z. anorg. Chem., 1929, 179, 309—320).—Polemical against Müller (this vol., 13).
H. F. Gillbe.

Structure of the CH_4 molecule. G. W. Brindley (Nature, 1929, 123, 760—761).—The results of Hogness and Kvalnes (this vol., 242) accord with the view that the four chemical linkings in methane consist of pairs of shared electrons, each pair being formed by an *L*-electron of the carbon atom and a hydrogen electron. Since there are two 2_1 and two 2_2 electrons in the carbon atom, two of the linkings will differ from the other two (Lonsdale, A., 1928, 1079). Models of the methane molecule having either a C^{4-} or a C^{4+} central ion are unacceptable.
A. A. Eldridge.

Rectilinear diameter of ethylene. E. Mathias, C. A. Crommelin, and H. G. Watts (Ann. Physique, 1929, [x], 11, 343—353).—The densities of liquid ethylene and of the saturated vapour were determined over a wide range of temperature and tabulated together with the calculated diameters. The observed and calculated vapour tensions and latent heat of vaporisation are similarly tabulated and good general agreement between the two sets of values is obtained.
N. M. Bligh.

Absolute velocity of a water molecule emitted on the dehydration of a crystalline hydrate. A. S. Predvoditelev (Z. Physik, 1929, 54, 159—160).—A correction of earlier calculations (cf. this vol., 21).
J. W. Smith.

Scattering of *X*-rays by graphite. W. Ehrenberg (Z. Physik, 1929, 53, 234—236).—Spectroscopic examination of *X*-ray scattering of graphite cannot confirm the results of Davis and Mitchell (A., 1928, 1168). No deviated lines are observed except the Compton line.
G. E. Wentworth.

Evaluation of Debye–Scherrer spectrograms. G. Kettmann (Z. Physik, 1929, 53, 198—209).—A graphical method is given for the evaluation of the grating constants in the Debye–Scherrer spectrograms. With substances giving only small interference the accuracy of the evaluation is increased by using radiations of several frequencies.
G. E. Wentworth.

Occurrence of structure lines at the *K*-absorption band edge of bromine. H. T. Meyer (Wiss. Veröff. Siemens-Konzern, 1929, 7, [2], 101—107).—At the *K*-absorption band edge of bromine obtained by absorption with sodium or potassium bromate in the solid state or in solution, structure lines have been recorded which do not appear when sodium or potassium bromide is used as the absorbing material. This is considered to be a striking example of the effect of chemical linking on the *K*-absorption, since the atomic number (35) is so high. The wave-length differences of the lines correspond with 39·6, 119·6, and 241·4 volts.
R. A. Morton.

Superposed *X*-radiations. *J*-Phenomenon. IX. C. G. Barkla and M. M. Sen Gupta (Phil. Mag., 1929, [vii], 7, 737—742).—Previous results of Barkla and Mackenzie on the *J*-discontinuities produced by the superposition of *X*-ray beams from separate sources have been confirmed by superimposing *X*-ray beams scattered from paper or paraffin wax. Precautions were taken to ensure that the two scattered beams did not become superimposed until in close proximity to the aluminium absorbers employed to detect the displacement of the *J*-discontinuities.
A. E. Mitchell.

***X*-Ray diffraction haloes in aqueous solutions of electrolytes.** H. Shiba and T. Watanabe (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, 10, 187—192; cf. Krishnamurti, A., 1928, 1079).—Results were tabulated for solutions of various concentrations of sulphuric acid, the hydroxides of lithium, sodium, potassium, and ammonium, the chlorides and nitrates of lithium, sodium, potassium, beryllium, and aluminium, and the chlorides of ammonium and magnesium. The electrolytes could be classified into three groups having, respectively, a halo approximately the same size as that of water, a halo which expands with concentration, and a halo which contracts as concentration increases. The halo contraction seemed to be closely related to the formation of a complex of the cation with water. In general, the diffraction at small angles becomes weak as the concentration is increased.
N. M. Bligh.

Total reflexion of *X*-rays from nickel films. II. H. W. Edwards (Physical Rev., 1929, [ii], 33, 463—466; cf. A., 1927, 921; this vol., 123).—The critical angle for thin nickel films sputtered on platinum which was sputtered on a glass support was found to decrease logarithmically with increasing thickness of nickel film except for an increase with the thinnest films. Results indicate that total reflexion is not purely a surface phenomenon.
N. M. Bligh.

Diffraction of *X*-rays in liquids and liquid mixtures. H. F. Hertlein (Z. Physik, 1929, 54, 341—346).—The *X*-ray diffraction in mixtures of methyl, ethyl, and propyl alcohols with water has been investigated. The results indicate that the effect is of an intermolecular nature, as supposed by

Stewart, Morrow, and Skinner (A., 1927, 1015; 1928, 224). J. W. Smith.

Spectral analytical determination of readily fusible and liquid substances by means of Lenard tubes. O. Eisenhut and E. Kaupp (Z. Physik, 1929, **54**, 427—432).—Details are given of a convenient method of excitation of characteristic *X*-rays by means of cathode rays from a Lenard tube, schemes for eliminating the usual experimental errors being fully described. This method has been tested with iron, selenium, and gallium, the wave-lengths of the *K* series of the last-named element, hitherto uncertain, having been measured carefully. The extreme sensitivity of the method is illustrated by measurements on iron with a very small admixture of mercuric oxide. J. W. Smith.

Fine structure of the normal scattered molybdenum $K\alpha$-radiation from graphite. D. Coster, I. Nitta, and W. J. Thijssen (Nature, 1929, **123**, 642).—The experiments of Davis and Mitchell (A., 1928, 1168) have been repeated, using the photographic method, but no difference between the structure of the primary radiation and that of the "undisplaced" scattered line was detected. If there should exist in the *X*-ray spectrum something analogous to the Raman effect in the optical region, it would be expected to give rise, not to lines, but to a continuous spectrum. A. A. Eldridge.

Violation of the selection principle for the principal quantum number. S. Idei (Nature, 1929, **123**, 643).—New measurements in the *L*-series for tantalum, tungsten, platinum, and gold give values of ν/R more accurate than those recorded by Thibaud and Soltan (A., 1927, 1000; 1928, 339). It appears that the doublets found by these authors may be due to transitions $N_{\text{IV}}\ N_{\text{VI}}$ and $N_{\text{V}}\ N_{\text{VI VII}}$. A. A. Eldridge.

Measurement of the K_a line of carbon. C. E. Howe (Proc. Nat. Acad. Sci., 1929, **15**, 251—253).—In view of previous divergent values the wave-length of the $K\alpha$ line of carbon was determined accurately by an improved method. An unweighted mean value of 44·60 correct to 0·04 Å. was obtained. N. M. Bligh.

Densitometric measurements of the $K\alpha$ line of carbon. C. B. Bazzoni, Faust, and Weatherby (Nature, 1929, **113**, 717).—Separation of components has been accomplished for the $K\alpha$ lines of carbon (four principal components, 44·2, 42·0, 45·4, 46·15 Å.) and boron. A. A. Eldridge.

Crystal structure of some binary compounds of the platinum metals. L. Thomassen (Z. physikal. Chem., 1929, B, **2**, 349—379).—A number of binary compounds of the platinum metals and antimony, tellurium, selenium, and sulphur were prepared and their crystalline structure was investigated by the powder method. The compounds were classified into three groups according to their structure. The pyrites group contains five new compounds: osmium ditelluride, $OsTe_2$ (a=6·369±0·003 Å.), osmium diselenide, $OsSe_2$ (a=5·933±0·002 Å.), ruthenium ditelluride, $RuTe_2$ (a=6·360±0·002 Å.), ruthenium diselenide, $RuSe_2$ (a=5·921±0·002 Å.), and platinum diantimonide, $PtSb_2$ (a=6·428±0·003 Å.). Systems with the compositions OsTe, OsSe, RuTe, and RuSe are shown to be mixtures of the corresponding di-compounds with the metal. The second group, cadmium iodide type, contains palladium ditelluride, $PdTe_2$ (a=4·028±0·003 Å.; c=5·118±0·004 Å.), platinum ditelluride, $PtTe_2$ (a=4·010±0·004 Å.; c=5·201±0·005 Å.), platinum diselenide, $PtSe_2$ (a=3·724±0·004 Å.; c=5·062±0·004 Å.), platinum disulphide, PtS_2 (a=3·537±0·004 Å.; c=5·019±0·005 Å.). It was possible to prepare only one member of the series containing palladium, viz., palladium ditelluride, $PdTe_2$. The third group, nickel arsenide type, contains palladium monotelluride, PdTe (a=4·127±0·004 Å.; c=5·663±0·005 Å.). Since there is a certain analogy between the structure of these compounds and that of the ferrous metals, it might be expected that they would possess ferromagnetic properties. On testing with a bar magnet, and with an electromagnet at liquid air temperature, no positive results could be obtained. Further compounds, similar to the above, have also been tested, and whilst weak para- or dia-magnetism was found there was no indication of ferromagnetism. A. J. Mee.

***X*-Ray diagram of native cellulose.** K. R. Andress (Z. physikal. Chem., 1929, B, **2**, 380—394).—The intensities of points on the *X*-ray diagram of native cellulose are examined. The intensities calculated from the position of the atoms in Meyer and Mark's model of the cellulose molecule are in satisfactory agreement with those actually observed. A. J. Mee.

Ionic arrangement. H. J. Kist (Rec. trav. chim., 1929, **48**, 310—311).—Calculations are made of the positions assumed by ions arranged around a positive nucleus. With three negative ions, the positions will be at the apices of an equilateral triangle in a great circle, with four, at the corners of a sphenoid of tetrahedral type. An octahedral arrangement is found in the case of six ions, and with eight ions positions are occupied at the corners of a tetragonal trapezohedron which is so truncated that eight corners are produced. F. G. Tryhorn.

Imperfections of crystals. F. Zwicky (Proc. Nat. Acad. Sci., 1929, **15**, 253—259).—Theoretical. It is shown that the discrepancy between the theoretical and experimental values for the breaking strength of dry crystals can be satisfactorily accounted for by the presence of microscopic cracks in the surface of the crystals and occurring between the blocks or "mosaics" of the crystal, in accordance with Smekal's views (cf. A., 1927, 192). This cracking is shown to be connected with the surface energy, and the shape and dimensions of the cracks can be deduced approximately. The theory explains the fact that the theoretical value of the breaking strength can be approached under suitable circumstances and surface conditions, and its bearing on crystal growth, chemical imperfections, and the absorption of gases by metals is considered. N. M. Bligh.

***X*-Ray study of surface or interfacial orientations by the tangential drop method.** J. J. Trillat (J. Phys. Radium, 1929, [vi], **10**, 32—43).—

The basis of the method is that a pencil of *X*-rays suffers diffraction at the surface of a drop. As this surface is curved, the same effect is obtained as when the rays are diffracted by a crystal which is turned slowly about an axis, except that all the diffraction rays are obtained simultaneously. This method can be applied to solid or liquid drops, surrounded either by air or by another liquid. With a layer of fatty acid on a drop of mercury it is found that the film of attack, composed of the mercury salt, consists first of a layer of molecules with their $\cdot CO_2Hg$ groups anchored to the mercury and the rest of the chain standing up. The next layer has its methyl groups adjacent to the methyl groups of the first layer and its $\cdot CO_2Hg$ adjacent to the $\cdot CO_2Hg$ of the third layer, and so on. It is also concluded that the carbon atoms in the fatty acid chain have a zig-zag formation and that the chains themselves are slightly inclined to the normal to the surface of the drop. The solid–air interfaces of some long-chain compounds have been examined by allowing a drop of the melted substance to solidify by slow cooling. It is found that the surface layer of the drop consists of perfectly oriented molecules, similar to the surface of contact with glass but probably with the methyl groups outermost. The modifications which lead oleate undergoes with change of temperature have been investigated.

J. L. BUCHAN.

Possible dissymmetry of corrosion figures obtained by an active isotropic liquid. L. ROYER (Compt. rend., 1929, **188**, 1176—1178).—The etching effects of malic, aspartic, gluconic, camphoric, glyceric, pyruvic, and mucic acids on a cleavage plane of calcite parallel to the reticular plane *p*(100) were examined. When the acids were optically active the corrosion figures were dissymmetrical with respect to the plane of symmetry *P* normal to the face under observation; when the liquids were inactive the figures were perfectly symmetrical (cf. Herzfeld and Hettich, A., 1926, 889).

J. GRANT.

Single crystals of silver. E. W. R. STEACIE and F. J. TOOLE (J. Amer. Chem. Soc., 1929, **51**, 1134—1135).—Very pure silver which has been fused and kept just below the m. p. for several days and then cooled very slowly dissolves non-uniformly in dilute nitric acid, gradually assuming the shape of an octagonal prism. The silver must not come into contact with oxygen during the operations. The crystal form of the prism is briefly described.

S. K. TWEEDY.

***X*-Ray investigation of the internal stress in carbon steels.** S. SEKITO (Sci. Rep. Tôhoku Imp. Univ., 1928, **17**, 1227—1236).—Lattice distortion in carbon steels containing 0·1, 0·3, and 0·5% C as the result of cold-drawing from 3·0 to 0·67 mm. diameter was determined from the broadening of the spectral lines. The maximum variation in the lattice parameter was 0·4%, corresponding with an internal stress of 84 kg./mm.^{2}, which is slightly less than the tensile strength of these steels.

C. J. SMITHELLS.

Crystal structure of strontium and barium. F. EBERT and H. HARTMANN (Z. anorg. Chem., 1929, **179**, 418—420).—Strontium crystallises in the cubic system, with a face-centred lattice having *a* 6·05 Å. Barium also crystallises in the cubic system, but the lattice is space-centred, with *a* 5·01 Å.; the atomic radii are: strontium, 2·135 Å., barium, 2·17 Å.

H. F. GILLBE.

Crystal structure of tetraethylammonium iodide. R. W. G. WYCKOFF (Z. Krist., 1928, **67**, 550—554; Chem. Zentr., 1928, ii, 2221).—Tetraethylammonium iodide has *a* 8·87, *c* 6·95 Å.; the unit cell contains two molecules of NEt_4I.

A. A. ELDRIDGE.

Crystal structure of titanium monoxide. H. BRÄKKEN (Z. Krist., 1928, **67**, 547—549; Chem. Zentr., 1928, ii, 2220).—The atomic lattice is face-centred cubic, *a* 4·235±0·005 Å.

A. A. ELDRIDGE.

Crystal structure of some rhombic compounds MX_2. H. BRÄKKEN and L. HARANG (Z. Krist., 1928, **68**, 123—138; Chem. Zentr., 1928, ii, 2219).—Lead chloride has a 4·49$_6$, b 7·66$_7$, c 9·15$_3$ Å.; axial ratio $a:b:c$=0·586 : 1 : 1·194. Lead bromide has a 4·70$_6$, b 7·98$_9$, c 9·47$_5$; $a:b:c$=0·589 : 1 : 1·186. In both cases the unit cell contains four molecules of PbX_2; space-group V_h^{16}. The structure is discussed. Mercuric chloride has a 4·30$_7$ b 5·93$_6$, c 12·66$_7$ Å.; $a:b:c$=0·7255 : 1 : 2·1336. The unit cell contains four molecules of $HgCl_2$; space-group V_h^{16}. The structure is considered to resemble that of the lead halides.

A. A. ELDRIDGE.

Distribution of foreign substances in single crystals of zinc. M. STRAUMANIS (Z. anorg. Chem., 1929, **180**, 1—10).—Single crystals of zinc deposited from molten zinc containing cadmium possess a banded structure owing to the simultaneous separation of cadmium in layers parallel to the basal faces of the crystals. There is also a slight separation in a perpendicular direction, showing that the cadmium forms a network. With as little as 0·2% Cd this structure can still be detected, so that, contrary to the findings of Rosbaud and Schmid (A., 1925, ii, 488), it must be concluded that even this small amount of cadmium does not form a mixed crystal. The cleavage of the crystals indicates that the cadmium assumes the same orientation as the zinc, and forms an integral part of the lattice. Aluminium, bismuth, magnesium, and tin behave in the same way as cadmium.

R. CUTHILL.

Crystal structure of thin metallic films. (MLLE.) S. DEMBINSKA (Z. Physik, 1929, **54**, 46—52).—Employing Bragg's method, the crystal structure of thin films (7—18 mμ thickness) of platinum, copper, and nickel crystals formed by cathodic or thermal spattering have been investigated. The films show definite orientation, but there is a dispersion of the reflexion line of the (111) plane, the magnitude of which depends on the nature of the plate supporting the metallic film.

J. W. SMITH.

Recrystallisation of single crystals of aluminium. II. Orientation of the crystals formed by recrystallisation under strong deformation. W. G. BURGERS and J. C. M. BASART (Z. Physik, 1929, **54**, 74—91; cf. this vol., 384).—If single aluminium crystals are stretched until they are one fourth their original thickness and then heated for a short time at 600°, the orientation of the crystals then formed shows a statistical anisotropy. The variation of this orientation with the treatment given to the crystals has been studied by stereoscopic *X*-ray spectrograms.

J. W. Smith.

Anomalous after-effect with quartz. H. Saegusa and S. Shimizu (Nature, 1929, **113**, 713—714).—An anomalous after-effect in the apparent resistivity of quartz is ascribed to some property of the atomic lattice.

A. A. Eldridge.

Change of electrical conductivity in strong magnetic fields. I. Experimental results. II. Analysis and interpretation of the experimental results. P. Kapitza (Proc. Roy. Soc., 1929, **A**, **123**, 292—341, 342—372).—I. By means of an improved form of the apparatus previously employed for measuring the change of resistance of bismuth crystals in magnetic fields up to 300 kilogauss (A., 1928, 825), a study has been made of the change of resistance in a transverse field at the ordinary temperature, at the temperature of solid carbon dioxide and ether, and at the temperature of liquid nitrogen for the following metals: lithium, sodium, copper, silver, gold, beryllium, magnesium, zinc, cadmium, mercury, aluminium, gallium, indium, thallium, graphite, germanium, tin, lead, titanium, zirconium, thorium, arsenic, antimony, bismuth, vanadium, tantalum, chromium, molybdenum, tungsten, tellurium, manganese, iron, nickel, palladium, platinum; and for a gold–silver alloy and a copper–arsenic alloy (Cu_3As). Measurements were also made in a parallel field with copper, cadmium, aluminium, gallium, and molybdenum. The metals were very highly purified. The influence of impurities on the phenomena studied was found to be very marked, particularly in the lighter elements, and invariably reduced the change of resistance. All the curves showing change of resistance with magnetic field, except those for iron and nickel (the latter being the only metal studied in which a decrease of resistance was observed instead of an increase), are exactly similar in character. The increase of the resistance at the beginning is proportional to the square of the magnetic field, but later is directly proportional to the field. This change from the square to the linear law takes place gradually after a critical field H_k which for different substances ranges from 5 to 250 kilogauss. The linear part of the curve appears to be independent of the crystalline state of the metal, and to be related to the position of the element in the periodic table. The results are compared with those of previous investigators. The suggestion that the strongly diamagnetic substances give a larger change of resistance (de Haas, Proc. Roy. Acad. Amsterdam, 1914, **16**, 1110) is not confirmed.

II. A general theory is developed of the phenomenon of change of resistance in a magnetic field. It is assumed that the change of resistance follows a linear law which is fully established only when the field is well above the critical value (H_k), and is masked below H_k by an initial disturbance, already existing in the metal, equivalent to that produced by a magnetic field distributed at random in the conductor. When the outside field is applied, the disturbance causing the increase of resistance is now the vectorial sum of these two disturbances and the increase of resistance is proportional to this sum. Expressions are derived which represent the experimental facts within the limits of error, and by means of which the "ideal" resistance R_i may be separated from the "additional" resistance ΔR_0 produced by internal disturbances. R_i is found to be a constant for a given temperature, independent of the physical and chemical state of the metal, but diminishes rapidly with fall of temperature, whilst ΔR_0 is independent of the temperature but is affected by the physical state of the conductor, having a higher value in a hard-drawn wire than in an annealed wire. ΔR_0 is identified with the "residual" resistance (Kamerlingh Onnes) which is observed near the absolute zero. A comparison of ΔR_0 for the superconductors mercury, thallium, tin, lead, and indium with the resistance near the threshold of superconductivity shows that the values lie within the limits of the variation of the resistance at the threshold observed by Kamerlingh Onnes for different specimens of the same superconductor. This indicates that the phenomenon of superconductivity consists in the disappearance of the additional resistance, the resistance of the conductor then being equal to R_i. It is concluded that superconductivity is a general phenomenon in all metals, but is masked by the additional resistance which disappears at very low temperatures in certain metals.

L. L. Bircumshaw.

Susceptibility and change in resistivity of metals in a magnetic field. F. Block (Z. Physik, 1929, **53**, 216—227).—The paramagnetic behaviour of metals is investigated from the point of view of the conception that the so-called "free electrons," responsible for the electrical conductivity, are not free but move in a periodic field of force. It is shown also that the change of resistance in a magnetic field can be formulated to the correct order of magnitude if the spin orientation is considered with the Sommerfeld formula for the periodic field of force.

G. E. Wentworth.

Influence of grain-size on the magnetic properties of iron. O. von Auwers (Wiss. Veröff. Siemens-Konzern, 1929, **7**, [2], 197—209).—The fall in watt/kg. for electrolytic iron decreases as the cube root of the grain-size, but this relationship is strongly influenced by heat-treatment. Grain-size also affects coercivity forces, remanence, and permeability curves, but saturation value and specific resistance are uninfluenced. The rôle of grain-size is less important after heating in hydrogen, and is further reduced by heating in a moderately good vacuum (oxygen). Chemical effects between oxygen and carbon are important. The influence of grain-size on magnetic properties is essentially secondary in nature, depending on surface contamination by oxides and carbides.

R. A. Morton.

Method of measuring the electrical resistances of alloys. A. L. Norbury (Phil. Mag., 1929, [vii], **7**, 662—669).—The method consists in determining the electrical resistance between the equator of a ball or the shoulder of a 90° cone of a metal, such as steel or copper, and the plane surface of the metal under test into which it is pressed by loading, and measuring the diameter of the impression so made. Calibration curves are made by measuring these quantities with combinations of metals of known resistance, and these are employed to give the results for other metals. Contact resistances are eliminated by the etching of the surfaces to be brought into contact. The method has the advantage that it can be used in the determination of the resistances of materials of which only small pieces are available. The plane surface required need not exceed an area of 5 by 0·5 mm. A. E. MITCHELL.

Preparation, optical and magneto-optical properties of very thin iron layers. M. CAU (Ann. Physique, 1929, [x], 11, 354—449).—The transparency, reflecting power, optical and geometric thickness, and Faraday and Kerr effects were studied for thin iron films prepared by distillation in a vacuum and by cathodic deposition. The optical effects were calculated theoretically and plotted as functions of film thickness. Comparison of calculated and experimental results shows, in the case of deposited iron, a general agreement, the constants being the same as for iron in bulk. In the case of the distilled films the results, as well as those for the magneto-optical effects, are somewhat discordant, and the classical optical theory of metals is apparently not applicable. The reflexion effects can be calculated from the transmission effects on simple theoretical grounds and show good agreement with experimental results. It is concluded that the deposited films, in spite of discrepancies due to differences of crystal structure, are more regular than the distilled films and approximate more closely to iron in bulk. Classical optical theory is applicable to a close approximation. Distilled films, which are more allied to the amorphous state, and of complex structure, give different results. N. M. BLIGH.

Fundamental law of paramagnetic magnetisation of a crystal, and the law of paramagnetic rotatory dispersion. J. BECQUEREL and W. J. DE HAAS (Compt. rend., 1929, 188, 1156—1158).—Ladenburg's formula expressing the rotation in terms of the wave-lengths of the activated absorption bands (A., 1927, 493) is confirmed in the case of tysonite (A., 1928, 823) between 4·21° and 1·95° Abs. to within 0·1%, and also for parisite. It is concluded that the high paramagnetic rotation of tysonite compared with its diamagnetic rotation is due to the $\mathrm{Ce}^{\cdots}$ ion, the hyperbolic tangent law established in this case (*loc. cit.*) being an indication of the reversal of the sense of the magnetic moment. J. GRANT.

Magnetisation of single crystals of cobalt. S. KAYA (Sci. Rep. Tôhoku Imp. Univ., 1928, 17, 1157—1177).—Large single crystals of cobalt were prepared by slow cooling through the transformation point at 470°, and two discs 4·5 mm. in diameter were cut so as to present (0001) and $(10\bar{1}0)$ planes, respectively. In the $(10\bar{1}0)$ plane magnetisation was easy in the [0001] direction but difficult in the $[10\bar{1}0]$ direction, the maximum permeabilities being 380 and 4, respectively. The parallel and perpendicular components of magnetisation vary with a period of 180° in this plane. In the (0001) plane magnetisation was difficult in the directions of both the principal axes $[10\bar{1}0]$ and $[11\bar{2}0]$. The saturation value for a single crystal rod having its axis parallel to direction of easy magnetisation [0001] was 1422 at 26°. The results are in agreement with the theory of Honda and Okubo (*ibid.*, 1926, 15, 449). C. J. SMITHELLS.

Connexion between size of crystal nucleus and magnetic properties of pure nickel. G. J. SIZOO (Z. Physik, 1929, 53, 449—457).—The conditions of recrystallisation of nickel are studied. The manganese content must be below 0·2% before recrystallisation phenomena may be produced by mechanical and thermal processes. Twin crystals then form easily. A study of the magnetic properties in connexion with the size of the crystal nucleus gives the same results as were obtained with iron. G. E. WENTWORTH.

Influence of pressure from all sides on metallic conductivity of low temperature. H. J. SEEMANN (Physikal. Z., 1929, 30, 256—258).—The pressure coefficient γ, where $\gamma=\Delta w/w\,.\,p$, Δw being the change of the resistance w under a pressure p, has been given by Onnes and Beckmann (Comm. Leiden, 1912, 312) as $\gamma=-17\times10^{-16}$ at −252·7° and $-22{\cdot}5\times10^{-6}$ at −183°, whilst Lisell found $\gamma=-14{\cdot}4\times10^{-6}$ at 0°, the metal being lead. In the present work, the pressure coefficient for copper has been determined over the range 50—150 kg./cm.^{2} and at 0° $\gamma=-2{\cdot}14(\pm0{\cdot}013)\times10^{-6}$, whilst at −195° $\gamma=-5{\cdot}17\times10^{-6}$, the extreme determinations being 20% from the mean. It is probable that reduction of temperature will, in general, increase the pressure coefficient of the resistance of a metal. R. A. MORTON.

Crystal structure and ferromagnetism. W. SCHMIDT (Physikal. Z., 1929, 30, 259—261).—Temperature discontinuities in various physical properties of iron conform with considerable accuracy with the relation $T=nT_s/m$, T_s being the m. p. of iron (ca. 1803° Abs.), $m=14$, n being an integer less than 14, and T corresponding with an experimental discontinuity. The temperature 901·6° Abs., for instance, corresponds with 883° Abs., at which point the line expressing the variation between atomic distance and temperature for α- and δ-iron is intersected by the extrapolated similar line for γ-iron. There do not appear to be experimental data corresponding with $n=1$, 5, or 6. The expression may be of more general significance to critical temperatures of metals; *e.g.*, tin melts at 504·9° Abs., and discontinuities at 434° and 291° are consistent with $m=14$. R. A. MORTON.

Coercive power. I. Coercive power and mechanical hardness. A. KUSSMANN and B. SCHARNOW (Z. Physik, 1929, 54, 1—15).—The dependence of the coercive power (magnetic hardness) on the mechanical hardness and on the structure of alloys has been investigated. It has been established that in solid solution (mixed crystals) in which mechanical hardness, electrical resistance, etc. are considerably higher than with the pure metals, the coercive power is only slightly changed, and that no direct relation with the mechanical hardness of the alloy exists. In heterogeneous mixtures the coercive power is always much higher, independently of the mechanical hardness. This is attributed to the tension set up by contraction of the ferromagnetic material in the mixture. J. W. SMITH.

Piezo-electric effect of diamond. W. A. WOOSTER (Min. Mag., 1929, 22, 65—59).—An even pressure of about 300 g. was applied by means of an electro-magnet on an octahedral face of diamond. The results show that, within the limits of error of the experiment, diamond is not piezo-electric, the electrical charge developed being less than 0·005 of that obtained when a plate of quartz cut perpendicular to an electric axis was used. L. J. Spencer.

Optical activity of quartz perpendicular to the optic axis. G. Szivessy and C. Schweers (Ann. Physik, 1929, [v], **1**, 891—947).—First, the results of the crystal lattice theory as applied to the problem are given. The optical behaviour of any non-absorbing, active crystal is known if the position of the symmetry-axis system, the principal refractive indices, and the components of the gyration tensors along the optical symmetry axes are known. The laws relating to the propagation of light in non-absorbing, active crystals are collected. The components of the gyration tensors for trigonal enantiomorphic crystals are worked out. For a crystal of this class the gyration surface is an ellipsoid or a hyperboloid with the optic axis as axis of rotation. The numerical values for the components of the gyration tensors are obtained for α-quartz. The results do not agree with those of Voigt or of Wever, for the methods used by these workers are in error. The experimental method and apparatus are described. The component of the gyration tensor perpendicular to the optic axis for α-quartz is very small. The gyration surface is a very elongated ellipsoid with a vanishingly small equatorial diameter. A critical examination of the methods of Voigt and Wever is given, and the sources of inaccuracy are pointed out. A. J. Mee.

Behaviour of a single crystal of zinc subjected to alternating torsional stresses. H. J. Gough and H. L. Cox (Proc. Roy. Soc., 1929, **A**, **123**, 143—167).—A single zinc crystal was subjected to alternating torsional stressing. The principal slip plane was the basal (0001) plane, the direction of slip being that of the most highly stressed (shear stress) primitive direction contained by the basal plane. The specimen showed a clearly defined " visible slip limit " at a range of stress between ±0·87 and ±0·98 ton/inch^2, and a limiting range of resolved shear stress between ±1·0 and ±1·3 tons/inch^2. The twinning plane was identified as first order pyramidal (0112 type), producing a twinned basal plane making an angle of 94° 5′ with the original basal plane. The observed twin formation occurs as a result of the previous basal plane slip, and is not due to slip on the twinning plane. The particular twinning planes (of the six available sets) operative are determined principally by the direction of slip on the basal plane and probably by normal stress considerations. It is shown that twinning can be accomplished by small atomic translations confined to a plane normal to the twinning plane. Fracture consisted of one main crack which followed three directions. It is shown clearly that the prismatic planes are neither slip nor cleavage planes, and it is considered probable that what have been interpreted in the past as cleavages on prismatic planes have been fractures along the twinned basal planes. L. L. Bircumshaw.

Influence of finely-divided particles on the coercive force. W. Köster (Z. anorg. Chem., 1929, **179**, 297—308).—The size and arrangement of finely-divided particles in a ferromagnetic alloy have considerable influence on its magnetic properties. Experiments with iron–carbon and iron–nitrogen mixtures are described. H. F. Gillbe.

Stretching of cadmium crystals. W. Boas and E. Schmid (Z. Physik, 1929, **54**, 16—45).—The solidification of metallic crystals is discussed from the point of view of the critical limiting tension of plastic deformation. *X*-Ray investigations on stretched cadmium crystals show that the velocity of crystallisation exerts a very important influence on the readiness of slip along the basic translational plane. The diminution of the critical tension by tempering, the energy change on slipping, and mechanical twin formation were also investigated and the change in the space lattice of cadmium and zinc crystals on stretching was deduced. J. W. Smith.

Crystallographic slip on stretching zinc and cadmium. G. Masing (Wiss. Veröff. Siemens-Konzern, 1929, **7**, [2], 210—216).—Twin formation occurs to a considerable extent when zinc and cadmium are stretched. The effect can be followed in relation to the longitudinal extension. R. A. Morton.

Electrical conductivity of vapours of salts. H. Querengässer (Z. Elektrochem., 1929, **35**, 199—206).—Various forms of apparatus are described for the measurement of the conductivity of vapours of salts, *e.g.*, mercuric, ammonium, lithium, and ferric chlorides, cadmium iodide, and carbon tetrachloride. Curves are given showing the relationship between current and the *P.D.* applied, and also the diminution with time of current which can be passed through mercuric chloride vapour when subjected to a constant *P.D.* The surface of the glass vessel in which the vapour was enclosed, and also the conductivity of the glass used, had an important influence on the conductivity of the vapours. H. T. S. Britton.

Change of conductivity of cuprous oxide. H. Kost (Z. Physik, 1929, **54**, 367—371).—The difference in conductivity of a cuprous oxide film with polarity has been investigated by using the oxidised copper strip as one electrode and another pure copper strip as the other. The non-symmetrical conductivity of the cuprous oxide film does not appear when the latter is produced by heating the copper strip, excepting to a slight extent at the mid-point of the copper strip, the most strongly heated part It is concluded that the cuprous oxide crystals orient themselves as they grow out of the mother copper and that these crystals conduct more freely in one direction than in the other. The variation in the resistance of such films with temperature has also been investigated over the range −20° to +100°. J. W. Smith.

Variation of density and refractive index [of liquids] with the temperature. W. Herz (Z. anorg. Chem., 1929, **180**, 159—160).—The expansion coefficient, α, and the temperature coefficient of the refractive index, β, of 23 liquids have been calculated at two temperatures, t and t_1, which are 8/12 and 7/12, respectively, of the corresponding critical temperature, by means of the relationships $\alpha=[1/(t_1-t)][(d-d_1)/d_1]$ and $\beta=[1/(t_1-t)][(n-n_1)/n_1]$, where d is the density and n the refractive index. The ratio $\alpha:\beta$ has a value in the neighbourhood of 3 for most of the liquids.

O. J. WALKER.

Measurement of refractive index of water between wave-lengths of 23 and 73 cm. E. FRANKENBERGER (Ann. Physik, 1929, [v], **1**, 948—962).—An apparatus is described for measuring the refractive index of water for electric waves in the wave-length range 23—73 cm. The accuracy of the method is discussed, and it is shown that the use of Drude's second method is attended with a systematic error, which in the case of water amounts to 3—3·5 parts per thousand. The results with distilled water show that the index is practically constant over the range examined. In order to verify earlier work on the anomalous dispersion of sodium silicate solutions (A., 1927, 295), experiments were made with a colloidal solution of silicic acid, a solution of sodium metadisilicate ($Na_2Si_2O_5,2H_2O$), a solution of sodium metasilicate ($Na_2SiO_3,6H_2O$), and dilute sodium hydroxide solution. These solutions were examined only in the range 50—60 cm. No bands of anomalous dispersion were found.

A. J. MEE.

Refractive index of sodium vapour and width of D_1 in absorption. S. A. KORFF (Physical Rev., 1929, [ii], **33**, 584—588)—A continuation of the work of Stewart and Korff (cf. A., 1928, 1310). The variation of refractive index and the relation of dispersion to the width of the *D* lines in absorption are found to agree approximately with the classical formulæ. These optical methods give a value of the order 10^{-13} cm. for the radius of the electron.

N. M. BLIGH.

Specific heats of acetone, methyl, ethyl, and *n*-propyl alcohols at low temperatures. S. MITSUKURI and K. HARA (Bull. Chem. Soc. Japan, 1929, **4**, 77—80; cf. this vol., 386).—The specific heats are recorded of the above substances at temperatures between 160° and 270° Abs., over which range an approximately linear relationship holds.

A description is given of the calorimeter system employed in which a Dewar vessel, containing light petroleum, cooled by the circulation of liquid air through a copper spiral, serves as a jacket to the calorimeter proper, a metal cylinder suspended in a brass tube, and heated by a manganin spiral. The cooling stream is cut off at the beginning of the experiment, and the true heating curve for the system is derived from the observed by making the assumption that the temperature of the Dewar jacket remains constant during the heating period.

F. G. TRYHORN.

Specific heat of superheated steam for pressures between 30 and 120 atm. and at saturation temperatures to 450°. O. KNOBLAUCH and W. KOCH (Naturwiss., 1929, **17**, 269—270).—The c_p isobars in the c_p–t diagram have been determined at 30, 40, 60, 80, and 120 atm. over the range 225—450°.

R. A. MORTON.

Specific heats of some condensed gases between 10° Abs. and their triple points. K. CLUSIUS (Z. physikal. Chem., 1929, **B**, **3**, 41—79).—An apparatus for the measurement of the specific heats of condensed gases below 10° Abs. is described. The specific heats of nitrogen, oxygen, carbon monoxide, methane, and hydrogen chloride were determined from 10° Abs. down to their triple points. The results of other workers are in general agreement, but those of Giauque and Wiebe (A., 1928, 228) on hydrogen chloride show a systematic deviation lying outside the limits of experimental error, which must be ascribed to an error in their temperature scale. The heats of fusion of the gases were determined afresh. For methane a new transition point was found at 20·4° Abs. The lead resistance thermometer is described, and a table of its resistance ratios down to 9° Abs. is given.

A. J. MEE.

Heat capacities of ethyl and hexyl alcohols from 16° to 298° Abs. and the corresponding entropies and free energies. K. K. KELLEY (J. Amer. Chem. Soc., 1929, **51**, 779—786).—The specific heats of ethyl alcohol (including the glacial form) and of hexyl alcohol are recorded. The m. p., molal heats of fusion (g.-cal.), molal entropies (g.-cal./1° at 25°), and molal free energies (g.-cal. at 25°) are, respectively, for ethyl alcohol: 158·5° Abs., 1200, 38·4, and —43,300, and for hexyl alcohol: 225·8° Abs., 3676, 68·6, and —41,700. Parks' conclusions on the entropy relations between members of a homologous series of saturated aliphatic compounds (A., 1926, 784) are qualitatively confirmed.

S. K. TWEEDY.

Heat capacities of *iso*propyl alcohol and acetone from 16° to 298° Abs. and the corresponding entropies and free energies. K. K. KELLEY (J. Amer. Chem. Soc., 1929, **51**, 1145—1150).—The specific heat curve for acetone exhibits an irregularity at 126° Abs., indicating that a transition occurs in the crystals. The specific heat of liquid acetone passes through a minimum just above the m. p. The following molar quantities were determined for *iso*propyl alcohol and acetone, respectively: m. p., 184·67°, 176·62° Abs.; heat of fusion at m. p. (g.-cal.), 1284, 1366; entropy (g.-cal./1°) at 298·1° Abs., 43·0, 47·9; free energy (g.-cal.) at 298·1° Abs., —48100, —36700. The free energy and entropy for the thermal decomposition of *iso*propyl alcohol vapour are calculated (cf. A., 1928, 709).

S. K. TWEEDY.

Apparent influence of an electric field on the b. p. of benzene. J. W. SMITH (J.C.S., 1929, 788—791, cf. Baker, *ibid.*, 1928, 1051).—When an electric field is applied to benzene in a tube heated in an oil-bath, a thermometer in the liquid indicates an apparent rise of b. p., the vapour temperature remaining normal. This experiment is repeated and extended. The effect is considerably reduced by stirring, and is not observed when the tube is heated directly with a small flame (cf. Smits. A., 1928, 1189). The abnormality is attributed to superheating induced by the removal of charged nuclei from the system. No change in vapour pressure occurs when benzene is subjected to an electric field.

N. M. BLIGH.

Ebullioscopic paradox. A. BERTHOUD, E. BRINER, and A. SCHIDLOF (J. Chim. phys., 1929, **26**, 149—151; cf. A., 1927, 1029).—A reply to Mazzucchelli (A., 1928, 128) and to Verschaffelt (Wis. en nat. Tijds., 1928, **4**, 1).

C. W. GIBBY.

Solid helium at high temperatures. F. Simon (Naturwiss., 1929, **17**, 256).—The m. p./pressure curve of helium has been studied further (cf. this vol., 386, 497). The m. p. at 1800 kg./cm.^{2} is 20° Abs., and at 36·90 kg./cm.^{2}, 32° Abs. Unless a critical transition region is approached, the theoretical reasoning which is valid up to 32° indicates that at 80° Abs. and the ordinary temperature, pressures of 15,000 and 100,000 kg./cm.^{2}, respectively, should effect solidification of helium. R. A. Morton.

Volatilisation at the cathode of the mercury arc light. E. Kobel (Physikal. Z., 1929, **30**, 233—235; cf. von Issendorf, this vol., 227).—The mercury lost from the cathode of a rectifier is accounted for by volatilisation distributed over the entire surface and not localised at the focal spot. If the movement of the focus is arrested the vaporisation decreases, since the change in the loss from the cathode is greater than can be ascribed to the cessation of sputtering. In order to test the hypothesis that the mean stationary surface temperature of the cathode is greater for a moving focus than for a steady focus, an experiment was carried out on the effect of a motionless jet of flame as compared with the same flame sweeping over a surface of water at a constant height. It was found that the rise in temperature and the loss of weight from a definite initial volume were both less for the stationary than for the moving jet. This experiment indicates that the mean surface temperature of the mercury cathode is the controlling factor. The rate of evaporation in the mercury surface at different temperatures apart from the focal spot has been compared with the loss at the focal spot as calculated by Gunther-Schulze. By means of efficient cooling, the volatilisation can be reduced to a small fraction of the amount calculated on the Gunther-Schulze basis, without materially affecting the electrical properties of the arc. R. A. Morton.

Upper limit of energy density and the degradation of gas at high temperatures. S. Suzuki (Proc. Imp. Acad. Tokyo, 1929, **5**, 64—67).—Mathematical. The equation of state of a gas in the state of degradation at high temperatures is derived, assuming the existence of an upper limit of energy density. O. J. Walker.

Statistics of Bose and Einstein and of Fermi and Dirac and the upper limit of energy density. S. Suzuki (Proc. Imp. Acad. Tokyo, 1929, **5**, 68—71).—Mathematical. O. J. Walker.

Thermal expansions of mercury and vitreous silica. F. J. Harlow (Phil. Mag., 1929, [vii], **7**, 674—685).—Various results of different observers for the coefficients of expansion of mercury and vitreous silica have been examined and the most probable values deduced. The most probable value of the linear coefficient of thermal expansion of vitreous silica is given by the expression $S_0{}^t=\{66{\cdot}3-3879/(t+103)\}\times 10^{-8}$ or for the range 0—300° $V_t/V_0=1+10^{-8}\{93{\cdot}6t+0{\cdot}7776t^2-0{\cdot}003315t^3+0{\cdot}000005244t^4\}$, where V_t is the volume of 1 c.c. at 0° measured at t^0. Over the same temperature range the values for mercury fit two different curves. For the range 0—100°, $V_t/V_0=1+10^{-8}\{18153{\cdot}8t+0{\cdot}7548t^2+0{\cdot}001533t^3+0{\cdot}00000536t^4\}$ and for the range 100—300° $V_t/V_0=1+10^{-8}\{17559{\cdot}1+369555/(634{\cdot}7-t)\}t$. A table of values of V_t/V_0 for mercury is given. A. E. Mitchell.

Determination of vapour densities at the ordinary temperature. E. F. Linhorst (J. Amer. Chem. Soc., 1929, **51**, 1165—1167).—w g. of liquid, mol. wt. M, are evaporated at the ordinary temperature in a vessel, volume v, connected by means of an oil manometer with another, similar, vessel, the pressures in the two vessels being equal and well below one atmosphere. If p is the pressure registered by the manometer, than $pvM=wRT$. S. K. Tweedy.

Vapour pressure at high temperatures. C. Zwikker (Physica, 1928, **8**, 241—250; Chem. Zentr., 1928, ii, 2108).—In the vapour-pressure equation for high temperatures, log $p=-A/T+B$, B has practically the same value for all metals. The relation $B=-\frac{1}{2}\log T+3\log\theta-1/2{\cdot}303+1{\cdot}29+3/2\log M$, where M is the mol. wt., $\theta=136{\cdot}1\sqrt{\text{m. p.}\times(MV^{2/3})}$, and log T is a mean value for the temperature range concerned, gives for fifteen metals almost constant values for B (approx. 9·33). The mean value of B for 20 metals is 9·7. A. A. Eldridge.

Vapour pressure and vapour density of intensively dried ammonium chloride. W. H. Rodebush and J. C. Michalek (J. Amer. Chem. Soc., 1929, **51**, 748—789; cf. A., 1928, 469).—The vapour pressure of ammonium chloride was measured at varying degrees of dryness over the temperature range 470—560° Abs. Intensive drying seems not to affect the vapour pressure, and the results are all reproduced to within 1% by the equation log p (mm.)$=10{\cdot}1070-4402{\cdot}1/T$. The vapour is probably completely dissociated under all conditions. The vapour density was measured by the Knudsen method, but the slowness of evaporation of the salt in a vacuum vitiated the results. The vapour densities measured by Stock's buoyancy method (A., 1924, ii, 405) indicated complete dissociation. A high-capacity mercury-vapour pump is described in which volatile matter is removed from the condensed mercury before it reaches the reservoir. An improved glass diaphragm manometer is also described. S. K. Tweedy.

Vapour pressures of ethyl selenide, tin tetramethyl, and lead tetramethyl. Y. Tanaka and Y. Nagai (Proc. Imp. Acad. Tokyo, 1929, **5**, 78—79).—The vapour pressures of these compounds have been measured by a statical method at 25° and 35°. The values of L/T coincide closely with those calculated from the revised rule of Trouton, showing that these liquids are all normal. Equations are given showing the relations between vapour pressure and temperature. O. J. Walker.

Hydrated aluminium silicates. II. Dehydration vapour pressure of kaolin. C. J. van Nieuwenburg and H. A. J. Pieters (Rec. trav. chim., 1929, **48**, 406—416; cf. this vol., 280).—The vapour pressure of kaolin was determined at different temperatures and for different water content of the surrounding atmosphere. The dissociation pressure was found to be a function of the water content over the whole range. Temperature–pressure–water content diagrams were determined by three different methods. A. Freiman.

One-component system silica. III. Stability regions of quartz, tridymite, and cristobalite. C. J. van Nieuwenburg (Rec. trav. chim., 1929, 48, 402—405; cf. A., 1928, 709).—The stability regions of the different solid phases in the system silica were re-investigated by a new method using only 1% of lithium carbonate as a catalyst. The presence of tridymite and cristobalite was investigated by constructing thermal dilation diagrams. The stability regions of quartz, tridymite, and cristobalite as described by Fenner (A., 1913, ii, 133) were confirmed.

A. Freiman.

Isotonic liquids. F. A. H. Schreinemakers (Rec. trav. chim., 1929, 48, 393—401).—Theoretical. A generalised definition of isotonic liquids is given. Introducing a conception of osmotic water attraction the influence of temperature and pressure on this property is considered and the relation between f. p., vapour pressure, and osmotic pressure and isotonic liquids is deduced as well as the influence of temperature and pressure on isotonic liquids. A. Freiman.

Physical properties of liquids. I. Sonic interferometer. Velocity of sound in some organic liquids and their compressibilities. E. B. Freyer [with J. C. Hubbard and D. H. Andrews] (J. Amer. Chem. Soc., 1929, 51, 759—770). —The velocity of sound in some organic liquids was measured at 10° intervals up to 50° by the method of Hubbard and Loomis. The sonic interferometer previously described (A., 1928, 828) was further developed with particular reference to temperature control, and to prevention of evaporation of the liquid and of contamination of the liquid with water vapour from the air. The velocity of sound is a linear function of temperature for each liquid; in the case of benzene, aniline, and α-bromonaphthalene slight divergences from linearity occur just before the m. p., indicating that orientation of some kind occurs before freezing. The adiabatic compressibilities are calculated from the results. S. K. Tweedy.

Propagation of sound in gases. D. G. Bourgin (Phil. Mag., 1929, [vii], 7, 821—841).—Theoretical.

Internal resistance in instantaneous processes in relation to the entropy changes taking place in them. N. V. Tancov (J. Russ. Phys. Chem. Soc., 1929, 61, 41—52).—The crystallisation of supercooled liquids and of supersaturated solutions, the condensation of supersaturated vapours, and spontaneous chemical processes are considered from the point of view of the author's law of minimum change of entropy (cf. A., 1917, ii, 367; 1925, ii, 868) and are found to accord with it. A. Freiman.

Atomic volume relations in certain isomorphous series. III. A. F. Hallimond (Min. Mag., 1929, 22, 70—76).—From the atomic volumes previously deduced (A., 1928, 107, 942) and the observed compressibilities of the metals, compressibilities for the alkali halides which are in agreement with observed values are calculated. L. J. Spencer.

Viscosity of liquids above their b. p. V. T. Titani (Bull. Chem. Soc. Japan, 1929, 4, 68—75; cf. A., 1927, 1019).—The formula relating molecular fluidity to molecular volume and temperature, previously derived, has been tested further by its application to recent data for the viscosity of ethyl ether and acetone with satisfactory results.

F. G. Tryhorn.

Molecular dimensions of organic compounds. I. General considerations. T. M. Lowry and A. G. Nasini (Proc. Roy. Soc., 1929, A, 123, 686—691).—With the object of determining if the persistent similarity of b. p. observed by Victor Meyer for benzene and thiophen and their derivatives extends also to their other properties, a comparative examination has been made of the physical properties of benzene and thiophen, toluene and 2-methylthiophen, and benzene and *cyclo*hexane (the b. p. and f. p. of the last pair differing by less than 1°). In particular, a comparison has been made of the collision areas ($\bar{A}$) of the molecules, as deduced from the viscosities of the vapours. Some striking regularities are observed. Thus a decrease in A of about 2 Å.^{2} occurs on passing from benzene to thiophen and from toluene to 2-methylthiophen, whilst the replacement of H by Me is accompanied by a constant increment of 3 Å.^{2} Also on passing from benzene to pyridine an increase of about 1 Å.^{2} is found. A result of these small successive changes is to produce an almost complete identity in the values of $\bar{A}$ for pyridine and 2-methylthiophen. A marked similarity is also observed between other physical properties (*e. g.*, b. p. and f. p.) of these two compounds. In no case is the marked similarity of properties which Langmuir found in the case of "isosteric" substances observed; the vapours show regular increments rather than identity of properties, and the physical properties of the liquids and solids show even wider differences. L. L. Bircumshaw.

Molecular dimensions of organic compounds. II. Viscosity of vapours: benzene, toluene, and *cyclo*hexane. III. Viscosity of vapours: thiophen and 2-methylthiophen, pyridine, and thiazole. A. G. Nasini (Proc. Roy. Soc., 1929, A, 123, 692—704, 704—713; cf. preceding abstract).—II. Details are given of a modified form of Rankine's apparatus for measuring the viscosity of vapours, by means of which the viscosities of benzene, toluene, and *cyclo*hexane have been determined from 15° to 251°, 61° to 252°, and 46° to 205°, respectively. The values are found to be independent of the pressure over a fairly wide range. On plotting against the temperature, straight lines are obtained passing through the origin. The following values are deduced for Sutherland's constant S and the mean collision area $\bar{A}$: benzene, $S=380$, $\bar{A}=19{\cdot}0$ Å.^{2}; toluene, $S=370$, $\bar{A}=21{\cdot}8$ Å.^{2}; *cyclo*hexane, $S=330$, $\bar{A}=22{\cdot}3$ Å.^{2} The values of $\bar{A}$ for benzene and toluene are compared with those deduced from Bragg's crystal models (cf. Mack, A., 1925, ii, 1124). Although the absolute values differ by about 50%, the differences are of similar magnitude.

III. The viscosity apparatus is further modified for use with substances available only in small quantities. By reducing the "condensation pressure" to zero, the viscosity of a vapour can be determined without also determining the vapour-pressure curves. It is shown both theoretically and experimentally that this method leads to trustworthy results. The viscosities of thiophen, methylthiophen, and pyridine are recorded over the temperature ranges 20—245·5°, 50—250°, and 96—268°, respectively, and some provisional values are given for thiazole. When plotted against the temperature, the viscosity data fall on a straight line passing through the origin, with the exception of the thiazole values. The following values are deduced for S and $\bar{A}$; thiophen, $S=407$, $\bar{A}=16·7$ Å.^{2}; methylthiophen, $S=400$, $\bar{A}=19·9$ Å.^{2}; pyridine, $S=320$, $\bar{A}=20·0$ Å.^{2} The following new data are also recorded for 2-methylthiophen: d_4^{20} 1·016, b. p. 112·1°, m. p. −51°, t_c 321°, η_{25} 0·00667 (of liquid), $\gamma_{24·5}$ 30·8 dynes/cm.^{2}

L. L. BIRCUMSHAW.

Gaseous mixtures. N. CARRARA (Nuovo Cim., 1928, 5, 224—233; Chem. Zentr., 1928, ii, 2217).—For mixtures of non-reacting gases the conditions of equilibrium are calculated from the original state of the individual gases and the conditions of preparation of the mixture. A. A. ELDRIDGE.

Densities of butyric acid–water mixtures. J. GRINDLEY and C. R. BURY (J.C.S., 1929, 679—684).—The densities of butyric acid–water mixtures at 0°, 12°, 18°, 25°, and 34·94° have been determined. If the contraction due to mixing is plotted against the composition of the mixture, the resulting curve undergoes an abrupt change in slope at a point corresponding with a concentration of about 15% of acid. This is attributed to the presence of micelles in the mixtures, a conclusion which receives further support from a calculation of the partial specific volumes of the components. R. CUTHILL.

Surface tension of mixtures of associated and non-associated liquids. K. M. STACHORSKY (Z. Elektrochem., 1929, 35, 185—186).—Equations are derived which permit the calculation of (1) the surface tension of a binary mixture, composed of an associated and a non-associated liquid, from the surface tensions of the components and the molecular proportions in which they are present, and (2) the degree of association of an associated liquid, from the surface tension for a mixture containing this and a non-associated liquid. H. T. S. BRITTON.

Determination of parachors of substances in solution. D. L. HAMMICK and L. W. ANDREW (J.C.S., 1929, 754—759).—The parachors of binary mixtures of organic liquids are additively constituted of the parachors of the constituents, provided that these have surface tensions not differing by more than about 5—6 dynes/cm. If the difference is greater, there may be a slight divergence from the mixture rule, but the value for the pure solute can then be obtained by linear extrapolation. R. CUTHILL.

Raoult's law. W. D. BANCROFT and H. L. DAVIS (J. Physical Chem., 1929, 33, 361—370).—When Raoult's equation is applied to concentrated solutions, the mol. wts. are theoretically those of the two components in the condition of vapour. In the equation actually used by Raoult the mol. wt. of one of the components in the liquid phase is introduced, a fact which has not been recognised, since, in ideal solutions, the mol. wt. of liquid and vapour are supposed to be identical. In view of this, most of the experimental work dealing with variations from the law needs revision. Consideration of the data of previous investigators for the systems methyl alcohol–water, methyl alcohol–acetone, water–acetone, and acetone–ether shows that the equation $(G_1/G_2)^a=K(p_2-p'_2)/p'_2$, where G_1 and G_2 are the weights of the components in the solution, and p_2 and p'_2 are the vapour pressure and partial pressure of the pure solvent and solvent in the solution, respectively, holds over a wide range of concentration even for associated liquids. When $a=1$, and $K=M_1/M_2$, this equation reduces to Raoult's law. In the new equation a is a measure of the relative polymerisation and is independent of the units, whilst K depends mainly on the units used, the mol. wt. in the vapour phase, and the solubility. Dobson's data for ethyl alcohol and water (J.C.S., 1925, 127, 2866) have been calculated up to a mol. fraction of alcohol equal to 0·6 without recourse to variations from the gas laws or to the activity concept, and the distribution of acetone between water and methyl alcohol separated by a rubber membrane (Morton, this vol., 502) has also been calculated. Finally, it is pointed out that Henry's law and Nernst's distribution law should be expressed in mass and not volume concentrations as is usually the case.

L. S. THEOBALD.

Systems *n*-butyl alcohol–water and *n*-butyl alcohol–acetone–water. D. C. JONES (J.C.S., 1929, 799—813).—Investigation of the miscibility of *n*-butyl alcohol and water from the critical solution temperature (124·75°) to about −15° by the synthetic method shows that the solubility of the alcohol in water is minimal at about 52°, whereas the solubility of water in the alcohol decreases with falling temperature throughout; there is no indication of the existence of a lower critical solution temperature. By means of similar experiments with water and mixtures of the alcohol with acetone, the binodal surface for the ternary system between the same temperatures has been obtained, and here also no tendency for the formation of closed solubility rings is observed. The ternary critical solution temperatures for water, *n*-butyl alcohol, and hydrogen chloride are much more sensitive to traces of impurities than is the binary critical solution temperature for water and *n*-butyl alcohol. The factors determining the miscibility of liquids are discussed. R. CUTHILL.

Diffusion velocity of silver in silver telluride, antimonide, and stannide. G. VON HEVESY and W. SEITH (Z. anorg. Chem., 1929, 180, 150—158).—The diffusion velocities of silver in the above compounds have been derived from measurements of the diffusion coefficients of the latter in the corresponding compounds of copper. The diffusion constant, D, of silver telluride in copper telluride varies with the temperature, T, according to $D=A\,.\,e^{-B/T}$, where $A=2·027\times10^5$ and $B=10430$. At 581° $D=1$ cm.^{2}/day. At temperatures which are the same fraction of their m. p. the diffusion velocities of silver antimonide and silver stannide are of the order of 10^{-2} and 10^{-4} cm.^{2}/day, respectively. In heteropolar compounds and in metals the diffusion velocities of the atoms are exceedingly small, whereas in substances which are intermediate between these two types they are large.

O. J. WALKER.

Solid solutions, isomorphism, and symmorphism among the oxides of bivalent metals. I. The systems CaO–CdO, CaO–MnO, CaO–CoO, CaO–NiO, and CaO–MgO. G. Natta and L. Passerini. **II. The systems CoO–NiO, CoO–MgO, CoO–MnO, CoO–CdO, NiO–MgO, NiO–MnO, and NiO–CdO.** L. Passerini (Gazzetta, 1929, **59**, 129—143, 144—154).—I. An examination has been made by the *X*-ray powder method of a number of binary systems of bivalent metallic oxides. In general a mixture of the precipitated hydroxides was heated at a temperature somewhat above that at which complete dehydration occurred. The photograms given by these calcined products were compared with those given by the oxides separately and by mechanical mixtures of the pairs of oxides.

Complete miscibility in the solid state occurs in the system CaO–CdO and, within the limits of experimental error, the deformation of the lattice is proportional to the composition of the solid solution. By keeping a mechanical mixture of these two oxides at a temperature above 600° a solid solution is formed by diffusion identical with that formed from the mixed precipitated hydroxides.

Partial miscibility, little dependent on temperature, occurs in the system CaO–MnO. No evidence of the formation of solid solutions was found with the systems CaO–NiO, CaO–CdO, and CaO–MgO. In the last-named system a temperature of 1500° did not bring about dissolution.

II. Complete miscibility, with deformation of the lattice proportionate to the composition, occurs in the systems CoO–NiO, CoO–MgO, CoO–MnO, and NiO–MgO. Miscibility is partial in the system NiO–MnO, and is absent from the systems CoO–CdO and NiO–CdO.

A comparison of the results shows that in these systems of oxides possessing similar lattices the solubility in the solid state decreases rapidly with increase in the diameter of the metal ions.

F. G. Tryhorn.

Partition law. III. Application of van Laar's partition law to a condensed system derived from molten metals. R. Lorenz and G. Schulz [with F. Erbe] (Z. anorg. Chem., 1929, **179**, 339—344).—Van Laar's partition law yields a satisfactory constant for the partition of silver between molten aluminium and molten lead over a range of 0·9—30 at.-% Ag in aluminium. H. F. Gillbe.

Solubility of antimony in water. J. Grant (Analyst, 1929, **54**, 227—228).—Finely-divided antimony is soluble in distilled water in the presence of oxygen, and this property is regarded as a possible source of error in the Clarke method (this vol., 417) and in any analytical procedure where deposits of antimony (*e.g.*, those produced electrolytically) have to be washed. D. G. Hewer.

Sorption of hydrogen by the platinum metals. E. Müller and K. Schwabe (Z. Elektrochem., 1929, **35**, 165—184)—The authors have measured the amounts of hydrogen sorbed by the metals of the platinum group immediately after their formation by the reduction of the oxides by hydrogen at different temperatures. The apparatus used was similar to that of Mond, Ramsay, and Shields (A., 1895, ii, 492). The methods used in the preparation of ruthenium dioxide, the hydrated dioxides of osmium, iridium, and platinum, hydrated palladous oxide, and rhodium sesquioxide are described. These oxides were subjected to the action of hydrogen under various conditions and the volumes of gas occluded by the metals so formed were ascertained by subtracting the volumes of hydrogen required for reduction from the respective total volumes of hydrogen taken up. The data indicate that the quantity of occluded hydrogen depends on the temperature at which the oxide is reduced and on the time taken, on the method of preparing the oxide, and on the rate at which the metals are treated with hydrogen. Moreover, the platinum metals were found to be capable of sorbing greater quantities of hydrogen immediately after their formation than after they have been kept for some time. The previously published figures relating to the capacities which these metals have for occluding hydrogen are without real meaning, for as with charcoal, much depends on the surface area per unit mass. Thus with osmium the amounts of hydrogen taken up by 1 volume of the metal varied from 660 to 2000 volumes. H. T. S. Britton.

Adsorption of hydrogen on the surface of an electrodeless discharge tube. M. C. Johnson (Proc. Roy. Soc., 1929, **A**, **123**, 603—613).—Measurements have been made of the progressive decrease in the rate at which hydrogen disappears (the fatigue) under the action of the electrodeless discharge (cf. Thomson, A., 1928, 3). The hydrogen, contained in a glass bulb which could be evacuated to the cathode-ray stage and baked during evacuation up to 300°, was excited and dissociated by the high-frequency currents induced from a surrounding solenoid, and the fatigue was followed by means of a continuous reading micromanometer. The resulting sequences of curves indicate that the fatigue is a two-fold phenomenon. There is (*a*) a saturation observable in any one curve and almost completed in about 4 min., and (*b*) a decrease in the depth reached by this saturation curve on repetition of the experiment after re-baking. The capacity of the glass surface is obviously never greater than when newly made and first gassed out, and the surface is saturated when the hydrogen layer is unimolecular but not closely packed. The average separation of atomic centres in the adsorbed layer on two specimens at saturation is calculated to be 1·3 and 1·8 × 10^{-8} cm., respectively. Closest packing of Bohr orbits would give 1·06 × 10^{-8} cm., whilst attachment to the solid atom by atom, assuming all spaces occupied, would give a probable minimum value of 1·9 × 10^{-8} cm. The structure of the adsorbed layer is discussed. The heat of adsorption of hydrogen on glass, calculated by means of Frenkel's formula (A., 1925, ii, 194), is found to be 1·115 and 1·06 × 10^4 g.-cal./g.-mol., respectively, for the two specimens.

L. L. Bircumshaw.

Adsorption of gases by glass surfaces. M. Crespi (Anal. Fis. Quim., 1929, **27**, 108—119).—The apparatus used previously has been modified by replacing the system of small tubes by small bulbs equal in total volume to the large comparison bulb; measurements may thus be made with gases exhibiting a high degree of adsorption. The adsorption of carbon dioxide at 13° is given by $0{\cdot}93\times10^{-8}\,.\,p^{0{\cdot}444}$ from 1 to 0·25 atm.; the number of moles of carbon dioxide adsorbed per cm.^{2} at 760 mm. and the ordinary temperature is $2{\cdot}7\times10^{-15}$, as compared with $2{\cdot}4\times10^{-15}$ for chloroform. H. F. Gillbe.

Behaviour of outgassed activated charcoal with electrolytes. R. Burstein and A. Frumkin (Z. physikal. Chem., 1929, **141**, 219—220).—Sugar charcoal was heated to 1000° in a vacuum, and was then placed in contact with a solution of an electrolyte also in a vacuum. There was no hydrolytic adsorption. When, however, the charcoal was exposed to air it at once began to adsorb acids. A. J. Mee.

Relationship between gas content and adsorption of electrolytes by activated charcoal. I. B. Bruns and A. Frumkin (Z. physikal. Chem., 1929, **141**, 141—157).—Activated sugar charcoal was prepared, and part of it was platinised. The adsorbing power of this charcoal for acids and bases was then determined. It was found that the adsorption of acids by unplatinised charcoal in a hydrogen atmosphere is different from that in an air atmosphere, but that the difference is not very great. If platinised charcoal is used the difference is very much increased; indeed, with a sufficiently high concentration of platinum the adsorption of hydrochloric acid in the presence of hydrogen is reduced to zero. These conclusions were supported by observations on the adsorption of other acids (viz., sulphuric and phosphoric acids), when similar results were obtained. The amount of acid adsorbed by platinised charcoal in an atmosphere of air is much greater than that adsorbed by platinum-free charcoal under the same conditions. These phenomena must be ionic in nature because the adsorption of benzoic acid is unaffected by the atmosphere or type of charcoal used. In the case of bases (sodium hydroxide was used) there was no adsorption by charcoal, platinised or platinum-free, in the presence of air, but in the presence of hydrogen the amount adsorbed increased with increasing platinum content. An attempt is made to explain these facts on electrochemical theory. The activated charcoal behaves in aqueous solutions as a gas electrode, the adsorption of strong electrolytes being due to the formation of an electrical double layer at the carbon–solution interface. In the presence of air the activated charcoal sends out hydroxyl ions into the solution, becomes positively charged, and attracts anions. Hence acids will be adsorbed. Charcoal containing a certain quantity of platinum will discharge hydrogen ions into the solution if it is in an atmosphere of hydrogen. It will thereby become charged negatively and will attract cations. The formation of the double layer will, in this case, be bound up with adsorption of alkali. A. J. Mee.

Relationship between gas content and adsorption of electrolytes by activated charcoal. II. R. Burstein and A. Frumkin (Z. physikal. Chem., 1929, **141**, 158—166).—Activated charcoal was heated to about 1000° in an atmosphere of hydrogen and was then introduced into an oxygen-free solution in complete exclusion of air. There was a complete inversion of the adsorptive properties of the charcoal. Whereas previously acid was adsorbed, no acid was now taken up. A neutral solution in contact with the charcoal became acid. On exposing the charcoal to air it took up oxygen and developed its original adsorbing powers. It was found that the presence of sulphur dioxide in the charcoal, adsorbed from the laboratory atmosphere, lowered the power of the charcoal to adsorb acids. This capacity was, however, restored on heating in a stream of hydrogen. It was also observed that adsorbed hydrochloric acid is more readily liberated when the charcoal is heated in a current of hydrogen than it is when the hydrogen is replaced by nitrogen. A. J. Mee.

Adsorption of hydroxybenzenes and other aromatic compounds and their replacing action on each other at the interface water–charcoal. I. M. Kolthoff and E. van der Goot (Rec. trav. chim., 1929, 48, 265—287).—A study of the adsorption of various aromatic compounds by charcoal from aqueous solution has been made to determine whether the number of polar groups in a molecule and the configuration of phenolic compounds bear any relation to the form of their adsorption isotherms, and whether the number of molecules adsorbed at an interface represents any real measure of the adsorption affinity. The adsorption of the following substances was investigated: phenol, aniline, methylaniline, dimethylaniline, *o*-cresol, resorcinol, quinol, pyrocatechol, pyrogallol, phloroglucinol, *p*- and *m*-nitrophenol, gallic acid, pyridine, antipyrine, picric acid, benzoic acid, salicylic acid, sulphosalicylic acid, and benzenesulphonic acid. In addition a series of measurements was made with solutions containing two solutes.

In almost all cases the Freundlich adsorption equation could be satisfactorily applied to the results. The index $1/n$ in this equation was found to be related to the number of polar groups in the adsorbed molecule. The values of the index for molecules containing one, two, or three polar groups were respectively in the ratios 3 : 2 : 1. The index falls to very small values as the number of polar groups is increased, indicating that the affinity between the charcoal and the adsorptive increases under such conditions. This behaviour at a water–charcoal surface is converse to that at a water–air interface for the same substances. The polar groups of the benzene derivatives are directed, not to the bulk of the solution, but to the charcoal face, probably as a result of the presence of a layer of adsorbed water molecules on the latter. No real measure of the adsorbability of a substance is obtained by expressing the amount adsorbed as millimols. per g. of charcoal. When milliequivalents are used as units for this purpose, the equivalent number for benzene derivatives of non-electrolyte character is proportional to the number of polar groups in the molecule. Di- and tri-hydroxybenzenes are almost without influence on the surface tension of a phenol solution, but at a charcoal surface phenol is replaced by di- and tri-hydroxybenzene derivatives.

Usually, but not without exception, the influence of sodium chloride is to increase the adsorption of aromatic compounds by charcoal.

F. G. Tryhorn.

Adsorption of phenols at the interfaces water–air, water–charcoal, and water–mercury. A. Frumkin (Rec. trav. chim., 1929, **48**, 288—290).—Data for the adsorption of hydroxybenzene derivatives at the interfaces water–air and water–mercury are compared with the unexpected results obtained by Kolthoff and van der Goot (cf. preceding abstract) for the adsorption of the same compounds at the interface water–charcoal. F. G. Tryhorn.

Dependence of adsorption of a dissolved substance on the properties of the solution and the solvent. W. Herz and L. Lorenz (Kolloid-Z., 1929, **47**, 331—334).—Solutions of iodine in benzene and in carbon tetrachloride were prepared and measurements were made of the densities and viscosities of the solutions and their mixtures. The solubility of iodine in these solvents was determined and also the densities and viscosities of the saturated solutions. Measurements were made of the adsorption of iodine from these solutions by finely-divided charcoal and the adsorption values were compared with the physical properties of the solutions mentioned above. Since both the solvents are non-polar, similar experiments were conducted with mixtures of heptane and dipropyl ether, where one constituent is a dipole, and further experiments were carried out in ethyl alcohol and absolute acetic acid as polar solvents. Similar results were obtained in all these cases, and it is concluded that constant relations exist between the adsorbability of a substance from organic solvents and their mixtures on the one hand and the solubility of the substance and the density and viscosity of the saturated solution and of the solvent on the other hand. E. S. Hedges.

Soap. VIII. Adsorption of soap at the contact surface of two liquid phases. M. Nonaka (J. Soc. Chem. Ind. Japan, 1928, **31**, 297—300).—The adsorption of soap at the contact surface between benzene or toluene and an aqueous solution of sodium oleate or palmitate is much greater than would be expected on the assumption of the formation of a unimolecular layer, and it is suggested that a unimicellar layer is formed. The adsorbed layer consists of neutral soap, whilst the free fatty acids are dissolved in the adsorbents. When air is used as adsorbent instead of benzene or toluene, the adsorbed layer consists of neutral soap together with free fatty acids. It is concluded that the aqueous soap solution consists of aggregates of hydrated soap molecules in admixture with an emulsion of the free fatty acids formed by the hydrolysis of the soap. From such solutions the fatty acid is first adsorbed, and when this has passed into the adsorbent, or is insufficient to cover the contact surface, then the aggregates are adsorbed. The adsorption phenomena are not the same when the adsorbent is changed. Therefore the washing properties of the soap, which are dependent on adsorption, will vary according to the nature of the washed material. Y. Nagai.

Soap solutions. VI. Composition of the substances adsorbed by various adsorbents. J. Mikumo (J. Soc. Chem. Ind. Japan, 1928, **31**, 410—416).—Solutions of sodium oleate were shaken with various adsorbents, allowed to settle, and then filtered. The filtrate was analysed for oleic acid and total alkali, and the composition of the adsorbed matter was calculated from these data. Carbon, fibres of filter paper, silk, artificial silk, wool, hide powder, kaolin, and Japanese acid clay were used as the adsorbents. All these adsorbents react with soap, the reaction being partly chemical, and the adsorption hydrolytic. The adsorbed matter is a mixture of sodium oleate, oleic acid, sodium hydroxide, and their dissociation products; its composition varies with the conditions of the experiment. Carbon has very large adsorbing capacity, and absorbs always only acidic soap, even from alkaline solution, whilst the others absorb basic substances. Potassium oleate behaves similarly to the sodium salt. The mechanism of the washing action of soap solution is considered to involve two main factors, wetting and peptising. The cleaning action is mainly due to the simple soap molecules, simple soap ions, and acid soap sol. Y. Nagai.

Dependence of surface tension and of heat of evaporation on density and temperature up to the critical temperature. J. J. van Laar (Z. anorg. Chem., 1929, **180**, 193—214).—Mathematical, giving a more detailed and extended presentation of earlier work. The relation between surface tension (γ) and density is given by $\gamma=0{\cdot}1100fd_1(d_1-d_2)^3\times p_c\sqrt[3]{v_c/N}$, where f is a correction factor and the other quantities have the usual significance. The available data for benzene and ether are used to verify the formula, which is valid up to the critical temperature. The variation of γ with temperature is discussed and the expression $\gamma_s=p_cv_s^{1/3}/10{\cdot}9$ is obtained for the surface tension at the b. p.; this is the same as the experimentally obtained Dutoit–Friderich expression. The internal (λ) and total (L) heats of evaporation for benzene are calculated. These give constant values for the expressions $\lambda/\gamma^{1/3}$ and $L/\gamma^{1/3}$, which are derived theoretically. A theoretical derivation is also given for the Ramsay and Shields molecular surface energy equation. O. J. Walker.

Deposition and surface tension. J. Wulff (Nature, 1929, **123**, 682).—A preliminary report of experiments on the influence of curvature and surface tension on the nature of adsorption and deposition of iodine (cf. Luce, this vol., 658).

A. A. Eldridge.

Interfacial tension between mineral oils and aqueous solutions. Influence of degree of refining and degree of alteration of oils. H. Weiss and E. Vellinger (Compt. rend., 1929, **188**, 1099—1101; cf. this vol., 503).—The p_H–interfacial tension curves of the system, mineral oil–aqueous solution of an electrolyte, vary with the degree of refinement of the oil. J. Grant.

Floating mercury on water. C. A. C. Burton (Nature, 1929, **123**, 759).—In Adam's conclusion (this vol., 391) that the mercury–air tension must have been reduced by the order of 100—200 dynes, the part played by curvature of the surfaces in determining conditions for equilibrium or spreading was neglected; this consideration is examined. A. A. Eldridge.

[Floating mercury on water.] H. H. Dixon (Nature, 1929, **123**, 759).—Mercury drops on water may be supported by flotation, and not by surface tension. A. A. Eldridge.

Effect of proteins in diminishing surface tension. F. Bottazzi (Arch. Sci. biol., 1927, **10**, 456—506; Chem. Zentr., 1928, ii, 1988).—Solutions of proteins which remain dissolved at the isoelectric point show at that point minimal surface tension. The increase of surface tension on each side of the isoelectric point depends on the dissociation of the protein salt, the protein (or other substance) in the form of undissociated molecules diminishing the surface tension to the greatest extent.

A. A. Eldridge.

Invisible oxide films on metals. H. C. H. Carpenter (Nature, 1929, **123**, 682).—The formation of invisible oxide films on copper, lead, and iron has been demonstrated by Vernon (A., 1926, 1108; B., 1927, 301; cf. Constable, this vol., 503).

A. A. Eldridge.

Formation of thin films of organic colloids on mercury surfaces. R. L. Keenan (Kolloid-Z., 1929, **47**, 289—294).—A method for the preparation of thin films of substances on a surface of mercury is described. Experiments have been carried out with several kinds of cellulose acetate of varying viscosity and in different solvents. In the case of nitrobenzene as solvent, the thickness of the film varies inversely as the viscosity of the solution. Further experiments were conducted with crêpe rubber and with isoelectric gelatin. The films of cellulose acetate and of gelatin were hard, whilst the rubber film was elastic. The limiting value of the thickness of the film increases with the number of different kinds of atoms in the molecule: thus, the thicknesses for rubber, cellulose acetate, and gelatin are, respectively, 1·5, 2·5—5·0, and 7·0 Å. The conclusion is reached that the molecules in the films are arranged in long chains or in the form of a network.

E. S. Hedges.

Osmosis of liquids. II. F. A. H. Schreinemakers (J. Gen. Physiol., 1929, **12**, 555—569).—Two solutions separated by a membrane are allowed to diffuse under osmotic forces and the resulting changes are followed by analysing small quantities withdrawn from each solution (cf. A., 1928, 233). The type of curve obtained is dependent on the membrane used, two different samples of pig's bladder giving different types of curves with the same solutions.

W. O. Kermack.

Ultrafiltration dialysis and osmometry by means of collodion sacs. M. Sigaud (Ann. Inst. Pasteur, 1929, **43**, 190—217).—A detailed description is given of the technique required in the preparation of collodion cells of convenient form for ultrafiltration, dialysis, and osmometry, especially when sterility and freedom from chemical contamination are required.

H. F. Gillbe.

Suspension of sand in water. H. E. Hurst (Proc. Roy. Soc., 1929, A, **124**, 196—201).—By means of an apparatus, somewhat similar to the paddle-wheel apparatus used by Joule to determine J, and designed to give, as far as possible, uniformly distributed turbulent motion without any steady flow, a study has been made of the laws governing the suspension in water of samples of rounded desert-sand. Three kinds of sand, of diameter 0·9, 0·4, and 0·2 mm., respectively, and many different speeds of the propeller were used. The results show that for a given sample of sand and propeller speed, the concentration of sand n at height h is given by $n=n_0\varepsilon^{-ah}$, where a is a function of the speed of the propeller and varies with the kind of sand. Curves are plotted showing the relation between the mean square velocity of agitation of the particles and the square of the revolutions of the propeller. The investigation indicates that the particles in suspension due to uniformly distributed turbulent motion in a liquid behave like the molecules in a gas.

L. L. Bircumshaw.

Equilibria between acids and bases in a gaseous phase. Volatility product of salts. Applications. A. Tian (J. Chim. phys., 1929, **26**, 91—116).—A theoretical study has been made of the formation of smokes by the interaction of volatile acids and bases. Such a reaction is always reversible, and the precipitation of the salt forming the smoke must obey a law of the mass action type. The expression [acid]×[base]$=P$ is derived, where P is the "volatility product" of the salt formed, and is analogous to the solubility product in solutions. This expression is verified experimentally from a study of the interaction of acetic acid and pyridine in the vapour state. The dissociation in the vapour phase of salts formed from volatile constituents is considered. The strengths of the acidic and basic constituents are the important factors which determine precipitation of the salt. If a mixture of two salt vapours can give rise to a salt with strong constituents, then this salt tends to be precipitated as a smoke. The validity of this statement, which forms a general law, is verified experimentally.

The conditions favourable for the formation of smokes are investigated, and a method is developed for the determination of small amounts of acidic and basic constituents of a gaseous mixture. Investigation has also been made of the effect of water vapour, which for strong acids and bases increases the sensitivity of the method. O. J. Walker.

Chemical composition and dispersity of crystalline particles. Wo. Ostwald and A. von Buzágh (Kolloid-Z., 1929, **47**, 314—323).—The composition of the elementary cell of a crystal as disclosed by X-ray examination differs from the stoicheiometric composition of large crystals, the two merging into one another as the size of the crystal increases. This progression with increasing size of crystal has been investigated and is illustrated by means of curves for some typical forms of space lattice (rock salt, fluorspar, cæsium chloride, cuprite, and rutile). The convergence of the two compositions occurs in crystals having a length of about 10^{-6} to 10^{-5} cm., *i.e.*, typical colloidal dimensions. It follows that the composition of the colloidal particles in sols and highly disperse precipitates can vary with the size of the particles, *e.g.*, a highly disperse calcium fluoride sol prepared by a condensation method may be richer in calcium ions than a similar sol of lower dispersity. The difficulties inherent in an experimental verification of these views are discussed. It is suggested that the "lattice blocks" of Smekal's theory of crystal structure are identical with crystallites which have reached a stoicheiometric composition, the progression from the fine-structure composition to the stoicheiometric composition being marked by a stabilisation of the crystallites. E. S. Hedges.

Preparation of many-coloured silver sols by means of hydrogen peroxide. E. Wiegel (Kolloid-Z., 1929, **47**, 323—325).—Silver sols which appear yellow, red, violet, or blue in transmitted light may be prepared without the aid of gelatin as a protective colloid. The method consists of adding hydrogen peroxide to a highly disperse Carey Lea's silver sol containing a small quantity of dextrin. The colour produced after the catalytic decomposition of the hydrogen peroxide depends on the amount of hydrogen peroxide used and on the rate of addition. The colour of the sols in reflected light is complementary to that in transmitted light.

E. S. Hedges.

Spontaneous formation of nuclei in dilute, highly supersaturated gold solutions. P. A. Thiessen (Z. anorg. Chem., 1929, **180**, 57—64).—When a dilute aqueous solution of chloroauric acid is being reduced with hydrogen peroxide, carbon monoxide, potassium thiocyanate, or ultra-violet light, the number of gold nuclei present at any particular moment may be determined by adding hydroxylamine hydrochloride, or hydrazine sulphate, which cause existing nuclei to grow so large that they can be counted under the ultramicroscope, yet do not themselves give rise to an appreciable number of new nuclei. The rate of formation of nuclei increases for a short time after reduction has started, then becomes fairly steady, and ultimately diminishes. In explanation of the period of induction, it is suggested that the rate of formation of nuclei increases with increase in the degree of supersaturation, which initially rises steadily owing to the progress of the reduction. Soon, however, the products of reaction reach such a concentration as would bring the reaction to a standstill if they were not removed as nuclei, the rate of formation of which therefore becomes constant. Finally, the concentration of chloroauric acid becomes so small that this degree of supersaturation cannot be maintained, and the rate therefore starts to diminish. With ultra-violet light, the number of nuclei ultimately starts to decrease again, apparently owing to coagulation. From the foregoing it becomes possible to prepare gold hydrosols with particles of any desired size without the aid of nuclei by starting with a suitable concentration of gold, and developing the nuclei at the appropriate point. R. Cuthill.

Smallest crystal nuclei in highly supersaturated gold solutions. P. A. Thiessen (Z. anorg. Chem., 1929, **180**, 110—114).—When auric chloride is reduced with potassium thiocyanate, the smallest gold particles which will serve as nuclei for the formation of a gold sol (cf. preceding abstract) are of approximately the same dimensions as the smallest gold crystals capable of growth. R. Cuthill.

Colloidal behaviour of the sulphides and hydroxides of cadmium and zinc. (Miss) W. Daus and O. F. Tower (J. Physical Chem., 1929, **33**, 605—612; cf. Hausmann, A., 1904, ii, 547).—Liesegang's rings of cadmium and zinc sulphides are formed in 1% agar-agar and in 5% gelatin, but not in silica gel. The sulphide ion must be in the gel and the metallic ion above in order to obtain good banding, which occurs at an optimum concentration in each case. The results can be explained by Bradford's theory of ring formation (A., 1922, ii, 358) with the proviso that sulphide ions are adsorbed more strongly than the metallic ions by the precipitated sulphides. Colloidal solutions of cadmium and zinc hydroxides have been prepared by a method analogous to that used for nickel hydroxide (Tower, A., 1924, ii, 237). The cadmium hydroxide is stable and positively charged, whilst the zinc hydroxide is somewhat unstable. Gels of these two hydroxides in glycerol have also been obtained by the method used for nickel hydroxide gel (Tower and Cooke, A., 1922, ii, 853).

L. S. Theobald.

Electrolyte-free colloidal ferric oxide. P. A. Thiessen and O. Koerner (Z. anorg. Chem., 1929, **180**, 115—119).—Electrolyte-free ferric oxide sols prepared by hydrolysis of ferric ethoxide are markedly lyophobic, being extremely sensitive to electrolytes; the disperse particles are negatively charged. Acids and ferric chloride alter the sign of the charge, and impart to the sol the characteristics of ordinary ferric oxide sols prepared by hydrolysis of ferric compounds and dialysis, so that the lyophilic nature of such sols is to be attributed to the traces of electrolytes present. Small amounts of alkali have a stabilising effect without influencing the charge, but larger amounts cause coagulation. R. Cuthill.

Equilibrium in the system colloidal ferric hydroxide–hydrochloric acid–water. E. Heymann (Kolloid-Z., 1929, **47**, 325—330; cf. this vol., 260).—An experimental investigation has been made of the equilibrium between colloidal ferric hydroxide and hydrochloric acid, and the results show that for a given concentration of hydrochloric acid the amount of ferric chloride formed increases with the concentration of ferric hydroxide used. The expression $[HCl]^3/[FeCl_3]=K$ is therefore only approximate. The active mass of the colloidal hydrolysis product of ferric chloride is not regarded as constant, but increases with the concentration of the colloid. The reaction between colloidal ferric hydroxide and hydrochloric acid takes place, not only on the surface of the particles, but also within the surface. The equilibrium is also influenced by the degree of dispersion of the ferric hydroxide: thus, coarsely disperse ferric hydroxide is in equilibrium with a smaller concentration of ferric chloride than the highly disperse colloid. The dispersity varies with age, and by altering this condition micelles of different chemical composition can be produced. The micelles richest in chlorine are obtained by the ageing of ferric chloride solutions and those poorest in chlorine by mixing ferric hydroxide sol (prepared from iron pentacarbonyl by the method of Freundlich) with hydrochloric acid.

E. S. Hedges.

Colloidal platinum. V. Coagulation by electrolytes in acid solution. VI. Behaviour

of platinum sols in basic solution. S. W. Pennycuick (J.C.S., 1929, 618—623, 623—633; cf. A., 1928, 1090).—V. Conductivity measurements show that when salts are added to acid platinum sols the salt cation partly replaces the hydrogen ion in the surface hexahydroxy-acid. With increase in the salt concentration the activity of the colloid ion is reduced to such a point that coagulation can occur, the relation between the coagulative power of an ion and its valency being explicable in terms of its attraction for the colloid ion. The amount of a particular salt required to effect coagulation decreases with increase in the acidity of the sol, probably due to the acid as well as the salt playing a part in such coagulations. With ferric chloride and aluminium sulphate at very low concentrations, it is apparently the free acid produced by hydrolysis which is the coagulant; the hydroxide plays no part.

VI. When platinum sols are titrated with barium hydroxide, the amount of alkali taken up is much greater than corresponds with the hexahydroxy-acid on the surface of the colloid particles. This excess of alkali is apparently fixed on the surface by lower oxides of platinum which are too weak to form acids with water, yet are able to form salts with bases. If salts bring about coagulation by repressing the ionisation of the salt of the hexahydroxy-acid, their effect will be opposed by alkalis, which will render the lower oxides ionogenic, and so tend to maintain the charge on the colloid particles. The coagulative powers of salts prove, in fact, to be much reduced by addition of alkalis, which will also frequently peptise the coagula produced by salts. Sometimes peptisation can be achieved by washing with water only.

R. Cuthill.

Peptisation of ignited ferric oxides and formation of a ferric oxide mirror. A. Krause (Z. anorg. Chem., 1929, 180, 120—126).—Ferric ferrite, obtained by the interaction of ortho- and meta-ferric hydroxides, is, after being ignited, readily peptised by dilute acids. The resulting "*c*-ferric oxide" sol contains positively-charged particles, and its hydrophobic nature is evident from the readiness with which it deposits a ferric oxide mirror on the walls of the containing vessel. Ortho-ferric hydroxide partly converted into ferric ferrite by ageing under water or sodium hydroxide solution yields the same sol after ignition. Ortho- and meta-ferric oxides are not peptised by acids after ignition, but the meta-oxide, unlike ferric ferrite and the ortho-oxide, is peptised by dilute ammonia solution after ignition. The meta-ferric acetate hydrosol has only a slight tendency to produce a mirror, and the ortho-acetate hydrosol has none, and even exerts a stabilising influence on the meta- and *c*-sols. It may therefore be concluded that there are three series of ferric oxides and hydroxides.

R. Cuthill.

Lyophilic colloids. I. Osmotic experiments and viscosity measurements with caoutchouc solutions. H. Kroepelin (Kolloid-Z., 1929, 47, 294—304).—Measurements of the osmotic pressure of caoutchouc solutions have been made at 11° and 40° and from the results the vapour pressure and its temperature coefficient and also the heat of dilution have been calculated. The material used was a cold ethereal extract of the substance extracted by acetone from crêpe. The micellar weight of caoutchouc has been calculated from a simplified van der Waals equation and leads to the value 200,000. Viscosity measurements were conducted, using capillaries of various diameters, and the results show that the apparent viscosity is a definite function of the middle velocity gradients: measurements with different capillaries give the same value so long as the middle velocity gradients are chosen. In all the caoutchouc solutions examined, the apparent viscosity is a linear function of the logarithm of the velocity gradient. No simple relation has been found between viscosity and osmotic pressure in these solution.

E. S. Hedges.

[Effect of ethyl alcohol on] silver sols. S. Klosky (J. Physical Chem., 1929, 33, 621—626).—The composition and physical properties of silver sols prepared by the method of Carmody (Thesis, Catholic University, U.S.A.) and containing various percentages of ethyl alcohol have been investigated. The densities are almost identical with those of the dispersion media, but contrary to Woudstra (A., 1908, ii, 818), the viscosities are slightly less. The migration velocities decrease with an increase in the alcohol content up to 20% by weight and then remain constant up to 40%. Alcohol also sensitises the sols towards coagulation by potassium, calcium, and aluminium ions. The calculated values of the boundary potential rise after the addition of 25% of alcohol.

L. S. Theobald.

Dispersoidological investigations. XXIV. Dispersoidology of gold. P. P. von Weimarn (Repts. Imp. Ind. Inst. Osaka, 1929, 9, No. 7, 9—79).—The relation between the size of crystals and the concentrations of the reacting solutions is discussed and the views of Zsigmondy are shown to be opposed to those of the author. It is shown that the increase in the mean size of crystals with increase of concentration of the reacting solutions observed in some cases is an indication of the existence of some anomaly in the course of the precipitation process. An account is given of the preparation of colloidal solutions of "gold iodide," "gold thiocyanate," and "gold citrate" and of their transformation into gold sols. The chemical composition of these substances is not constant. It is suggested that colloidal gold iodide may find an application in medicine. The existing simple view of the mechanism of the formation of gold sols as a spontaneous crystallisation from supersaturated solutions of gold is considered to be insufficient, in particular because it cannot account for the different results obtained by using equal concentrations of different salts and gold compounds. The question is considered whether it is possible to obtain colloidal solutions of gold without the preliminary formation of colloidal solutions of sparingly soluble gold compounds. Methods are given for the preparation of gold sols of orange-red and pure orange colour. The orange sols retain their orange colour only for a few hours, but the orange-red sols retain their colour for some months, ultimately becoming pure red. The particles producing the orange coloration are smaller than those present in red gold sols. The ammonia test (a blue ring produced at the boundary of contact of concentrated ammonia solutions and a red gold sol containing small quantities of gold compounds) is criticised. The gold compounds concerned are divided into three groups: (*a*) those which give a blue ring after a short time, (*b*) those giving no ring at all, (*c*) those giving a coloured ring slowly and with the colour changing from purplish-red to blue. It is pointed out that gold is far from being one of the simplest subjects for dispersoidological investigations; it is inclined to the formation of complex compounds and these are not characterised by stability and they undergo rapid changes in their chemical composition.

E. S. HEDGES.

Coagulation and particle size. P. A. THIESSEN, K. L. THATER, and B. KANDELAKY (Z. anorg. Chem., 1929, **180**, 11—18).—By determining the minimum amounts of a particular electrolyte necessary to coagulate gold sols of various degrees of dispersity, and also comparing the rates of coagulation by a particular concentration of electrolyte, it has been found that with decrease in the size of the colloid particles the stability in respect of coagulation by electrolytes increases. Since the electrokinetic potential of the particles varies with the composition of the intermicellar liquid, it must be concluded that the critical potential for coagulation depends on the degree of dispersity.

R. CUTHILL.

Conductivity–diffusion method for studying the coagulation of colloidal ferric oxide. C. H. SORUM (J. Amer. Chem. Soc., 1929, **51**, 1154—1162). —Attempts were made to determine the critical electrolyte concentration necessary to coagulate ferric hydroxide sols by increasing the electrolyte concentration very gradually and determining the effect on the conductivity of the sol. Since coagulation is considered to be accompanied or preceded by the adsorption of the coagulating ion, the conductivity should fall abruptly at the critical point. The graphs of resistance against time for experiments in which the gradual addition of the electrolyte was effected by a diffusion process do indeed show discontinuities, but although these may be attributable to the cause mentioned, they may also be due to the sudden localised coagulation preventing uniform distribution of the electrolyte. Gradual concentration of the electrolyte by evaporation was found to be unsatisfactory.

S. K. TWEEDY.

Morphology of chemical reactions in colloidal media. M. S. DUNIN and F. M. SCHEMJAKIN (Kolloid-Z., 1929, **47**, 335—341).—A study has been made of the interaction of solutions of potassium ferrocyanide and silver nitrate at various concentrations in 5% gelatin. The experiments were carried out by placing a drop of a saturated solution of one of the reagents on a thin layer of gelatin containing a dilute solution of the other reagent and observing the nature of the field of diffusion. It is concluded that reactions of this type in gels fall into one of three classes: (*a*) the diffusion field consists of periodic rings (typified by silver nitrate and potassium dichromate), (*b*) the diffusion field is in the form of a rosette and rings form inside the drop (silver nitrate and potassium ferrocyanide), (*c*) the diffusion field is homogeneous (silver nitrate and potassium chloride). In the reaction between silver nitrate and potassium ferrocyanide the conditions for the formation of rosettes are most favourable when potassium ferrocyanide is the inner electrolyte and at a concentration of 0·05—0·01N. Rosettes are not formed when silver nitrate is the inner electrolyte, but are formed when a saturated solution of copper sulphate is used in place of silver nitrate. The morphology of the structures also depends on the quality of the gelatin.

E. S. HEDGES.

Method of investigating coagulation and peptisation phenomena. A. VON BUZÁGH (Kolloid-Z., 1929, **47**, 370—372).—A preliminary communication of a method for following the process of coagulation and peptisation by direct observation.

E. S. HEDGES.

Influence of dimensions of the capillary on the streaming anomalies of colloidal liquids in the capillary viscosimeter. W. HALLER and V. TRAKAS (Kolloid-Z., 1929, **47**, 304—310).—In the streaming of colloidal liquids a critical value is derived, which is characteristic for the appearance of structure viscosity, resembling Reynolds' value for turbulence. An explanation of some viscosity anomalies of colloidal solutions is offered. The equation of de Waele and Wo. Ostwald has been reduced, so that the two constants involved are no longer dependent on the dimensions of the apparatus, but only on the substances.

E. S. HEDGES.

Capillarity. X. Further formulation of capillary structures. K. SCHULTZE (Kolloid-Z., 1929, **47**, 310—313; cf. A., 1928, 232).—A theoretical consideration of different types of capillaries.

E. S. HEDGES.

Diffusibility and dispersity of dyes and their relation to colour at various hydrogen-ion concentrations. A. PISCHINGER (Z. Zellforsch. Mikros. Anat., 1927, **5**, 347—385; Chem. Zentr., 1928, ii, 1865—1866).—The speed of diffusion of methylene-blue in gelatin gels diminishes, and that of crystal-ponceau increases from the acid side towards neutrality; that of methylene-blue in water is constant between p_H 2·5 and 7·8. Hence the variations depend on the change of adsorptive power of the gelatin with change in p_H. The relation between the charge of the dye and the colloid protein determines the flocculating effect; methylene-blue displaces the optimum for denatured serum-albumin slightly towards the alkaline side, and crystal-ponceau slightly towards the acid side. Colour changes due to the formation of adsorption compounds, *e.g.*, of nucleic acid and methylene-blue, are discussed.

A. A. ELDRIDGE.

Rennin action in relation to electrokinetic phenomena. G. A. RICHARDSON and L. S. PALMER (J. Physical Chem., 1928, **33**, 557—576).—The isoelectric point of rennin determined by a cataphoretic method lies at p_H 6·9—7·0. The addition of rennin to sols of calcium caseinogenate having p_H 6·1—6·9 reduces the rate of migration of the caseinogenate micelles, indicating that rennin lowers the electrical charge on negatively-charged, semilyophilic micelles. At p_H 7·0—7·25 the rate of migration increases, but at p_H 7·5—7·69 no change occurs. The addition of rennin to calcium caseinate solutions with p_H

6·45 also has no effect on migration. Heating neutral and slightly acid caseinogenate sols increases the rate of migration, indicating an increase in charge of the protein micelles, and the action of rennin on such heated sols is to decrease the rate of migration, but not to the extent which is observed with unheated sols.

L. S. Theobald.

Action of caffeine on absorption of water by colloids. J. Szeloczey (Biochem. Z., 1929, 206, 290—300).—The gelation temperature of a gelatin solution is depressed by the addition of caffeine. The caffeine raises the proportion of " free " water and this action depends not only on the concentration of the caffeine and on the p_H of the solution, but also on the nature of the colloid. C. C. N. Vass.

Influence of a second liquid on the formation of soap gels. H. N. Holmes and R. N. Maxson (5th Coll. Symp. Mon., 1928, 287—300).—Traces of water assist the dispersion of potassium stearate in turpentine and the formation of a gel on cooling. Addition of a small quantity of water increases the ability of sodium stearate, but decreases that of sodium oleate, to hold turpentine. Potassium oleate does not readily disperse in turpentine. Oleic acid assists sodium oleate or stearate to hold turpentine; oleic or stearic acid depresses gel formation with sodium stearate, and assists it with calcium stearate, in paraffin oil. With sodium stearate and benzene, oleic acid aids dispersion; with stearic acid there is a critical zone above which no gels are formed, although gels are not formed without stearic acid.

Chemical Abstracts.

Structure of solutions of gelatin. Marinesco (Compt. rend., 1929, 188, 1163—1165; cf. A., 1928, 1321).—The dielectric constant at 20° of solutions of commercial gelatin (ash 0·4%) for λ 6·50 m. increases rapidly and linearly with concentration and reaches a sharp maximum for a 0·75% solution (ε=108). It then falls rapidly. This maximum corresponds with the transformation of the gelatin from one to the other of the two forms in which according to Smith (A., 1919, i, 179) it may exist. It is shown that in concentrations of 2—3%, one gram of solid gelatin fixes approximately 9 c.c. of water. J. Grant.

Setting of gelatin sols. A. Lottermoser and W. Matthaes (Z. physikal. Chem., 1929, 141, 129—136).—The cooling curves of gelatin solutions of varying concentrations (10, 20, 30, and 60%) were compared with those for corresponding quantities of water, and the temperature differences as indicated by the curves were then plotted against temperature. In all cases there are inflexions in these difference curves. In the case of the 10%, 20%, and 30% solutions the initial rise in temperature occurred at 31°, 36°, and 38°, respectively; the most rapid rises were between 26° and 27°, 30·5° and 32°, and between 32° and 33·5°, respectively; and the total rises were 1·4°, 1·55°, and 1·8°, respectively. The more concentrated the solution the less sudden was the rise. This may be due to viscosity or hysteresis phenomena. Similar experiments were carried out with potassium palmitate solutions with analogous results. It is probable that this phenomenon occurs with all temperature-reversible colloids. A. J. Mee.

Swelling of gelatin and the volume of surrounding solution. J. H. Northrop and M. Kunitz (J. Gen. Physiol., 1929, 12, 537—542).—When various quantities of acid of different concentrations are added to purified isoelectric gelatin the degree of swelling of the gelatin is dependent solely on the final p_H of the supernatant acid, a result in accordance with the theories of Procter, Wilson, and Loeb. If, however, the gelatin contains salts, the final concentration of these salts will depend on the amount of acid used and so the degree of swelling will be determined, not only by the final p_H of the supernatant fluid, but also by the quantity of acid added. This conclusion is confirmed by experiment.

W. O. Kermack.

Influence of size, shape, and conductivity of microscopically visible particles on cataphoretic mobility. H. A. Abramson and L. Michaelis (J. Gen. Physiol., 1929, 12, 587—598).—The cataphoretic mobilities of globules of nujol, benzyl alcohol, paraffin oil, cacao butter, or castor oil suspended in a solution of sucrose of approximately the same density containing a small quantity of an electrolyte have been determined by a microscopical method. In each case the mobility is independent of the size of the particles. Needle-shaped particles of asbestos likewise move with a speed independent of their length and during cataphoresis do not orient themselves in any particular direction relatively to the potential gradient. In presence of gelatin, which ensures that the electrokinetic potential is independent of the substance composing the particle, spherical globules of paraffin oil or mastic and needles of asbestos or *m*-aminobenzoic acid migrate with equal mobilities, thus demonstrating that under the same electrokinetic potential the velocities of cylinders and of spheres are equal, a conclusion which is opposed to that reached theoretically by Debye and Hückel. Paraffin droplets, quartz particles, droplets of benzyl alcohol, carbon particles, and particles of agar, in spite of their different conductivities, possess equal mobilities when suspended in a medium containing gelatin.

W. O. Kermack.

Hydrolysis of gelatin by means of acid and alkali. I. S. Yaitschnikov (J. Russ. Phys. Chem. Soc., 1929, 61, 109—118).—Gelatin was hydrolysed by means of either *N*- or 0·2*N*-sulphuric acid or -sodium hydroxide solution at 37° or 100° and for periods up to 16 hrs. The action is more vigorous at higher concentrations and higher temperatures, and alkali has been found to be the more efficient hydrolysing agent. A graphic method is described which permits the progress of hydrolysis to be determined.

A. Freiman.

Chemical and physical changes in gelatin solutions during hydrolysis. J. H. Northrop (J. Gen. Physiol., 1929, 12, 529—535).—The physical and chemical changes occurring in gelatin as the result of hydrolysis by pepsin have been followed by determining the viscosity at various hydrogen-ion concentrations and also the " formol " titration values. A slight increase in formol titration value corresponds with a large decrease in viscosity. The greatest degree of physical change relative to chemical change occurs in 1% gelatin at a low p_H when the initial

viscosity is high. These results are in conformity with the theory of Loeb and Kunitz (A., 1927, 726) relative to the structure of gelatin solutions.
W. O. Kermack.

Combination of gelatin with hydrochloric acid. II. New determinations of the isoelectric point and combining capacity of a purified gelatin. D. I. Hitchcock (J. Gen. Physiol., 1929, **12**, 495—509).—The isoelectric point of a purified sample of Cooper's gelatin was determined by ascertaining the points of minimum osmotic pressure and of maximum turbidity. These methods both show the isoelectric point to be at p_H 5·05. Fairly concentrated solutions of gelatin were used to determine the hydrogen ions and chlorine ions combined with this protein at a p_H between 1 and 2. Over this range the quantity of combined hydrogen ion is constant and equal to $9{\cdot}4\times10^{-4}$ equiv. of hydrogen per gram of gelatin, whilst in 0·1*M*-hydrochloric acid 1 g. of gelatin combines with $1{\cdot}7\times10^{-4}$ equiv. of chlorine.
W. O. Kermack.

Chemical antagonism of ions. III. Effect of salt mixtures on gelatin activity. H. S. Simms (J. Gen. Physiol., 1929, **12**, 511—528).—To a 1·25% solution of sodium (or potassium) gelatinate (p_H 7·37) various quantities of sodium chloride, potassium chloride, and magnesium chloride were added either separately, in pairs, or all three together, and the p_H of the resulting solutions was determined. Sodium chloride at all the concentrations used (up to *M*) lowers the p_H of the sodium gelatinate solution and potassium chloride lowers the p_H up to 0·01*M*, but more concentrated solutions raise it. The results obtained with mixtures show that the effect is not the sum of the effects of the separate salts, but that the action of one salt may antagonise that of the other, even when both salts have univalent cations. W. O. Kermack.

Properties of fibres of coagulated gelatin. R. Collin (Compt. rend. Soc. Biol., 1928, **98**, 1353—1355; Chem. Zentr., 1928, ii, 1963).—Fibres obtained by dropping glass beads from a 10% gelatin solution into absolute alcohol exhibit double refraction. The colour reactions of the coagulated gelatin are the same as those of collagen fibrils; a close physico-chemical relation is indicated. A. A. Eldridge.

Colloidal chemical reactions between sols of proteins and polymeric carbohydrates. II. Wo. Ostwald and R. H. Hertel (Kolloid-Z., 1929, **47**, 357—370; cf. this vol., 507).—Experiments have been conducted on the influence of acids, alkalis, neutral salts, and salts at various hydrogen-ion concentrations on the separation of a mixture of sols of gelatin and starch. The volume of the new phase produced is related to the hydrogen-ion concentration in a similar way to other colloid chemical properties, *e.g.*, swelling. A minimum is observed in approximately neutral and weakly alkaline regions, whilst a maximum appears in acid and also in strongly alkaline regions. The influence of salts, particularly with regard to the anions, is in conformity with their place in the Hofmeister series. The phenomenon is considered to be due to flocculation as a result of the mutual dehydration of two sols and this idea is discussed in connexion with other mutual precipitations such as serological precipitation reactions. The kind of starch used affects the results considerably: the starches used appear in the following order of degree of hydration: potato-, rice-, maize-, wheat-starch.
E. S. Hedges.

Thermodynamic activities of the proteins. G. S. Adair (J. Amer. Chem. Soc., 1929, **51**, 696—707; cf. A., 1928, 1326).—Formulæ are derived correlating the thermodynamic activities of protein salts with their observed osmotic pressures. Provisional values for the activity coefficients of a salt of hæmoglobin (Hb) designated by the formula $Hb(Na+K)_{8{\cdot}5}$ have been determined.
S. K. Tweedy.

Physico-chemical properties of antitoxic and normal sera. S. Kasarnovsky (Kolloid-Z., 1929, **47**, 351—357).—In regard to the antagonistic effects of normal and immune sera on hydrophobic colloids, the coagulating and peptising influences of diphtheria immune sera are stronger than those of normal sera. The diphtheria sera are also more readily gelatinised.
E. S. Hedges.

Calculation of molecular polarisation of dissolved substances at infinite dilution. G. Hedestrand (Z. physikal. Chem., 1929, **B**, **2**, 428—444).—A formula is derived from which the molecular polarisation and dipole moments of substances at infinite dilution can be calculated from a knowledge of the dielectric constant and density of the solution as a function of concentration. The formula is applied to the calculation of the dipole moments of a number of organic substances in different solvents.
A. J. Mee.

B. p. of aqueous solutions. W. D. Bancroft and H. L. Davis (J. Physical Chem., 1929, **33**, 591—604).—The Washburn–Read modification of the Cottrell b.-p. apparatus is shown not to inhibit the superheating of water—a test for which is described—but a new modification is described which permits the accurate determination of the b. p. of dilute aqueous solutions. Dilute solutions of potassium nitrate and the potassium halides are now found to be completely dissociated at infinite dilution. An apparatus for the determination of the b. p. of aqueous solutions under pressures from 10 to 20 atm. is described, together with some preliminary results for boric acid and potassium chloride; the latter appears to be as abnormal at higher temperatures as it is at 0° or 100°. The divergences from commonly accepted theories revealed by a study of b.-p. data (cf. Kahlenberg, A., 1901, ii, 540) are discussed. L. S. Theobald.

Relation between specific rotatory power and refractive index of a solution. A. P. Perschke (J. Russ. Phys. Chem. Soc., 1929, **61**, 119—122).—It is shown that the specific rotatory power and the refractive index are connected by the same logarithmic expression $\log [\alpha]=a+b \log n$ which applies to a pure liquid. A. Freiman.

Natural rotation of polarised light by optically active bases. II. Rotation of *d*-α-phenylethylamine and its hydrochloride in solution: rotation of active tetrahydro-2-methylquinoline. W. Leithe (Monatsh., 1929, 51, 381—385).—Solvents which produce little change in the optical rotation of *d*-α-pipecoline (A., 1928, 1022), such as ether, *cyclo*hexane, *n*-heptane, and benzene, cause a slight increase in the specific rotation of *d*-α-phenylethylamine (d^{15} 0·9561; $[\alpha]_D^{15}$ +40·67° in the liquid state); carbon tetrachloride, chloroform, ethyl acetate, and pyridine cause a slight decrease, whilst solvents of the alcohol–water type cause a decrease of 10—15°. Solvents which affect the rotation of *d*-α-pipecoline have less influence on *d*-α-phenylethylamine. The specific rotation of the hydrochloride, which is also dextrorotatory ($[\alpha]_D^{15}$ +7·4° in 24·93 wt.-% aqueous solution), also varies slightly with the concentration of the solution and the solvent used. The phenyl group thus has an appreciable effect on the rotation and on the solvent effect. With the exception of ether and water, variation in the specific volume of the solutions runs parallel with the change in rotation, especially in the case of the hydrochloride. The opposite effects of different solvents, salt formation, and benzoylation on the rotations of *l*-α-methylindoline and *l*-tetrahydro-2-methylquinoline (Pope and others, J.C.S., 1899, **75**, 1116; 1904, **85**, 1330) are discussed and it is suggested that lævorotatory tetrahydro-2-methylquinoline has really a *d*-configuration, the lævorotation being due to secondary influences such as the solvent. J. W. Baker.

Van der Waals' equation and thermodynamics. J. E. Verschaffelt (Compt. rend., 1929, **188**, 1037—1039).—Polemical against Karpen (this vol., 387), and an amplification of the author's original deductions. J. Grant.

Calculation of van der Waals' *a* constants from Dühring's specific factors derived from van Laar's formula for the vapour-pressure curve. R. Lorenz (Z. anorg. Chem., 1929, **179**, 293—296).—Mathematical. The quantity A in the simple vapour-pressure equation $\log p=-A/T+C$ may be calculated for any substance from the value A' for another similar substance by means of the equation $q=A/A'$, where q is the "specific factor." H. F. Gillbe.

Thermodynamics of gases which show degeneracy. G. N. Lewis and J. E. Mayer (Proc. Nat. Acad. Sci., 1929, **15**, 208—218; cf. A., 1928, 1096).—Theoretical. An extension, based on previous simple statistical assumptions, to all types of molecules, of the work of Bose on photons and of Einstein on monatomic molecules. Boltzmann's equation for distribution with respect to energy is shown to be not generally valid, and from an investigation on molecules possessing internal energy a generalised form of this equation is deduced. The case of an arbitrarily quantised system, an ideal monatomic gas, is considered and the equation $S=5E/3T-kN\log A$ is derived for the entropy; in this A may be regarded as a measure of the degeneracy. A simple generalised equation is also obtained for the total entropy of a gas in terms of the total number of molecules, the total translational energy, and the total internal energy. N. M. Bligh.

Electrolytic solution tension and the ionic states. VI. K. Fredenhagen (Z. physikal. Chem., 1929, **141**, 195—216; cf. this vol., 513).—By comparing the theories of interionic force and solution force, it is shown that whilst they originate from different assumptions, they lead ultimately to the same result, viz., that in the region of dilute solutions the solution force must increase with increasing concentration. Objections are raised against the underlying assumption of the theory of interionic force, viz., that ions in a solution are solvated gas ions, and that the interaction between solvent and solute is independent of the concentration. The deviations from the dilution law are examined on the basis of a solution force changing with concentration. It is shown that the conception of the existence of ionic states can explain the characteristics of the absorption spectra of strong and weak electrolytes. A. J. Mee.

Dissociation and the colour of free radicals. C. B. Wooster (J. Amer. Chem. Soc., 1929, **51**, 1163—1165).—The degrees of dissociation derived from cryoscopic measurements do not warrant the conclusion that the equilibrium constant of a tautomeric process varies with dilution. The conclusions reached by Gomberg and Sullivan (A., 1922, i, 929) from their experimental results, therefore, are incompatible with the evidence on which they are based. Calculation shows that the measurements of these experimenters are not sufficiently accurate to test thoroughly the relation between colour and dissociation. S. K. Tweedy.

Equilibrium in aqueous solution between ammonium acetate, acetamide, and water. E. E. Lineken and G. H. Burrows (J. Amer. Chem. Soc., 1929, **51**, 1106—1112).—The components were heated at 172°, 184°, or 193° in a sealed glass tube, the equilibrium concentration being determined by conductivity measurements. The results indicate that the amide is formed through the ions of the ammonium acetate (cf. Walker and Hambley, J.C.S., 1895, **67**, 753). The effect of heating at 184° and 193° in a pyrex vessel on the conductivity of water is recorded. S. K. Tweedy.

Cryoscopic determination of the molecular equilibria of resorcinol in aqueous solutions of potassium chloride. F. Bourion and C. Tuttle (Compt. rend., 1929, **188**, 1110—1111; cf. A., 1927, 515).—Measurements by Raoult's method, slightly modified, suggest that resorcinol in 0·5 and 1·225*M*-potassium chloride solution forms simple, double, and triple molecules, whilst in pure water the last two only are observed. The fact that the cryoscopic constant is higher than in water and increases with the chloride concentration may be attributed to the adsorption of water by the salt. J. Grant.

Combination of proteins and amino-acids with acids and alkalis. II. Titration curves of amino-acids in presence of formaldehyde. L. J. Harris (Proc. Roy. Soc., 1929, **B**, **104**, 412—439).—The titration curves of various amino-acids determined in presence of 16% formaldehyde are consistent with the view that the apparent acid dissociation constant of the ampholyte is about a thousand times as great as that of the amino-acid in the absence of formaldehyde. With smaller concentrations of formaldehyde the apparent dissociation constant depends on the concentration of formaldehyde present, and up to about 8%, gradually increases with increase

in the formaldehyde. The results are best explained on the zwitterion theory of amino-acids, according to which the apparent acid dissociation constant is really dependent on the amino-group, whilst the apparent basic dissociation constant is dependent on the acidic group. In presence of formaldehyde, which combines with the amino-group, the apparent basic dissociation constant remains practically unchanged, whilst the apparent acid dissociation constant is increased. The conditions most favourable for carrying out the Sørensen formol titration are detailed.
W. O. Kermack.

Equilibrium in the liquid state between potassium, sodium, and their bromides. E. Rinck (Compt. rend., 1929, **188**, 1108—1109).—The law of mass action holds for the reaction $KBr+Na=K+NaBr$, the value $c=28{\cdot}8$ being obtained between 800° and 1000° (maximum variation 20%). The thermal value of the direct reaction is $-9{\cdot}5$ g.-cal. at the ordinary temperature and zero at 800—1000°.
J. Grant.

Activity coefficients of ions in very dilute methyl alcohol solutions. J. W. Williams (J. Amer. Chem. Soc., 1929, **51**, 1112—1119).—The activity coefficients in methyl alcohol at 20° of sparingly soluble cobaltammine salts of two valency types were determined by the solubility method. In sufficiently dilute solutions the limiting law of Debye and Hückel is approximately obeyed. The range of applicability of the theory seems to depend on the nature of the solute. As the dielectric constant of the solvent decreases, the highest concentration at which the simple activity theory is obeyed probably decreases also.
S. K. Tweedy.

Activity coefficients of diacetone alcohol in aqueous salt solutions. G. Åkerlöf (J. Amer. Chem. Soc., 1929, **51**, 984—997).—The activity coefficients, γ, of diacetone alcohol in solutions of alkali metal, magnesium, and aluminium salts were measured at 24° by the distribution method, the concentration changes being determined interferometrically. The values of γ are independent of the concentration of the alcohol in the salt solution. The quotient $(\log \gamma)/N$ is constant for a given salt, N being the concentration of the salt solution (cf. Randall and Failey, Chem. Rev., 1927, **4**, 291). The activity coefficients are of the same order of magnitude as those obtained for ethyl acetate and for some gases in the same salt solutions. No satisfactory explanation can be offered for the changes of the decomposition velocity of diacetone alcohol in various solutions of strong electrolytes (cf. A., 1928, 716).
S. K. Tweedy.

Osmotic and activity coefficients. R. C. Cantelo (J. Physical Chem., 1929, **33**, 627—632).—Mathematical. Alternative derivations of the Debye–Hückel equations for activity and osmotic coefficients are presented.
L. S. Theobald.

Significance of internal diffusion in the regulation of chemical equilibria. G. Tammann (Nachr. Ges. Wiss. Göttingen, 1927, 394—406; Chem. Zentr., 1928, ii, 1853—1854).—A discussion.
A. A. Eldridge.

Transformation of supercooled liquids into glasses. G. Tammann (Nachr. Ges. Wiss. Göttingen, 1927, 457—464; Chem. Zentr., 1928, ii, 1855—1856).—In the transitions between viscous liquids and glasses there is a lower limiting temperature, t_f, recognisable for the former, and an upper limiting temperature, t_g, for the latter. Between t_f and t_g individual properties of the substance change to an abnormally great extent. This is ascribed, not to molecular changes, but to a great increase of the internal pressure.
A. A. Eldridge.

Alkalinity of soap solutions as measured by indicators. J. W. McBain and (Miss) K. Hay (J.C.S., 1929, 589—601).—Very few indicators can be used to measure the p_H of soap solutions, but by means of alizarin-yellow *G* and phenolphthalein, which are the most satisfactory, the hydroxyl-ion concentrations in solutions of sodium and potassium soaps at 20° and 90° over a wide range of concentrations have been determined. The results agree with the view that the alkalinity is due to the formation of acid soap, whereby an excess of free hydroxyl ions results in the solution. In sufficiently dilute solution, the soap is crystalloidal, and the degree of hydrolysis depends simply on the mol. wt. With increase in concentration the hydroxyl-ion concentration rises to a flat maximum and ultimately falls again, presumably owing to replacement of the simple fatty ions by micelles, which are hydrolysed to a smaller extent.
R. Cuthill.

Amphoteric character of lead oxide and peroxide. H. Töpelmann (J. pr. Chem., 1929, [ii], **121**, 320—363).—Measurements of the solubilities in water and in sodium hydroxide solutions ($1\times10^{-4}-1N$) have been made at 25° and the conductivities of the solutions determined. Sources of error, arising from the disintegration of the particles by rotation of the vessel, the slowness with which the equilibrium is established, the dissolution of alkali from the glass (greatest in aqueous solutions), and the resulting silicification of the particles have been studied. From these observations a technique involving a shortened reaction period with very slow rotation in waxed glass vessels (with control in platinum vessels) is evolved, and the solubility and conductivity data are compared with those in the literature. The olive, red, and white (hydrated) forms of lead oxide (PbO) were each investigated, their solubilities in N- and $0{\cdot}01N$-sodium hydroxide and water at 25° being, respectively, $5{\cdot}82\times10^{-2}$, $7{\cdot}05\times10^{-4}$, $3{\cdot}35\times10^{-4}$ (olive); $3{\cdot}71\times10^{-2}$, $>4{\cdot}5\times10^{-4}$, $2{\cdot}14\times10^{-4}$ (red); and $7{\cdot}29\times10^{-2}$, $9{\cdot}49\times10^{-4}$, $5{\cdot}72\times10^{-4}$ mol./litre, and the specific conductances 30—35, —, and $38{\cdot}2\times10^{-6}$ ohm^{-1}, respectively. The solubility in very dilute alkali is less than that in water, the lead cation concentration diminishing with increasing hydroxyl-ion concentration, but above a $0{\cdot}01N$-concentration of sodium hydroxide the solubility rapidly increases owing to chemical interaction between the hydroxyl ions and the lead anions, indicating the amphoteric nature of this oxide. The dissolution of lead peroxide in alkali occurs much more slowly, the solubilities at 25° in $5{\cdot}01$, $1{\cdot}0$, and $0{\cdot}1N$-sodium hydroxide being, respectively, $8{\cdot}1\times10^{-3}$, 9×10^{-5}, and 1×10^{-6} mol./litre. On the basis of these results the dissociation constant of white, hydrated lead oxide as a monobasic acid (k_a) is

$8{\cdot}1\times10^{-12}$, and as a mono-acid base (k_b) $9{\cdot}6\times10^{-4}$, whence the measurement of its amphoteric character, obtained by the ratio k_a/k_b, is $8{\cdot}4\times10^{-9}$, the basic character being much more strongly pronounced. The solubility products, $C_{PbO_2H'}\times C_{H^\cdot}$, and $C_{PbOH^\cdot}\times C_{OH'}$, for the white, hydrated oxide are, respectively, $10{\cdot}1\times10^{-16}$ and $2{\cdot}56\times10^{-8}$, whilst the value of the former for the olive form is $7{\cdot}9\times10^{-16}$. The relations between the chemical properties and amphoteric character of the two lead oxides are discussed with reference to their atomic structure, and it would seem that the peroxide is the more acidic, the value of k_a/k_b being greater than unity, although the actual dissociation constants cannot be compared, since the quantity of dissolved, undissociated peroxide is unknown. The activity product of lead peroxide as a dibasic acid, $[A_{H^\cdot}]^2\times A_{PbO_4H_2''}$, has the value $4{\cdot}4\times10^{-33}$.
J. W. Baker.

Dissociation pressure of vanadium pentoxide. E. F. Milan (J. Physical Chem., 1929, **33**, 498—508).—The oxygen pressures of initially pure vanadium pentoxide have been measured over the range 25—1125°, together with the pressures of different mixtures of vanadium pentoxide and tetroxide over the range 700—1125°. The pentoxide is unstable above its m. p. The dissociation pressure at a given temperature depends on the composition of the mass. The pressure for fused masses containing practically 100% V_2O_5 is much greater than for those containing 10% V_2O_4 or more. The variations of oxygen pressure are not in accord with Raoult's law. Curves showing the relation between pressure, composition, and temperature are given.
L. S. Theobald.

Phase diagram of calcium–sodium. R. Lorenz and R. Winzer (Z. anorg. Chem., 1929, **179**, 281—286).—The m. p. of calcium (98·76%) is 809°. With sodium a eutectic mixture is formed containing 86 at.-% Ca and having m. p. 700°.
H. F. Gillbe.

Ceramics of highly refractory substances. II. System ZrO_2–CaO. O. Ruff, F. Ebert, and E. Stephan (Z. anorg. Chem., 1929, **180**, 215—224; cf. B., 1929, 474).—The m.-p. diagram of the system ZrO_2–CaO has been determined by means of a special oven with an oxy-acetylene burner. The existence of a compound $CaZrO_3$ is indicated and confirmed by means of Debye–Scherrer *X*-ray measurements. Calcium oxide forms mixed crystals with zirconium oxide from 0 to 40 mol.-%CaO. The compound has a monoclinic structure and *d* 4·78±0·05 ($d_{calc.}$ 4·74±0·05). The systems ZrO_2–MgO and ZrO_2–CaO are compared.
O. J. Walker.

Solubilities of lead phosphates. H. Millet and M. Jowett (J. Amer. Chem. Soc., 1929, **51**, 997—1004).—The solubility products (in terms of activity) of lead orthophosphate, s_3, and of lead hydrogen orthophosphate, $PbHPO_4$, s_2, have been determined by measuring the *E.M.F.* of cells of the type Pb|Pb salt soln.|satd.KCl|*N*-calomel electrode, and ascertaining the hydrogen-ion activity of the lead solution by means of the quinhydrone electrode. The values found were: $\log s_3=-42{\cdot}1$ at 25° and $-42{\cdot}0$ at 37·5°; $\log s_2=-9{\cdot}9$ at 25° and $-9{\cdot}62$ at 37·5°. The logarithm of the second ionisation constant of orthophosphoric acid is $-7{\cdot}127$ at 25°, and $-7{\cdot}058$ at 37·5°. The calculated heat of dissolution of the hydrogen salt is −10,000 g.-cal. at infinite dilution. Calculation shows that the normal orthophosphate is the stable lead phosphate under the conditions prevailing in the human body, and that a slight shift to the acid side does not convert this salt into the hydrogen phosphate.
S. K. Tweedy.

Ionisation constants of orthophosphoric acid. M. Jowett and H. Millet (J. Amer. Chem. Soc., 1929, **51**, 1004—1010).—The logarithm of the first ionisation constant is −2·10 at 25° and −2·16 at 37·5°. From previously published data the logarithm of the third ionisation constant is calculated to be −12·1 at 20° (cf. preceding abstract). The calculated heats (evolved) of the following reactions: $H_3PO_4\longrightarrow H^\cdot+H_2PO_4'$ and $H_2PO_4'\longrightarrow H^\cdot+HPO_4''$ are +2000 and −2300 g.-cal., respectively.
S. K. Tweedy.

Heterogeneous equilibria at 97° in systems containing water, sodium sulphate, and sulphates of the vitriol type. A. Benrath and H. Benrath (Z. anorg. Chem., 1929, **179**, 369—378).—Isotherms for ternary systems containing water and sodium sulphate, together with zinc, cadmium, ferrous, manganous, cobaltous, nickelous, or copper sulphate have been determined from 0° to 100°. At 97° all these sulphates, except those of copper and nickel, exist as monohydrates. Double sulphates are formed in all cases: $ZnSO_4,Na_2SO_4,4H_2O$, $CoSO_4,Na_2SO_4,4H_2O$, and $NiSO_4,Na_2SO_4,4H_2O$ are of the astrakanite type; $FeSO_4,Na_2SO_4,2H_2O$, $MnSO_4,Na_2SO_4,2H_2O$, $MgSO_4,Na_2SO_4,2H_2O$, and $CuSO_4,Na_2SO_4,2H_2O$ of the löweite type, whilst $CdSO_4,Na_2SO_4$ is of the glauberite type. Double salts of the vanthoffite composition are formed from those components which give rise to salts of the glauberite and löweite types.
H. F. Gillbe.

Ternary system potassium perchlorate–sodium nitrate–water from 0° to 100°. E. Cornec and A. Neumeister (Caliche, 1929, **11**, 488—491).—The solubility of sodium nitrate is increased slightly by the addition of potassium perchlorate, and that of the latter to a large extent by the addition of sodium nitrate. A saturated solution at 0° contains sodium nitrate and potassium perchlorate in the ratio 4·4 : 95·6. When saturated solutions are cooled, mixtures of the two salts separate in which the percentage of potassium perchlorate is greater the higher is the initial temperature. Separation of the two salts by a cyclic process may be readily effected.
H. F. Gillbe.

System potassium perchlorate–sodium chloride–water from 0° to 100°. E. Cornec and A. Neumeister (Caliche, 1929, **11**, 492—494).—Potassium perchlorate and sodium chloride diminish the solubility of each other in water. A solution saturated with both salts yields on cooling a mixture which always contains a greater proportion of perchlorate. Separation of the two salts may be effected by a cyclic process.
H. F. Gillbe.

System sodium nitrate–sodium chloride–potassium perchlorate–water from 0° to 100°. E. Cornec and A. Neumeister (Caliche, 1929, **11**,

494—499).—A single cycle is described whereby the three salts may be separated from a solution saturated with regard to sodium nitrate and sodium chloride, but unsaturated with regard to potassium perchlorate.
H. F. Gillbe.

Ternary system: water, sodium sulphate, sodium nitrate. A. Chrétien (Compt. rend., 1929, 188, 1047—1050).—The double salt $Na_2SO_4,NaNO_3,H_2O$ identical with darapskite can exist as a solid phase between 13° and 74°. No other double salt was detected. The three solid-phase equilibria observed were: (1) Na_2SO_4–$Na_2SO_4,10H_2O$–darapskite at 24·3°; (2) $NaNO_3$–Na_2SO_4–darapskite at 74°; (3) $Na_2SO_4,10H_2O$–$NaNO_3$–darapskite at 13°.
J. Grant.

Double salt isotherms. R. M. Caven and W. Johnston (J. Roy. Tech. Coll. Glasgow, 1929, 2, [i], 30—35).—See A., 1928, 1191.

System $Fe(NO_3)_3$–HNO_3–H_2O at 25°. G. Malquori (Atti R. Accad. Lincei, 1929, [vi], 9, 324—325).—The system has been investigated in the region of high nitric acid concentrations. The compounds $Fe(NO_3)_3,9H_2O$ and $Fe(NO_3)_3,6H_2O$ were identified. The latter may be prepared by the action of nitric anhydride on a saturated solution of the former in nitric acid of *d* 1·52.
F. G. Tryhorn.

System $Fe(NO_3)_3$–KNO_3–HNO_3–H_2O. G. Malquori (Atti R. Accad. Lincei, 1929, [vi], 9, 414—416; cf. preceding abstract).—A portion of the 25° isotherm for this system has been investigated with reference to the fractional crystallisation of the liquor obtained by the extraction of leucite with nitric acid. The following sets of solid phases are stable in contact with solutions of the compositions given by the figures in parentheses, which refer respectively to the percentages of ferric nitrate, potassium nitrate, nitric acid, and water: $Fe(NO_3)_3,9H_2O+Fe(NO_3)_3,6H_2O$, (28·2, 0, 54·23, 17·75): $Fe(NO_3)_3,9H_2O+Fe(NO_3)_3,6H_2O+Fe(NO_3)_3,2KNO_3,4H_2O$, (27·0, 17·30, 39·11, 16·59): $Fe(NO_3)_3,9H_2O+KNO_3$, (39·05, 11·02, 0, 49·03): $Fe(NO_3)_3,9H_2O+KNO_3+Fe(NO_3)_3,2KNO_3,4H_2O$, (24·91, 26·50, 26·71, 21·88): $Fe(NO_3)_3,2KNO_3,4H_2O+KNO_3$, (7·80, 43·95, 46·15, 2·10). The compound $Fe(NO_3)_3,2KNO_3,4H_2O$ is the first example of a double nitrate of an alkali metal and tervalent iron.
F. G. Tryhorn.

Systems: strontium oxide–phosphorus pentoxide–water, and barium oxide–phosphorus pentoxide–water at 25° (acid region). H. V. Tartar and J. R. Lorah (J. Amer. Chem. Soc., 1929, 51, 1091—1097).—The isotherms for 25° have been determined for the above two systems.
S. K. Tweedy.

Double decomposition in the absence of a solvent. VII. Equilibrium in the systems formed from thallous sulphate and mercury halides. N. K. Voskressenskaja (J. Russ. Phys. Chem. Soc., 1929, 61, 79—87).—The systems thallous sulphate–mercuric chloride, bromide, or iodide have been examined in reference to the conditions of equilibrium. Their behaviour resembles that of binary systems. Thallous sulphate forms no complexes with either the bromide or the iodide, but with the chloride it combines to form a complex $3Tl_2SO_4,HgCl_2$, m. p. 269°. The composition cannot, however, be regarded as definitely settled on account of experimental difficulties. The reaction between thallous sulphate and the three mercuric salts in water was also examined. In the case of mercuric chloride a compound of the approximate composition $5HgCl_2,2Tl_2SO_4$ is formed, but no double decomposition appears to take place.
A. Freiman.

Double decomposition in the absence of a solvent. VIII. Unusual irreversible system $TlNO_3+KBr \longrightarrow TlBr \longrightarrow KNO_3$. A. P. Rostkovski (J. Russ. Phys. Chem. Soc., 1929, 61, 89—107).—The equilibrium relations are described. It has been found that the reaction goes irreversibly in the direction of the formation of thallous bromide. The critical temperature of complete miscibility of the components is 535°. Complex formation occurs only in the case of potassium nitrate and potassium bromide: the compound KNO_3,KBr has m. p. 342° (decomp.).
A. Freiman.

Carbon dioxide–carbon monoxide equilibrium over copper. F. Halla (Z. anorg. Chem., 1929, 180, 83—88).—The equilibrium pressure for the system $Cu_2O \rightleftharpoons 2Cu+0{\cdot}5O_2$ indicated by the experimental data of Ishikawa and Kimura (A., 1928, 246) is, contrary to the assumption made by Brody and Millner (A., 1927, 939), much less than the pressure corresponding with the equilibrium $2CuO \rightleftharpoons Cu_2O+0{\cdot}5O_2$ at the same temperature. By means of the new figures, the constant for the equilibrium $2Cu+CO_2 \rightleftharpoons Cu_2O+CO$ between 200° and 700° has been recalculated.
R. Cuthill.

Heterogeneous equilibrium of tungsten and its oxides with carbon monoxide and carbon dioxide. Z. Shibata (Tech. Rep. Tôhoku, 1929, 8, 129—144).—The reduction of tungsten trioxide by mixtures of carbon monoxide and dioxide takes place in three stages through the intermediate oxides W_2O_5 and WO_2; between each oxide and the next lower and between WO_2 and metal there is a limited series of solid solutions. The constants for the successive stages of equilibrium have been determined.
A. R. Powell.

Heterogeneous equilibrium of tungsten and its oxides with hydrogen and water vapour and the dissociation pressure of the oxides. Z. Shibata (Tech. Rep. Tôhoku, 1929, 8, 145—151).—Equations have been derived which express the equilibria in the successive stages of the reduction of tungsten trioxide by hydrogen, and the dissociation pressure of the three oxides of tungsten have been calculated. The heats of formation of WO_2 and WO_3 are respectively 138·2 and 199·9 g.-cal. and the heat of the reaction $2WO_2+0{\cdot}5O_2=W_2O_5$ is 62·9 g.-cal. These values are in close agreement with those found by earlier investigators.
A. R. Powell.

Heat of dissociation of nitrogen. J. Kaplan (Proc. Nat. Acad. Sci., 1929, 15, 226—229).—Theoretical. Arguments are presented in support of Gaviola (cf. A., 1928, 1075) and others, that the heat of dissociation of nitrogen is less than the accepted value of 11·4 volts. The value 9·0 volts seems to be indicated.
N. M. Bligh.

Specific heats of sodium and potassium hydroxide solutions [at 18°]. T. W. Richards and L. P. Hall (J. Amer. Chem. Soc., 1929, 51, 707—712).—Experiments already recorded were repeated and extended, the results previously obtained being confirmed (cf. Richards and Gucker, A., 1925, ii, 848; Richards and Rowe, A., 1913, ii, 920). The method of determining sodium as a chloride residue is subject to error on account of the retention of water by the crystals; only fusion of the salt will remove this water. Sodium hydroxide may be completely freed from potassium by two crystallisations.
S. K. Tweedy.

Heats of dilution of sodium hydroxide, acetic acid, and sodium acetate, and their bearing on heat capacities and heat of neutralisation. T. W. Richards and F. T. Gucker, jun. (J. Amer. Chem. Soc., 1929, 51, 712—727).—The method previously described was improved and used to determine the specific heats and heats of dilution at 16° and 20° of sodium acetate, sodium hydroxide, and acetic acid (Richards and Rowe, A., 1921, ii, 380). Dilution of sodium acetate and acetic acid is attended by evolution of heat; the same applies to sodium hydroxide at concentrations below 1 mol. of salt in 400 mols. of water, at which concentration the heat of dilution changes sign. Dilution of concentrated acetic acid solutions is accompanied by an increase in heat capacity. The heat of neutralisation of acetic acid increases with the dilution, but for all acids the value 13,600 g.-cal./mol. is approached at infinite dilution.
S. K. Tweedy.

Heats of dilution and heat capacities of hydrochloric acid solutions. T. W. Richards, B. J. Mair, and L. P. Hall (J. Amer. Chem. Soc., 1929, 51, 727—730).—The specific heats at 18° and the heats of dilution at 16° and 20° of some hydrochloric acid solutions were measured, and from the results the specific heats at other dilutions were calculated. The values for the heats of dilution substantially agree with those previously found (cf. Richards and Rowe, A., 1920, ii, 584).
S. K. Tweedy.

Thermochemical behaviour of weak electrolytes. T. W. Richards and B. J. Mair (J. Amer. Chem. Soc., 1929, 51, 740—748).—The heats of dilution of citric acid, sodium citrate, and the two sodium hydrogen citrates were determined over a wide range of dilution. The replacement of hydrogen by sodium does not produce any regular effect on the heat of dilution, and the latter decreases for each compound as the ionisation increases. Each replacement of hydrogen in citric acid by sodium is accompanied by an almost regular increase in the loss of heat capacity of the solution, which latter quantity seems to depend very largely on the degree of dissociation. Contrary to the behaviour of strong inorganic acids, the heat capacities of the solutions decrease as hydrogen is replaced by sodium. The heats of neutralisation of citric acid and the two hydrogen citrates are recorded; they are smaller, and their temperature coefficients are smaller, than the corresponding values for strong acids.
S. K. Tweedy.

Heats of dilution and specific heats of barium and calcium chloride solutions. T. W. Richards and M. Dole (J. Amer. Chem. Soc., 1929, 51, 794—802).—The specific heats increase between 20° and 25°. As required by the Debye–Hückel theory (Bjerrum, A., 1926, 476), both calcium and barium chlorides have positive heats of dilution at very small concentration. The heats of dissolution of calcium, strontium, and barium chlorides show a regular decrease in magnitude as the at. wt. of the metal increases.
S. K. Tweedy.

Thermolysis of solid salts (Ludwig-Soret phenomenon). H. Reinhold (Z. physikal. Chem., 1929, A, 141, 137—140).—Continuing earlier work on thermo-electric phenomena in solid salts, thermolytic experiments were carried out with mixed crystals of cuprous and silver iodides. Cylinders containing 25% of cuprous iodide and 75% of silver iodide were prepared and made homogeneous, being heated for some time at 250° in an atmosphere of nitrogen. Two cylinders with their ends in contact were then heated for 4 days so that the temperature difference between one end and the other was in the neighbourhood of 100—120°. There was a change in weight of the cylinders, the hotter cylinder becoming heavier. The total weight of the two remained unchanged. By transposing the hot and cold cylinders the change was made to take place in the reverse direction, the cylinders regaining their original weights. There is an exchange of ions from one cylinder to the other. Copper ions travel with the temperature gradient; silver ions travel against it. Hence the colder cylinder will become lighter as the silver ions are replaced by the lighter copper ions. In the case of silver and copper ions with their abnormally high mobilities the effect is considerable.
A. J. Mee.

Superconducting mixture made up of non-superconducting elements. W. J. de Haas, E. von Aubel, and J. Voogd (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 226—230).—The resistance of a eutectic mixture of gold and bismuth (17·9% Au) has been determined down to 2·041° Abs. The mixture appears to be superconducting. There are two possibilities. In the first place, either gold or bismuth may be superconducting at very low temperatures, or, secondly, the superconductivity may be due to impurities. The transition point from ordinary to superconduction, however, does not agree with that of any known superconductor. The temperature–resistance curve has the same character as that for ordinary superconductors.
A. J. Mee.

Variation of the conductivity of coloured solutions during decolorisation. N. Zchodro (J. Chim. phys., 1929, 26, 117—119).—The electrical resistance of solutions of cyanine and of gallocyanine in benzene decreases when the solution is exposed to light. On removing the source of light the resistance slowly returns to its initial value. Monochromatic light is effective only within the limits of the absorption band of a solution of cyanine in benzene.
O. J. Walker.

Conductometric titrations and the measurement of the resistances of electrolytes by a visual method. G. Jander and O. Pfundt (Z. Elektrochem., 1929, 35, 206—208).—An alternating-current method is described which dispenses with the use of a telephone and the adjustment of the position of the sliding contact on the wire of the Wheatstone bridge at each stage of the titration. In this method the sliding contact is first placed in a suitable position and a transformer is inserted in the position normally occupied by the telephone. A "thermocross" is placed in the secondary circuit of the transformer and is also included in the circuit of a mirror-galvanometer. The variation in current produced in the main Wheatstone bridge circuit by the addition of reactant to the titration cell results in the heating of the "cross" in the galvanometer circuit, giving rise to a thermoelectric current, which causes the galvanometer needle to be deflected in such a way that the deflexion bears a simple relation to the conductivity of the liquid undergoing titration. Details are also given of the procedure to be adopted to use the apparatus as a null-point instrument for the exact measurement of conductivity. H. T. S. Britton.

Electrode potential of nickel. II. Effect of occluded hydrogen on the electrode potential of nickel. III. Mechanism of the reactivation of the passive state of nickel. K. Murata (Tech. Rep. Tôhoku, 1929, 8, 71—82, 83—94).—II. Prolonged cathodic polarisation of nickel in dilute sulphuric acid solution causes a slight decrease in the initial value of the *E.M.F.* of the cell $Ni|NiSO_4(0{\cdot}05M)||KCl(0{\cdot}1N),Hg_2Cl_2|Hg$; the decrease is attributed to the introduction of traces of free acid. The potential of a nickel electrode in an atmosphere of nitrogen and hydrogen is the same as that in nitrogen. These results indicate that occluded hydrogen has no effect on the potential of nickel; the true value of this potential can be determined only in the complete absence of oxygen, however, as even traces of oxygen reduce the potential by 30 millivolts.

III. The reactivation of passive nickel electrodes by hydrogen is explained on the assumption that nickel acts as a catalyst in the combination of hydrogen and oxygen. From thermodynamic considerations the equilibrium conditions in the nickel half cells have been deduced to be such that the activity product ($a_{Ni}\times a^2{}_{OH}$) reaches the solubility product of nickel hydroxide when the partial pressure of hydrogen is 0·22 atm. The free energies of several reactions in the system nickel–oxygen–hydrogen have been determined. A. R. Powell.

***E.M.F.* of silver–silver chloride–calomel cells.** W. M. Mazel (Amer. Electrochem. Soc., May 1929. Advance copy, 8 pp.).—The dependence of the potential of the silver–silver chloride electrode on the mode of preparation of the silver and the silver chloride has been investigated. Coarsely crystalline silver prepared by electrolysis of a 20% silver nitrate solution shows a more positive potential against silver nitrate solution than silver prepared in other ways and this potential is unchanged by heating at 400—500°, whereas other samples all change in potential on such treatment. Of several preparations of silver chloride the least soluble was that made by fusing a carefully washed sample. Using the coarsely crystalline electrodeposited silver and the least soluble preparation of silver chloride, the *E.M.F.* of the cell $Hg|Hg_2Cl_2,0{\cdot}1N\text{-}KCl,AgCl|Ag$ is 0·0466 volt at 25° and is reproducible to 0·1 millivolt. Values as low as 0·0422 volt were obtained with silver chloride prepared in other ways. H. J. T. Ellingham.

***E.M.F.* of the reversible cell in a non-aqueous solution.** T. Yoshida (Sci. Rep. Tôhoku, 1928, 7, 1279—1287).—Reversible cells of the type Cd amalgam|saturated solution, $CdI_2|HgI|Hg$ were prepared with water, acetone, methyl, ethyl, and propyl alcohols as solvents. Measurements at various temperatures show that the *E.M.F.* is independent of the solvent. C. J. Smithells.

Solubility of galena and some lead concentration cells. L. F. Nims and W. D. Bonner (J. Physical Chem., 1929, 33, 586—590).—The *E.M.F.* of cells of the type $Pb(Hg)|PbX_2$ (sat.), PbY_2 (sat.)$|Pb(Hg)$ have been determined at 25°. When X and Y respectively are Cl and Br, Cl and I, Br and I, Cl and $0{\cdot}5SO_4$, Br and $0{\cdot}5SO_4$, I and $0{\cdot}5SO_4$, and $0{\cdot}5SO_4$ and S, the *E.M.F.* are 0·0077, 0·0495, 0·0420, 0·1030, 0·0955, 0·0530, and 0·0670 volt, respectively. For the first three cells, the observed values agree with those calculated; from the value of the last, the solubility of galena is found to be approximately $0{\cdot}94\times10^{-6}$ g.-mol./1000 g. of water at 25°. L. S. Theobald.

Reversible *E.M.F.* of electrolysis. J. Vuillermoz (Compt. rend., 1929, 188, 1098—1099).—The *P.D.* between 2*N*-sulphuric acid and a platinum electrode polarised negatively with a current density of 0·2—2·0 milliamp./cm.^{2} has been determined at the instant of interruption of the current and for the first half second of spontaneous depolarisation. Interruption produces no instantaneous variation in *P.D.* unless it is accompanied by a static discharge across the electrode–electrolyte contact, when the variation increases with the intensity of the discharge. The resulting depolarisation curves, which are divisible into two types each tending asymptotically towards the same straight line, indicate that normal depolarisation is the superposition of an electrostatic and a chemical effect. J. Grant.

Electrochemical behaviour of substances in very dilute solutions. F. Joliot (Compt. rend., 1929, 188, 1106—1108).—The rate of deposition of small quantities of substances from dilute solutions may be measured continuously by means of a photoelectric cell from the increase in optical density of a glass cathode on which a transparent deposit of gold or platinum (20—40 $\mu\mu$ in thickness) is produced by cathodic sputtering. If i is the cell current, x the thickness of metal deposited, and A and B are constants, $\log i=A-Bx$. The deposition potentials of bismuth and tellurium were determined, and the method was shown to be capable of detecting a change in weight of the deposit of 10^{-7} g. J. Grant.

Kučera's anomalies in electrocapillary curves. P. Herasymenko (Chem. Listy, 1929, 23, 121—124).—Polemical against Teige (this vol., 402). R. Truszkowski.

Photo-voltaic cells with silver–silver bromide electrodes. I. W. Vanselow and S. E. Sheppard (J. Physical Chem., 1929, 33, 331—353).—Photo-voltaic cells of Ag|AgBr electrodes in solutions of potassium bromide have been studied using a new vacuum tube voltmeter which is described. The shape of the *P.D.*–time curves depends on the thickness of the silver bromide layer and on the crystal size of the bromide particles, but, in general, the curve is the resultant of an initial negative effect superimposed on a positive. The *E.M.F.* between the illuminated and dark electrodes increases with an increase in concentration of the potassium bromide solution surrounding the electrodes. The results are explained by an extension of the hypothesis of Sheppard and Trivelli (cf. B., 1922, 79A) and Fajans and Frankenburger (A., 1923, ii, 109) in terms of the liberation of electrons and bromine atoms from bromide ions on absorption of light. This is supported by experiments in which the positive effect shown in the *P.D.*–time curves has been suppressed and the negative effect made more pronounced by the addition of bromine acceptors. The positive effect is also shown to be similar to that produced by allowing bromine to diffuse through the silver bromide layer to the silver. The preparation of trustworthy silver|silver bromide electrodes is described.

L. S. Theobald.

Electrolytic polarisation. VII. Complex cyanides: (*a*) silver. VIII. Complex cyanides: (*b*) copper. S. Glasstone (J.C.S., 1929, 690—702, 702—713; cf. A., 1927, 422).—VII. The variation with current density of the cathode potential and current efficiency for the deposition of silver from solutions of silver cyanide in sodium cyanide solutions with a silver cathode and a platinum anode has been investigated. When equivalent amounts of the two cyanides are present, the cathode potential increases fairly rapidly with increasing current density, since, as is shown by measurements of the static electrode potential, the potential at the equivalence point varies considerably with slight variations in the ratio of silver ions to cyanide ions. If, on the other hand, an excess of alkali cyanide is present, the cathode potential does not at first change very much with rise in current density, for in such solutions the static electrode potential is much less sensitive to variations in the relative amount of silver. In all solutions, with increasing current density a state is ultimately reached in which silver ions are deposited as rapidly as they are brought up to the electrode by diffusion and other processes. Further increase causes discharge of hydrogen ions on the electrode, resulting in the efficiency dropping below 100%, but owing to overvoltage effects gas is not evolved until a considerably higher potential is reached. Raising the temperature or stirring the solution increases the maximum current density for 100% efficiency, whereas diluting the solution has the opposite effect. Substitution of potassium cyanide for sodium cyanide has no material influence on the results. Addition of alkali carbonate renders the electrode potential for the higher current densities somewhat more negative, but the effect seems to be due mainly to the altered cathodic environment; under the conditions used technically the carbonate would have little influence. The electrodeposition of silver from argentocyanide solutions is best explained by assuming the presence in solution of complex cations such as $Ag_2CN^{\cdot}$ and $Ag_3CN^{\cdot\cdot}$, which on discharge at the cathode break down into neutral silver atoms and cyanide and silver ions.

VIII. Electrometric titration of cuprous cyanide with sodium cyanide using a copper electrode indicates that the cuprocyanide solution contains both $Cu(CN)_2'$ and $Cu(CN)_3''$ ions in comparable amounts, which agrees with the observation that about 1·5 equivalents of alkali cyanide are required to dissolve 1 equivalent of cuprous cyanide. Similar results are obtained using potassium cyanide instead of sodium cyanide. When sodium cuprocyanide solutions are electrolysed with a copper cathode, the cathodic potential increases quite rapidly with increase in current density, since the static electrode potential also increases rather rapidly with decrease in the ratio of copper to cyanide when this is below about 1 : 2. The current efficiency for the deposition of copper is almost always below 100%, largely because the reversible copper potential soon becomes more negative than the reversible potential for hydrogen evolution. Stirring the solution much reduces the polarisation and increases the efficiency, indicating that the complex ions present dissociate rapidly, a view which accords with the relatively slight effect of rise in temperature. The solution probably contains complex cations such as $Cu_2CN^{\cdot}$ and $Cu_3CN^{\cdot\cdot}$, which on discharge at the cathode yield copper. Potassium cuprocyanide solutions give results similar to the foregoing.

R. Cuthill.

Inflammability of hydrogen. VII. Dew point, density, and range of inflammability of treated hydrogen. Y. Tanaka and Y. Nagai (Proc. Imp. Acad. Tokyo, 1929, 5, 80—81; cf. A., 1928, 847).—Density, dew point, and range of inflammability values for hydrogen treated with various explosion suppressors are tabulated. Tin tetramethyl is considered to be the best explosion suppressor for hydrogen to be used in airships. Methyl selenide and ethyl bromide are also good, but ethyl ether and acetone are not suitable.

O. J. Walker.

Combustion of rigidly dried carbon monoxide–oxygen mixtures. W. A. Bone (Nature, 1929, 123, 644).—Explanatory.

A. A. Eldridge.

Thermal formation of hydrogen chloride. J. A. Christiansen (Z. physikal. Chem., 1929, B, 2, 405—427).—The formation of hydrogen chloride from its elements in the dark is investigated. A new type of micro-burette used in the work is described, and it is mentioned that in an electrical thermoregulator with iron–mercury contact the iron must be negative. The velocity of the reaction at 200° is practically independent of the hydrogen pressure at a definite oxygen pressure, approximately proportional to the chlorine pressure, and inversely proportional to the oxygen pressure. The theory of the reaction is also considered. The Nernst atom-chain mechanism can be used to interpret the results obtained if it is assumed that the reaction chains begin only on the walls of the vessel. Various phenomena, especially the low-temperature coefficient of the reaction, support this assumption. It may also explain, in part, the differences between the results of some earlier experiments. The presence of hydrogen chloride appears to inhibit the reaction somewhat. The effect of bromine on the reaction was also studied. As Pólányi and others have already observed, bromine does not inhibit the thermal formation of hydrogen chloride. A. J. Mee.

Reaction of atomic hydrogen with hydrocarbons. H. S. Taylor and D. G. Hill (Z. physikal. Chem., 1929, B, 2, 449—450).—Ethylene with an excess of hydrogen and in the presence of excited mercury atoms gives practically entirely ethane. If, however, relatively high concentrations of ethylene are used, the saturated hydrocarbons formed are more complex. The reaction may also furnish liquid condensation products of the composition $(CH_2)_n$. Methane is also formed and is acted on by hydrogen atoms under the influence of excited mercury atoms. The effect of atomic hydrogen on the saturated hydrocarbons varies with the mol. wt., being the more rapid the greater is the mol. wt. The velocity of the reaction between ethylene and hydrogen is accelerated considerably by increase in the hydrogen atom concentration, other things being equal. The reaction is therefore started by hydrogen atoms. With large excess of ethylene, acetylene is formed in considerable quantity, but with excess of hydrogen no acetylene is formed. The results are not in complete agreement with those of Bonhoeffer and Harteck (this vol., 409), which could, however, be repeated at low pressures and with large excess of hydrogen. The pressures used in the present work were up to atmospheric, and under these conditions all possible kinds of reaction product are formed. A. J. Mee.

Low-temperature oxidation of hydrocarbons. I. Pressure–temperature curves of amylene–oxygen mixtures. J. S. Lewis (J.C.S., 1929, 759—767).—Pressure–temperature curves of mixtures of amylene and oxygen show that a slight chemical action occurs up to 220—230°, followed by a more vigorous reaction up to 237—241° which is characterised by a fall of pressure to a minimum varying with the concentration of the gases in the mixture. Continued heating above the point of minimum pressure results in a rapid increase in pressure due to the oxidation of products formed in the preceding stage. The curves in this oxidation region are comparable with those of the paraffins (cf. Brunner and Rideal, A., 1928, 1350). The reaction products in the case of amylene appear to be primarily peroxides, the rate of formation of which is increased by a rise in temperature, which also increases their rate of decomposition into aldehydes etc. which polymerise and so account for the fall in pressure. At temperatures above the minimum points in the curves the unstable compounds present set up chain reactions and rapid oxidation. This oxidation can be accelerated by the presence of catalysts such as pumice or active charcoal, which cause detonation at the critical point in the curves. Inhibitors such as lead tetraethyl almost eliminate the contraction part of the curve. These results suggest that the second step in the combustion of a paraffin hydrocarbon is the oxidation of the primarily-formed unsaturated compound to a readily decomposed peroxide the energy of decomposition of which assists the further oxidation of the aldehydes formed during its decomposition. A. R. Powell.

Kinetics of the oxidation of organic compounds by bromine. I. Action of bromine on oxalic acid. E. Joséfowicz (Bull. Acad. Polonaise, 1929, A, 39—63).—See A., 1928, 715.

Unimolecular reaction in aqueous solution which can be followed thermometrically. W. O. Roth (Z. Elektrochem., 1929, 35, 186—189).—Dihydroxyacetone undergoes a keto–enol transformation. When freshly-distilled dihydroxyacetone was burnt its heat of combustion was 3810·3±0·7 g.-cal. per g., but on keeping this value became slowly diminished. This transformation readily takes place in aqueous solution and if placed in a calorimeter its course may be followed by observing the variations in temperature with a Beckmann thermometer with time. Calculations based on the corrected temperatures showed the reaction to be unimolecular. The rate depends on the age of the preparation; thus a freshly-distilled product underwent a 50% change in 0·5 min., whilst an old sample suffered about 30% transformation in that time. The heat of the keto–enol change is about +0·43 kg.-cal. per mol. H. T. S. Britton.

Nitric acid. IV. System nitric acid–nitrous acid during oxidation. Activation of nitric acid. A. Klemenc and L. Klima (Z. anorg. Chem., 1929, 179, 379—412).—The nitric acid in an aqueous solution of nitric and nitrous acids possesses towards the stannous ion a definite oxidising power, which, however, gradually falls to zero; on dilution the oxidising value again increases. This effect is ascribed to the production of activated nitric acid according to the equation $3HNO_2 \rightleftharpoons HNO_3 + 2NO + H_2O$; decomposition of the activated acid follows the unimolecular law. A direct relationship between reaction and activation has thus been established. H. F. Gillbe.

Velocity of hydrolysis of esters and lactones by sodium hydroxide in mixtures of two and three solvents. J. F. M. Caudri (Rec. trav. chim., 1929, 48, 422—460; cf. Tasman, A., 1928, 138).—The velocity of ring-opening of phthalide by sodium hydroxide at 25° in water and mixtures of water and methyl alcohol, water and ethyl alcohol, water and acetone, and water, ethyl alcohol, and ether was determined. In general the addition of an organic solvent decreases the velocity, except in the case of acetone, when a minimum is reached. The velocity of hydrolysis of ethyl acetate by sodium hydroxide at 25° in water and in mixtures of water and ethyl alcohol, water and methyl alcohol, water and acetone, and water, ethyl alcohol, and ether, and also of methyl acetate in a mixture of methyl alcohol and water, was also determined. The hydrolysis curves for the esters and phthalide were drawn and were found to agree fairly well. A. Freiman.

Velocities of esterification of alcohols in formic acid. A. Kailan and G. Brunner (Monatsh., 1929, 51, 334—368).—The velocity of the uncatalysed esterification of *tert.*-butyl and *iso*propyl alcohols, glycolmonoformin, and glycerol-αγ-diformin in formic acid containing various concentrations of water (w, 0·1—1·2 mols./litre), and in some cases with hydrogen chloride catalysis, has been determined at 25° and 15°. The progress of the esterification was followed by the increase in the f.-p. depression of the mixture. The values of the coefficients k_1+k_2w and k_1 (k_1=esterification coefficient, k_2=hydrolysis coefficient) for a reversible, unimolecular reaction are calculated and are expressed by intrapolation formulæ as functions of w. In the uncatalysed reaction the effect of the concentration of water is greatest with *tert.*-butyl alcohol and least with the secondary alcohols, an increase in w from 0·30 to 1·37 mols./litre depressing the value of k_1+k_2w and k_1 by, respectively, 46% and 43% with the tertiary alcohol, 15% and 11%, and 21% and 20%, respectively, for *iso*propyl alcohol and glyceroldiformin, and 30% and 25% with glycolmonoformin. The velocity of esterification is greatest with *iso*propyl alcohol, the values of k_1+k_2w and k_1 for *tert.*-butyl alcohol with almost anhydrous formic acid being, respectively, 64% and 51% (w=0·3) and 41% and 32% (w=1·37) of the corresponding values for *iso*propyl alcohol. With glycolmonoformin the velocity of esterification at w=0·3 is slightly less, and at w=1·37, slightly higher, than that of *tert.*-butyl alcohol, whilst the value of the velocity coefficient for glycerol-$\alpha\gamma$-diformin is only about 0·1 of that for *iso*propyl alcohol, the effect of substitution of the two methyl groups by the group $CH_2\cdot O_2CH$ being very great. The presence of 0·0085 mol./litre of hydrogen chloride quadruples the velocity of esterification in the case of glyceroldiformin, and doubles it with the other alcohols studied, whence it is concluded that steric effects play less part in the catalysed than in the uncatalysed esterification. The mean values (for w=0·30—1·37) of the temperature coefficients of k_1+k_2w and k_1 between 15° and 25° are, respectively, 3·2 and 3·5 for the uncatalysed esterification with *tert.*-butyl alcohol, and 2·4 and 2·5 for catalysis with 0·0085—0·01*N*-hydrogen chloride (w=0·22). The degree of esterification is 70—80% with *tert.*-butyl alcohol and glyceroldiformin, 80—90% with glycolmonoformin, and 92—100% with *iso*propyl alcohol. The significance of the results is discussed. J. W. Baker.

Oxidation [by potassium permanganate] of benz-*o*-toluidide at a benzene–water interface with special reference to the temperature coefficient of the reaction rate. L. S. Kassel and N. K. Schaffer (J. Amer. Chem. Soc., 1929, **51**, 965—974).—The kinetics of the above reaction, which is influenced by the rate of stirring and the presence of some catalyst, was investigated at 15—45°. The activation energy increases with temperature, indicating that more than one reaction is occurring. The temperature coefficient is 2; Bell (A., 1928, 848) found 13 for this quantity. The mechanism suggested by Bell is not in disagreement with the data, but other mechanisms are possible. S. K. Tweedy.

Decomposition of triphenylacetic acid by sulphuric acid. H. R. Dittmar (J. Physical Chem., 1929, **33**, 533—556).—The decomposition of triphenylacetic acid, in the form of its sodium salt, by sulphuric acid has been investigated by means of measurements of the rate of evolution of carbon monoxide. The reaction is unimolecular and at 12° $k=30\cdot7\times10^{-3}$. Water inhibits the reaction and its effect can be represented by the equation $\log k\times10^3=-0\cdot544M+3\cdot4688$. Sodium and potassium sulphates, acetic, benzoic, *o*-toluic, and crotonic acids, phenol, acetone, dimethylpyrone, *p*-cresol, and acetophenone also act as inhibitors; in general, the inhibitory effect increases exponentially with an increase in concentration and the inhibitors form an additive compound with the sulphuric acid. Hydrogen chloride in low concentration has no effect on k, but phosphoric acid at high concentration slightly inhibits the reaction. Although the temperature coefficients are affected irregularly by the presence of inhibitors, $k^{22^\circ}/k^{12^\circ}=2$ approx. Indirect evidence of the formation of an additive compound between triphenylacetic and sulphuric acids has been obtained and leads to an explanation of the decomposition based on the formation of an intermediate unstable additive complex, and the effect of inhibitors may be to disturb the equilibrium of the reaction by which this complex is formed. The results support Taylor's theory of the mechanism of negative catalysis. The relative ease with which sulphuric acid decomposes oxalic, formic, malic, or triphenylacetic acid is given by the critical increments of the reactions, and the similarity of these decompositions is pointed out, with the suggestion that the mechanism in each case is practically the same. *Sodium triphenylacetate monohydrate* forms efflorescent needles. The additive compound, $CPh_3\cdot OH,4H_2SO_4$, has been isolated during a concentration–temperature study of the system triphenylcarbinol–sulphuric acid. The solubility of triphenylacetic acid in acetic acid at 25° has also been determined. L. S. Theobald.

Reactions with very large apparent temperature coefficients. L. S. Kassel (J. Amer. Chem. Soc., 1929, **51**, 1136—1145).—Examination of the available data in light of the author's reaction rate theory (A., 1928, 715; Rice and Ramsperger, *ibid.*, 484) indicates that the dehydration of calcium carbonate hexahydrate in presence of liquid water is not a single reaction. The experimental results can be accounted for, however, on the basis of the general reaction rate theory on the supposition that the change occurs in a series of steps (perhaps 5). If the temperature coefficients of the intermediate dissociation reactions are assumed to be about 3, and those of the association reactions to be about 1·5, then the observed abnormal temperature coefficient of 12 is accounted for.

The abnormal temperature coefficients of the decomposition of menthyl and bornyl benzenesulphonates in organic solvents (Patterson and McAlpine, *ibid.*, 1253) are due to autocatalysis by the acid formed during the decomposition together with an accompanying homogeneous uncatalysed reaction and a heterogeneous catalysed reaction (? wall reaction). The nature of the solvent influences the predominance of one or other of the first two of these reactions, according as it forms complexes with hydrogen ions or not, and according to its electric moment. S. K. Tweedy.

Kinetics of the dissolution of aluminium and cadmium in hydrochloric acid. K. Jabłczyński, E. Hermanowicz, and H. Wajchselfisz (Z. anorg. Chem., 1929, 180, 184—192).—The rates of dissolution of aluminium and of cadmium in hydrochloric acid are independent of the rate of stirring. The temperature coefficients are 2·26 and 2·02, respectively. The dissolution process is therefore purely chemical and is not dependent on diffusion. In the case of aluminium, the rate of dissolution is directly proportional to the acid concentration. Dissolution is considered to take place by the following stages: $Al+H^{\cdot}=Al^{\cdot}+H$; $Al^{\cdot}+H^{\cdot}=Al^{\cdot\cdot}+H$; $Al^{\cdot\cdot}+H^{\cdot}=Al^{\cdot\cdot\cdot}+H$; $2H=H_2$. The velocity of the first stage is the lowest and is the velocity which is measured. If aluminium is activated by means of mercuric chloride it reacts much more readily with hydrochloric acid, and the reaction is converted into a true diffusion process. O. J. Walker.

Velocity of dissolution of tin and some tin–copper alloys in acids. M. Centnerszwer (Z. physikal. Chem., 1929, **A**, **141**, 167—179).—Tin will only dissolve with measurable velocity in hydrochloric acid of concentration greater than 6*N*. The reaction is complicated, the velocity indicating that it is of the fourth order. The effect of stirring and of temperature on the velocity was determined. Diffusion had only a subordinate effect on the velocity of dissolution. The temperature coefficient of the reaction is comparable with that for the dissolution of cadmium in hydrochloric acid, which is a fourth order reaction. Alloys of tin and copper dissolved more readily than tin itself, but only the tin went into solution, leaving behind the copper, or a compound of copper and tin. This increase in velocity is due to local action, and the reaction is accelerated by stirring. A. J. Mee.

Kinetics of the contact sulphuric acid process and modern views on adsorption. M. Bodenstein.—See B., 1929, 354.

Influence of nitrogen peroxide on the combination of hydrogen and oxygen. H. W. Thompson and C. N. Hinshelwood (Proc. Roy. Soc., 1929, **A**, **124**, 219—227).—The accelerating effect of traces of nitrogen peroxide on the union of hydrogen and oxygen has been further investigated (cf. Gibson and Hinshelwood, A., 1928, 1334), with the object of constructing a definite theory of the mechanism of the reaction. A study of the influence of temperature, pressure, proportion of oxygen to hydrogen, presence of nitrogen, and nature of the reaction vessel on the critical concentrations of nitrogen peroxide shows that (*a*) the lower critical concentration is raised and the upper lowered as the total pressure of hydrogen and oxygen is increased, (*b*) for a given total pressure the upper limit is lowered by an increase in the proportion of oxygen to hydrogen, (*c*) the upper limit is lowered by the presence of nitrogen, the lower limit being only slightly affected, and (*d*) the results are essentially the same in porcelain as in silica vessels. These results are interpreted in terms of a theory of "reaction chains" (cf. this vol., 403). The nitrogen peroxide reacts with hydrogen, yielding activated hydrogen peroxide which in turn reacts with hydrogen in the gas phase, giving rise to a cycle of processes whereby ultimately α (probably two) molecules of active hydrogen peroxide arise from each of the original ones. The reaction chain thus "branches," and the reaction velocity will increase indefinitely, and explosion ensue, except in so far as various deactivation processes keep the effect of the branching chains in check. The balancing of these various influences determines the critical limits of concentration between explosion and slow reaction. The interruption of the chains may be due to decomposition or reaction with hydrogen at the walls of the vessel, to mutual destruction of two hydrogen peroxide molecules, or to destruction of hydrogen peroxide by nitrogen peroxide. The latter mechanism is analogous to that which recent studies in combustion have indicated for the action of "anti-knocks."

L. L. Bircumshaw.

Inhibiting action of catalysts on the decomposition of hydrogen peroxide. S. Dunaeva (Pharm. J. Russia, 1928, No. 3, 23—24; Chem. Zentr., 1928, ii, 2323).—The decomposition of hydrogen peroxide is prevented by "luminal" or quinine sulphate (0·02%) for a much longer period than by phenacetin, antifebrin, or aspirin.

A. A. Eldridge.

Autoxidation of quinol catalysed by manganous salts in acid solutions. V. K. La Mer and J. W. Temple (Proc. Nat. Acad. Sci., 1929, **15**, 191—194).—A cell in which, by measuring the rate of change of *E.M.F.*, the kinetics of the quinol oxidation reaction can be followed, is described. Side reactions are eliminated. The values of the reaction velocity are plotted against a function of the percentage of quinol oxidised, proportional to the free energy content of the system, and a linear relation is obtained. The case is stated to be the first in which the velocity of a homogeneous reaction has proved to be proportional to the logarithms of the concentrations of the initial and final states, *i.e.*, to the energy levels of the system. N. M. Bligh.

Influence of protein on the catalytic properties of inorganic catalysts. M. J. Galvialo and R. Dobrotvorskaja (Biochem. Z., 1929, 207, 146—150).—Experiments on the oxidation of tincture of guaiacum and on the decomposition of hydrogen peroxide by inorganic catalysts in the presence of egg-albumin show that the latter has considerable influence on the processes. The decomposition of the peroxide by salts of manganese, nickel, gold, and platinum (but not that by salts of iron, cobalt, and copper) is accelerated by albumin, the reaction proceeding most rapidly when the salts are present in concentrations 0·001*M* to 0·0001*M*. Nothing is known of the influence on the anions. It is concluded that the albumin acts by holding the metal in suspension. W. McCartney.

Decomposition of aqueous bromine and bromic acid solutions by charcoal. I. M. Kolthoff (Rec. trav. chim., 1929, 48, 291—297).—In the adsorption of bromine by charcoal, part of the bromine may react according to the equations $2Br_2+2H_2O=4HBr+O_2$, $Br_2+H_2O \rightleftharpoons HBr+HBrO$. Experiment shows that 33—40% of the bromine in a 0·015*N*-solution is decomposed in contact with charcoal in a few minutes, according to the first equation. Hypobromous acid is not formed as an end-product, since this substance, as well as hypoiodous acid, is very rapidly decomposed in contact with charcoal. Consequently determinations of the adsorption isotherm of bromine by charcoal, and measurements of the effect of charcoal on the velocity of reactions in which bromine is involved, are subject to error. Iodine, on the other hand, does not react when adsorbed by charcoal from aqueous solution. Reaction is slight, or absent, when bromine is adsorbed from carbon tetrachloride solution. Bromic acid is rapidly decomposed when adsorbed by charcoal from acid solutions, and slowly decomposed even in weakly alkaline solutions, with the formation of hydrogen bromide. F. G. Tryhorn.

Influence of charcoal on the velocity of the reaction among iodide, iodate, and hydrogen ions, decomposition of thiosulphuric acid, and reaction between phenol and bromine. I. M. Kolthoff (Rec. trav. chim., 1929, **48**, 298—309).—When adsorbed on charcoal, hydrogen iodide does not react with iodate and hydrogen ions in aqueous solution. Ash-free charcoal adsorbs only hydrogen iodide from a solution of an alkali iodate and iodide. Measurements indicate a retardation by charcoal of the reaction $IO_3'+5I'+6H^+ \rightleftharpoons 3I_2+3H_2O$. The inhibition is only apparent, since if allowance is made for the strong adsorption of hydrogen and iodide ions, and especially of free iodine, calculation shows that the above reaction is actually accelerated by the charcoal. Great acceleration of the decomposition of a weakly acid solution of sodium thiosulphate was observed in the presence of charcoal. This was shown to be due to the instability of the undissociated thiosulphuric acid which is formed. The decomposition is rapid even in a neutral buffer solution. Little evidence was found of reaction between phenol and bromine in the adsorbed state, but reaction is rapid in the case of iodine and quinol. F. G. Tryhorn.

Conversion of water and iodine into hydriodic acid in the presence of charcoal. P. T. Danilitschenko and M. I. Ravitsch (J. Russ. Phys. Chem. Soc., 1929, **61**, 123—130).—When a mixture of iodine and water vapour is passed through a heated quartz tube containing a layer of wood charcoal hydriodic acid is formed. The temperature for the maximum yield (98%) is 795°. The maximum temperature is lowered if the porosity of the charcoal is increased. A. Freiman.

Influence of some physical and chemical factors on the activity of charcoal. E. V. Alexseevski and A. I. Avgastinik (J. Russ. Phys. Chem. Soc., 1929, **61**, 131—141).—Commercial wood and animal charcoals were impregnated with solutions of uranyl nitrate, thorium nitrate, or radium bromide and any change in their adsorptive powers towards acetic acid and acetylene was noted. Thorium nitrate was the least affected in that it retained its adsorptive powers unimpaired. Samples of birchwood were treated with solutions of uranyl nitrate, potassium nitrate, potassium carbonate, potassium hydroxide, potassium silicate, zinc chloride, ferric nitrate, cobaltous nitrate, and nickelous nitrate for 20 hrs., then burnt, and the charcoal was investigated for any changes in its adsorptive powers towards acetic acid, acetylene, benzene, phenol, and 1% indocarmine solution. Different solutions affect the adsorptive powers of the charcoal for the various substances differently. The effect of exposure of both wood and animal charcoal to ultra-violet light was also investigated. A. Freiman.

Influence of the curvature of solids on chemical and electrolytic phenomena. L. R. Luce (Ann. Physique, 1929, [x], **11**, 167—250).—The curvature of the surface of a solid reactant influences considerably the nature of the reaction, especially in liquid media. Reboul's formula for the thickness of deposits on silken threads has been verified quantitatively, and quantitative investigations show that in general the activity of a surface increases with its curvature. Two explanatory hypotheses have been developed, the one having regard to diffusion phenomena and the other to selective forces of adhesion or of affinity in the interface. H. F. Gillbe.

"Electrolysis with fluorine." W. D. Bancroft and N. C. Jones (Amer. Electrochem Soc., May 1929. Advance copy, 13 pp.).—It is claimed that any anode reaction not involving a time factor can be duplicated by the action of fluorine, except in so far as the hydrofluoric acid formed introduces a complication, and that any cathode reaction not involving a time factor can be duplicated by the action of a suitable metal, except in so far as the corrosion product introduces a complication. Experimental evidence is cited in support of these contentions and in opposition to statements made by Fichter (A., 1926, 925; 1927, 741; 1928, 382). It is concluded that oxidation with fluorine can be used with advantage instead of anodic oxidation in many cases where the solutions are poor conductors or where it is desirable to avoid having to deal with cathode reaction products. It is shown that the reason why lead peroxide is not obtained by the action of fluorine on acidified lead nitrate solution is that the lead tetrafluoride which is formed does not hydrolyse appreciably in slightly acid solutions. Lead peroxide is produced, however, by the action of fluorine on neutral or slightly alkaline solutions or suspensions of lead salts. When fluorine attacks organic substances it must displace the least negative radical or combine with the most positive radical, and it is suggested that this opens up a new method for studying organic compounds. A difficulty is that in reactions with fluorine an induction period may be followed by an explosive reaction, and methods of slowing down the reaction are being studied. The fluorine used was made by electrolysing fused potassium hydrogen fluoride in a Mathers cell consisting of a magnesium pot as cathode with a magnesium diaphragm surrounding a graphite anode. H. J. T. Ellingham.

Reaction between manganese dioxide and ammonium chloride. C. Drotschmann (Z. Elektrochem., 1929, **35**, 194—198).—Several series of experimental Leclanché cells were set up and discharged for different times through known resistances. The behaviour of different types of manganese dioxide—natural and artificial—was compared as regards (*a*) the amounts of manganese which dissolved in the electrolyte during the discharge of the cell, and (*b*) the attack on the zinc electrode. Abnormal amounts of manganese were found in the electrolytes in which artificial pyrolusite was used, although the dissolution of manganese did not appear to be a direct consequence of the depolarising action of the manganese dioxide. The enhanced chemical action of the artificial variety caused a greater attack on the zinc. The development of free ammonia in the electrolyte of a cell when kept for 14 days was greater when the zinc electrode was completely immersed than when it was partly exposed to the air. Less hydrogen was developed by a cell containing artificial manganese dioxide than by one containing the natural product when kept on open circuit. H. T. S. BRITTON.

Effect of the electric discharge on gases containing hydrocarbons at reduced pressure. F. FISCHER and K. PETERS (Z. physikal. Chem., 1929, **141**, 180—194).—An apparatus which is suitable for studying the effect of the electric discharge on gaseous mixtures at low pressures is described. A gas containing initially 0·4% H_2 and 93·6% CH_4 after being subjected to the discharge contained 92·1% H_2 and 3·3% CH_4. The methane was decomposed into acetylene and hydrogen according to the equation $2CH_4=C_2H_2+3H_2$. 97% of the mixture of gases condensed by liquid air after the discharge consisted of acetylene, the remaining 3% being hydrocarbons with 2, 3, or 4 carbon atoms. Using a mixture with a very much smaller methane content, there was still a large amount of acetylene formed, together with some hydrocyanic acid from nitrogen present in the original mixture. A. J. MEE.

Integration of light by photo-electrolysis. W. R. G. ATKINS and H. H. POOLE (Sci. Proc. Roy. Dubl. Soc., 1929, **19**, 159—164).—A Burt vacuum sodium cell was found suitable for the integration of light. The photo-electrolytic production of alkali in a dilute hydrogen carbonate solution and the photo-electric deposition of copper under various conditions of daylight and season are described. N. M. BLIGH.

Temperature coefficients of some photochemical reactions. G. B. KISTIAKOWSKY (Proc. Nat. Acad. Sci., 1929, **15**, 194—197).—Having regard to Semenov's thermal reaction chain theory (cf. A., 1928, 847), a study was made of the non-sensitised photochemical hydrogen–oxygen and oxygen–carbon monoxide reactions. The temperature coefficient is tabulated over sets of intervals from 25° to 527°. The results diverge widely from the Arrhenius equation and increase rapidly with rise of temperature, this being attributed to an increasing quantum yield. Semenov's theory is supported, and a general theory of the reaction mechanism is outlined. N. M. BLIGH.

Photochemical equilibrium between hydrogen, bromine, and hydrogen bromide. R. W. ARMOUR and E. B. LUDLAM (Proc. Roy. Soc. Edin., 1929, **49**, 91—96).—A mixture of hydrogen and bromine was subjected to light of the shortest wavelength possible with quartz apparatus (185 μμ), using an aluminium spark, which closely approximates to monochromatic light. At equilibrium, it was found that somewhat less than 1% by weight of bromine combines to give hydrogen bromide. N. M. BLIGH.

Photochemical formation of ammonium [type] salts. A. K. PLISOV (Gazzetta, 1929, **59**, 200—206).—Some preliminary experiments have been performed on the photochemical formation of salts of aromatic amines with alkyl halides in an attempt to determine whether the activation of the amine or of the halide is the determining factor in the reaction. Photochemical action is more evident in the combination of aniline with benzyl chloride than in the case of *o*-toluidine and benzyl chloride. In the former case, the yield in 3 hrs. increased from 15% for the dark reaction to 82% when illuminated in a quartz vessel by an electric arc. F. G. TRYHORN.

Photochemical decomposition of solutions of metallic salts in organic solvents. E. PUXEDDU (Gazzetta, 1929, **59**, 160—164).—Solutions of mercuric chloride, lead chloride, and titanium tetrachloride in anhydrous ether were exposed to sunlight for prolonged periods in sealed vessels. Little photochemical action was observed with the lead chloride solutions, but with mercuric chloride solutions, after 5½ months, a greyish-white precipitate separated which on heating was found to consist of mercury and calomel. In the solution remaining the presence of aldehydes and chloro-compounds as well as of hydrogen chloride was detected. Photochemical action was much more rapid in the titanium chloride solution. In two or three days the original clear yellow solution became deep brown, and later, clear green in colour. Attempts at crystallisation by evaporation of this solution at low temperatures were unsuccessful, although a colour change from green to violet occurred. F. G. TRYHORN.

Action of optically excited mercury atoms on hydrocarbon molecules. W. FRANKENBURGER and R. ZELL (Z. physikal. Chem., 1929, **B**, **2**, 395—398).—It was sought to discover whether when optically excited mercury atoms came into contact with hydrocarbon molecules there was any chemical reaction such as the breaking of the C–C linking or the C–H linking. A mixture of pentane vapour with some other gas (air, nitrogen, or carbon dioxide) was saturated with mercury vapour at 50°, and the radiation from a mercury-vapour lamp was passed through it. The products formed varied with the nature of the gas mixed with the pentane. With air a certain amount of hydrogen peroxide and aldehyde was formed, and the iodoform test gave a positive result. With nitrogen some higher hydrocarbons were produced, and with carbon dioxide the resulting mixture gave the aldehyde reactions. The primary reaction in all these cases can be traced to the breaking of a C–C or a C–H linking. The final products are the results of secondary reactions. In indifferent atmospheres (*e.g.*, nitrogen and, to a certain extent, carbon dioxide), the residues may combine with each other, forming hydrogen and higher or lower hydrocarbons. In the presence of air or carbon dioxide the hydrogen could form hydrogen peroxide, and organic compounds containing oxygen will be produced. A. J. Mee.

Photochemical reaction between mercury vapour and oxygen. W. A. Noyes, jun. (Z. physikal. Chem., 1929, **B**, 2, 445—448; cf. Leipunsky and Sagulin, this vol., 155).—The results obtained are compared with those of Leipunsky and Sagulin. The points of agreement are: (1) the oxygen pressure in a mixture of mercury vapour and oxygen decreases if the mixture is exposed to radiation containing the resonance wave-length of mercury (λ 2537 Å.); (2) a certain amount of mercury oxide is formed during the exposure, the layer being thickest on the side of the vessel nearest the lamp; (3) a decrease in the intensity of the λ 2537 Å. radiation causes a diminution in the velocity of decrease of pressure. The chief difference in the results of the two observations lies in the action of short wave-length radiation. Short wave-length radiation which causes direct formation of ozone influences the reaction. This was not found by Leipunsky and Sagulin. This difference may be due to the different apparatus used. Apart from this there is almost complete agreement. The mechanism of the reaction is discussed, and it is shown that that put forward by Leipunsky and Sagulin is probably incorrect. A series of reactions is proposed which will give a satisfactory explanation of all the results, but a definite decision is not possible. A. J. Mee.

Retarding action of heat on photochemical reactions of coloured solutions in benzene. N. Zchodro (J. Chim. phys., 1929, **26**, 178—181).—The rates of decolorisation of a solution of cyanine in benzene at 15°, 32°, and 45°, and of gallocyanine in benzene at 14·8° and 43·5°, have been measured. In each case rise in temperature retards the reaction.

C. W. Gibby.

Phototropic mercury compounds. S. V. R. Rao and H. E. Watson (J. Indian Inst. Sci., 1929, **12A**, 1—16).—The following compounds, which, with the exception of the last two, are phototropic, have been prepared, in most cases by crystallisation or precipitation from mixed solutions of the appropriate salts of potassium and mercury: *mercuric halogenocyanates*, $XHgCNO$ ($X=Cl$, Br, I), thiocyanates, $XHgCNS$, and *selenocyanates*, $XHgCNSe$; *mercuric hydrosulphoselenocyanate*, $HS\cdot Hg\cdot CNSe$; *trimercuric disulphodihalide*, $HgX_2,2HgS$; *trimercuric disulphodithiocyanate*, $Hg(CNS)_2,2HgS$; *trimercuric disulphodiselenocyanate*, $Hg(CNSe)_2,2HgS$; *trimercuric diselenodihalide*, $HgX_2,2HgSe$; *trimercuric dioxydithiocyanate*, $(HgCNS)_2,2HgO$; *mercuric hydroselenoselenocyanate*, $HSe\cdot Hg\cdot CNSe$; *mercuric hydroselenothiocyanate*, $HSe\cdot Hg\cdot CNS$. By spectroscopic examination of ten of the more sensitive of these compounds it has been found that with one exception they all are darkened by exposure to light of wave-length of the order of 5500 Å. or less, slight sensitivity extending into the ultra-violet to the limit of transmission of quartz. A broad but well-defined maximum of sensitivity is found, usually in the green, of which the position for related compounds tends to move towards the red with increase in the mol. wt. of the compound.

Reversal can be effected by exposure to red light in compounds previously darkened by exposure to light of shorter wave-length. There was a limiting wave-length on the short-wave side capable of producing reversal, but no evidence was found of a maximum efficiency in reversal. In several cases the limiting wave-length was too far in the red to be detected. A neutral zone in which no action occurs was found between the wave-lengths effective in reversal and those producing darkening. The effect of the medium in which the compound was suspended for examination was determined, and in most cases darkening was accelerated and reversal retarded by a medium such as gelatin. By suitably dyeing the compounds the region of sensitivity can be extended towards the red. For two compounds the mean temperature coefficients of the dark and light reactions were found to be 1·9 and 1·0, respectively. No induction period was observed, and the time of exposure required to produce a given effect was inversely proportional to the light intensity.

F. G. Tryhorn.

Primary process in the formation of the latent photographic image. F. C. Toy and G. B. Harrison (Nature, 1929, **123**, 679—680).—The photo-conductivity effect in layers of silver bromide made under conditions such that the bromine cannot escape is simply an expression of the primary photographic process (decomposition of silver bromide into silver and bromine), completely isolated from secondary chemical processes (removal of the bromine). The photo-current, due to liberated valency electrons when light passes through a thin layer of silver bromide fused between quartz plates, starts instantaneously on illumination and quickly reaches its final value. A. A. Eldridge.

Effect of photographic reactions on the Weigert effect in photochloride. H. Zocher and K. Coper (Z. physikal. Chem., 1929, **141**, 217—218).—It has been stated that the Weigert effect can be obtained only by the use of red light. The authors claim to have obtained it with white light.

A. J. Mee.

Helium. VI. Helium content of "moldavites" and artificial glasses. F. Paneth, K. W. Petersen, and J. Chloupek (Ber., 1929, **62**, [*B*], 801—809).—The rare gases are present in the products evolved when moldavites are ignited or fused with sodium carbonate, the proportion of helium being greater than that corresponding with its relationship to argon and neon in atmospheric air. Fresh determinations show the presence of $2\cdot19\times10^{-5}$ c.c. of neon + helium in 1 c.c. of air. If the relationship of the rare gases were the same as in atmospheric air, the amount of neon and helium must be derived from the amount of argon by multiplication by $2\cdot35\times10^{-3}$. Three moldavites of different origin exhibited an excess of helium above this value equal as an average to $1\cdot6\times10^{-5}$ c.c. per g. of material. The preponderance of helium can be detected qualitatively by observation of the neon–helium spectrum. The excess of helium in the gas from the moldavites is a direct consequence of their glassy nature, since artificial glasses have the power of concentrating helium greatly in comparison with neon; under rather less than atmospheric pressure they dissolve in equal times at the ordinary temperature approximately ten times as much helium as neon. In spite of the very small partial pressure of helium in atmospheric air, this action is sufficient to explain at any rate the greater part of the helium content of moldavites, since artificial glass, in which the helium cannot be of radioactive origin, but is necessarily derived from the air, has a "helium excess" amounting to $4{\cdot}2\times10^{-6}$ c.c. per g. It is therefore beyond doubt that the helium excess in moldavites is conditioned by the establishment of an equilibrium in the distribution of helium between the material and the atmosphere and does not depend in a simple manner on the geological age. Determination of the age of moldavites and other types of textites or of natural glassy products by the helium method is, in principle, impossible.

H. WREN.

Preparation of sodium-potassium alloy. T. MIDGLEY, jun., and A. L. HENNE (Ind. Eng. Chem. [Anal.], 1929, **1**, 751).—Freshly cut sodium and potassium are placed in slightly wet ether and gently agitated. Association with ether is less dangerous than association with benzene, the cooling effect of evaporation of the ether reducing the tendency for spontaneous ignition in the air. J. S. CARTER.

Decomposition of alkali carbonates in aqueous solution. B. L. VANZETTI (Gazzetta, 1929, **59**, 219—223; cf. A., 1925, ii, 421).—By passing a current of hydrogen free from carbon dioxide through a boiling solution of potassium or sodium carbonate (about $0{\cdot}2N$) as much as 70% of the carbonic acid may be removed in 5—6 days with the formation of free alkali. The amount of carbonate decomposed is proportional to the square root of the time. Analogous results are obtained if the solutions are boiled in open vessels by a current of superheated steam, the bulk of the solution being maintained with water free from carbon dioxide. At lower temperatures, under reduced pressure, the smaller yield of carbonic acid through reduced hydrolysis, and the lower dissociation pressure of the carbonic acid solution so formed, inhibit the loss of carbon dioxide. The decomposition increases with, but less quickly than, the concentration of the carbonate. F. G. TRYHORN.

Complex sulphites. G. JANTSCH and K. ABRESCH (Z. anorg. Chem., 1929, **179**, 345—356).—Lithium cobaltisulphite, $Li_3[Co(SO_3)_3],4H_2O$, has been prepared by treating a solution containing lithium nitrite and cobalt nitrate with acetic acid, and adding the resulting solution to a boiling solution of lithium sulphite. The complex salt crystallises out readily if the solution is kept hot (80—90°) for a short time. On exposure of the solution to air cobaltic hydroxide gradually precipitates. The insoluble potassium salt, crystallising with 6 mols. of water, may be obtained by direct precipitation. A solution of the lithium salt yields no precipitate when treated with cold ammonia solution, whereas with sodium hydroxide solution all the cobalt is precipitated as hydroxide. The solution has a very low conductivity and exhibits the Tyndall effect; after ultrafiltration the conductivity remains very small, and the Brownian movement is observable. The true solubility of the complex salt thus appears to be very small. Transport observations indicate the presence in the solution of the $Co(SO_3)_3'''$ ion. H. F. GILLBE.

Alkali perborates in the solid state. M. LE BLANC and R. ZELLMANN (Z. anorg. Chem., 1929, **180**, 127—128).—Polemical against Menzel (A., 1928, 32). R. CUTHILL.

Double carbonate of cobalt and potassium. F. DE CARLI (Atti R. Accad. Lincei, 1929, [vi], 9, 417—419).—The salt $CoCO_3,K_2CO_3,4H_2O$ is obtained as rose-coloured crystals from a mixed solution of cobalt nitrate and potassium carbonate. By dehydration at 100—120° in a current of carbon dioxide it is converted into the deep violet anhydrous compound. From measurements of the dissociation pressures at temperatures between 220° and 318°, a mean value of 13·74 kg.-cal. is obtained for the heat of dissociation. This figure includes the heat of dissociation of cobalt carbonate as well as that of the dissociation of the double carbonate. F. G. TRYHORN.

Action of potassium ferrocyanide on silver and several sparingly soluble silver compounds. E. BEUTEL and A. KUTZLNIGG (Monatsh., 1929, **51**, 369—380).—When finely-divided silver is boiled with a solution of potassium ferrocyanide in a current of air it passes into solution with the formation of potassium silver cyanide, ferric hydroxide is precipitated, the solution becoming alkaline, and some hydrogen cyanide is evolved. Quantitative examination shows that the amount of silver dissolved is not equivalent to the precipitated iron. Decomposition of the potassium ferrocyanide into ferric hydroxide and potassium cyanide occurs on boiling its solution, the potassium cyanide reacting with the silver, and a portion being hydrolysed with liberation of hydrogen cyanide. A similar reaction occurs with silver chloride, bromide, cyanide, ferrocyanide, oxide, carbonate, and chromate, the solution in these cases remaining neutral. Similar dissolution of silver and its sparingly soluble salts occurs more slowly in cold saturated potassium ferrocyanide solution, the ferric hydroxide formed remaining in colloidal solution. By measurements of the *P.D.* of concentration cells the solubility of silver ferrocyanide (which, contrary to statements in the literature, is readily soluble in hot, concentrated hydrochloric acid) is intermediate between that of the chloride and bromide. When well washed, precipitated silver cyanide is shaken with an equivalent quantity of dilute potassium ferrocyanide solution, the orange colour formed with nitric acid shows the presence of $Ag_4Fe(CN)_6$. If a slight excess of saturated potassium ferrocyanide is now added and shaking continued, the precipitate becomes definitely crystalline and consists of the *compound* $KAg_3Fe(CN)_6$, intermediate in the formation of potassium silver cyanide, and in the third stage of the reaction dissolves in the excess of potassium ferrocyanide, the total reaction being represented by the equation "$4AgCN+2K_4Fe(CN)_6+5H_2O=4KAg(CN)_2+2Fe(OH)_3+4HCN$." The application of these results to photographic processes, and the explanation of the processes involved in a silvering solution and in a ferrocyanide silver plating bath are discussed on the basis of these results.

J. W. BAKER.

Red phosphorescent alkaline-earth compounds. L. Vanino and F. Schmid (J. pr. Chem., 1929, [ii], **121**, 374—376).—The red luminescence of the alkali sulphide compounds obtained by Vanino and Zumbusch (A., 1909, ii, 731) is improved by partial substitution of cæsium for rubidium carbonate, but the most intense red phosphorescence is obtained by heating together 40 g. of barium oxide, 9 g. of sulphur, 0·7 g. of lithium phosphate, and 3·2 c.c. of a copper nitrate solution containing 0·38 g. of $Cu(NO_3),3H_2O$ in 100 c.c. of alcohol. J. W. Baker.

Action of calcium carbonate and of dolomite on zinc sulphate solutions. L. Cambi, G. Bozza, and D. Masperi.—See B., 1929, 354.

Sulphoaluminates of calcium. W. Lerch, F. W. Ashton, and R. H. Bogue (U.S. Bur. Stand. Res. Paper, 1929, No. 54, and Bur. Stand. J. Res., 1929, **2**, 715—731).—The existence of calcium sulphoaluminate, $3CaO,Al_2O_3,3CaSO_4,31H_2O$, d^{20} 1·48; refractive indices w_D 1·464, e_D 1·458, has been confirmed. The compound is stable in aqueous solution except in the presence of magnesium salts or carbonates. A new *calcium sulphoaluminate*, $2CaO,Al_2O_3,CaSO_4,12H_2O$, d^{20} 1·95, refractive indices w_D 1·504, e_D 1·488, has been isolated. It is much less stable than the former and under conditions occurring in concrete it is transformed into the more stable sulphoaluminate. In solution the transformation is retarded by hydroxyl ions. The existence of the calcium sulphosilicoaluminate of Lafuma (Ciment, 1925, **30**, 175) has not been confirmed. F. J. Wilkins.

Germanium. XXVII. Germanium dichloride. L. M. Dennis and H. L. Hunter (J. Amer. Chem. Soc., 1929, **51**, 1151—1154).—Germanium tetrachloride vapour reacts with metallic germanium at 350° to form germanium dichloride, a light yellow solid, which dissociates at 74·6°. The dichloride is insoluble in, or reacts with, many of the common solvents, although it does not attack 95% ethyl alcohol or chloroform. It is soluble in germanium tetrachloride, is hydrolysed by water, and is converted by ammonia solution into an orange-coloured substance. Concentrated hydrochloric acid converts it into trichloromonogermane. In dry oxygen, the reaction $2GeCl_2+O_2=GeO_2+GeCl_4$ occurs; in wet oxygen, germanochloroform is formed. The dichloride is converted by hydrogen sulphide into germanium sulphide, GeS, and bromine reacts with it to form a mixture of germanium tetrachloride and tetrabromide. Withdrawal of the elements of hydrogen chloride from germanochloroform does not produce germanium dichloride, nor does reduction of the tetrachloride with powerful reducing agents. S. K. Tweedy.

Phosphorous oxide. L. Wolf and H. Schmager (Ber., 1929, **62**, [*B*], 771—786).—When heated in a sealed tube, phosphorous oxide undergoes slow but sensible decomposition at 150°; with rising temperature, the rate of decomposition increases rapidly. The effect is due in part to temperature, in part to the vapour tension of the trioxide, which is greater than that of its decomposition products. Distillation of phosphorous oxide through a heated tube under greatly diminished pressure (0·01—0·001 mm.) shows that incipient decomposition takes place at 340—475°; below 500° the rate of change is slow but increases rapidly above this temperature. Favourable results in the preparation of phosphorous oxide depend on a favourable compromise between the period during which the trioxide remains in the flame and the lengthening of the flame. The yellow phosphorus is contained in a twice-bent quartz tube immersed in a vessel of water. A mixture of oxygen and nitrogen (25 and 75 vol.-%), dried by calcium chloride, soda-lime, phosphoric oxide, and sulphuric acid or carbon dioxide can be passed through the apparatus, the pressure of the gas being regulated by suitable pumps. The collecting apparatus consists of coarse and fine dust chambers followed by three U-tubes cooled respectively by ice and salt, carbon dioxide and acetone, and liquid air. Entry of dust into the pump is prevented by a long glass tube loosely packed with glass wool and connected with a U-tube cooled in liquid air. After the apparatus has been filled with carbon dioxide, the phosphorus is introduced. After evacuation, the phosphorus is warmed to about 50° and the water evolved is condensed in a subsidiary U-tube immersed in liquid air. The phosphorus is ignited and the quartz tube immersed in water at 46—50°. During the complete change, the pressure of the gas is maintained at 90 mm.; the rate of passage is 30 litres per hr. The product, which collects mainly in the coarse and fine dust chambers, is distilled at above 1 mm. into the U-tubes, a very slow current of carbon dioxide being helpful. It is contaminated by phosphoric oxide, probably phosphorus tetroxide, red and yellow phosphorus, from which (with the exception of yellow phosphorus) it can be freed by filtration through glass wool or a glass crucible in an atmosphere of carbon dioxide. Distillation from a special apparatus yields phosphorous oxide containing, as impurity, yellow phosphorus in amount not exceeding 0·2%. H. Wren.

Attempts to prepare phosphorus trioxide by a method other than by burning phosphorus. W. P. Jorissen and A. Tasman (Rec. trav. chim., 1929, **48**, 324—327; cf. Druten, this vol., 540).—Unsuccessful attempts have been made to prepare phosphorus trioxide by the action of phosphorus trichloride on phosphorous acid, or by the action of the same reagent on acetic, trichloroacetic, and butyric acids, and on sodium formate. F. G. Tryhorn.

Difluorophosphoric acid and its analogy to perchloric acid in salt formation. Monofluorophosphoric acid and the similarity of its salts to the sulphates. W. Lange (Ber., 1929, **62**, [*B*], 786—792; 793—801).—Hydrolysis of phosphoryl fluoride by cold, dilute alkali hydroxide results in the production of difluorophosphoric acid, HPO_2F_2, conveniently isolated as the nitron salt (cf. A., 1927, 532). More conveniently, phosphoric oxide is heated with 3 mols. of ammonium fluoride in a copper or nickel crucible at 135°; *ammonium difluorophosphate*, m. p. 213°, is obtained by extracting the cold product with alcohol. Addition of the requisite salts to dilute, aqueous solutions of ammonium difluorophosphate gives the corresponding *tetramethylammonium*, *strychnine*, *brucine*, *morphine*, and *cocaine* compounds; from very concentrated solutions the *potassium* and *cæsium* salts are prepared. Other salts are obtained by treating a hot solution of nitron difluorophosphate with the metallic nitrate, separation of nitron nitrate, and evaporation of the filtrate over sulphuric acid in a vacuum. They crystallise poorly, are hygroscopic, and, in part, become decomposed by hydrolysis during evaporation. The crystalline difluorophosphates are stable in air. They yield neutral solutions in water, in which they slowly undergo hydrolysis. Distillation of them with concentrated sulphuric acid does not afford difluorophosphoric acid, which has been prepared in dilute aqueous solution from the nitron salt and nitric acid or the silver salt and hydrochloric acid. Difluorophosphoric acid exhibits, in part, the properties of perchloric acid in a weakened form. The solubilities of its characteristic salts are generally considerable in comparison with those of the corresponding perchlorates; certain of them (*o*-toluenediazonium, pyridine, methylene-blue, malachite-green) cannot be prepared by precipitation, although the sparingly soluble perchlorates exist.

Salts of difluorophosphoric acid are completely hydrolysed by protracted heating with concentrated alkali hydroxide, whereas boiling, very dilute potassium hydroxide yields potassium fluoride and potassium monofluorophosphate. Addition of much solid silver nitrate to the resultant solution causes the separation of *silver monofluorophosphate*, Ag_2PO_3F, from which, by double decomposition with the requisite chloride, the corresponding *sodium*, *potassium*, and *ammonium* (monohydrate and anhydrous) salts are derived; the ammonium compound loses ammonia at 220°, yielding *ammonium hydrogen monofluorophosphate*, m. p. 225·5°. Aqueous solutions of the alkali salts are neutral to phenolphthalein but alkaline to methyl-orange, in the presence of which 1 mol. of salt requires 1 equivalent of acid for neutralisation. The salts are remarkably stable in neutral or alkaline solution, but are rapidly decomposed in hot acid solution. All cations which give sparingly soluble sulphates give characteristic monofluorophosphates. Other cations, including magnesium, zinc, and copper which yield sparingly soluble phosphates or fluorides, give freely soluble salts which have not been investigated further. The similarity is attributed to the identical valency of the anions co-ordination number and similar radii of the central atoms.

Monofluorophosphoric acid is present in the product of the action of phosphoric oxide and ammonium fluoride, from which it can be partly extracted by alcohol as the ammonium hydrogen salt. The optimal proportion of the reactants is the same as for the production of difluorophosphate, so that the change is formulated: $P_2O_5 + 3NH_4F = (NH_4)PO_2F_2 + (NH_4)_2PO_3F$. The mono-acid is also formed when phosphoric oxide is dissolved in 40% hydrofluoric acid or when metaphosphoric acid is treated with hydrofluoric acid or ammonium fluoride.

Treatment of silver monofluorophosphate with concentrated sulphuric acid causes the evolution of small quantities of a readily condensable gas, possibly the oxyfluoride, PO_2F. *Monofluorophosphoric acid* is readily prepared in dilute aqueous solution from the silver salt and hydrochloric acid; it is slowly but completely hydrolysed to orthophosphoric and hydrofluoric acid.

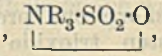
The *calcium* ($+2H_2O$), *strontium* ($+H_2O$), *barium*, *mercurous*, *lead*, and *benzidine monofluorophosphates* are described. H. WREN.

Combination of phosphorus pentachloride with bromine. V. A. PLOTNIKOV and S. I. JAKUBSON (J. Russ. Phys. Chem. Soc., 1928, 60, 1513—1515).—See this vol., 158.

Double sulphates and their components. III. Chromic sulphate. F. KRAUSS, H. QUERENGÄSSER, and P. WEYER (Z. anorg. Chem., 1929, 179, 413—417).—The existence of the following hydrates of chromic sulphate has been established: 18, 9, 3, anhydrous (violet); 6 (probably), and anhydrous (green, crystalline). The water in the green, amorphous form is in zeolitic combination.

H. F. GILLBE.

Sulpho-salts. VIII. Persulpho-salts. L. FERNANDES (Atti R. Accad. Lincei, 1919, [vi], 9, 409—414; cf. this vol., 525).—The formulæ of the type $S_3Mo\cdot S\cdot S\cdot S\cdot NH_4$, proposed by Hoffmann, for salts derived from the acids $HMoS_5$ and $HMoS_6$ are untenable. Instead, co-ordination formulæ of the type $(NH_4)_2[Mo_2S_7(S_5)]$ are suggested for the following *compounds* which have been prepared, chiefly by the action of hydrogen sulphide or ammonium polysulphide on solutions of the normal sulpho-salts of molybdenum and vanadium: NH_4MoS_6; NH_4MoS_6,H_2O; $[NH{:}C(NH_2)_2]MoS_6$; $(NH_4)_4V_2S_9,5H_2O$; $(NH_4)_3HV_2S_9,5H_2O$; $[NH{:}C(NH_2)_2]_3HV_2S_9,6H_2O$; $Tl_3HV_2S_2,3H_2O$; $K_3HV_2S_9,8H_2O$; $(NH_4)_2H_2(VS_5)_6,10H_2O$; $[NH{:}C(NH_2)_2]_4H_2(VS_5)_6,10H_2O$. F. G. TRYHORN.

Aminosulphonic acid and its trisubstituted derivatives. P. BAUMGARTEN (Ber., 1929, 62, [*B*], 820—826).—Trisubstituted derivatives of aminosulphonic acid,  $NR_3\cdot SO_2\cdot O$, form neutral solutions in water, without immediately suffering hydrolysis. Their stability towards water depends on the nature of the group R. They are decomposed more readily by alkali hydroxide, usually into tertiary amine and sulphate. With acids they are able to form salts and they can also yield complex compounds, as instanced by the *substances* $[NMe_3\cdot SO_3H]ClO_4,H_2O$ and $[NMe_3\cdot SO_3]_2,KI,I_5,2H_2O$. The structure $NH_2\cdot SO_3H$ for aminosulphonic acid rests mainly on the properties of its aqueous solution. Its high m. p., non-hygroscopicity, and limited solubility in water indicate a constitution differing from that of other sulphonic acids. Dissolution in water may be considered to cause the changes $\overset{+}{N}H_3\cdot SO_2\cdot\overset{-}{O}+H_2O \rightleftharpoons HO\cdot NH_3\cdot SO_2\cdot OH \rightleftharpoons NH_2\cdot SO_2\cdot OH$; the hypothesis receives support from the observation that aminosulphonic acid is precipitated from its solutions by mineral acids. The presence of the betaine form to a small extent in aqueous solution is deduced from the differing degree of stability of the sulphur–nitrogen linking towards hydrolytic agents in aminosulphonic acid and its alkali salts. The free acid passes in aqueous solution into ammonium hydrogen sulphate under conditions which do not affect the alkali salts. H. WREN.

Action of gases on metals. I. Kinetic study of the phenomena. G. Valensi (J. Chim. phys., 1929, **26**, 152—177).—Measurements have been made on the amounts of nitrogen absorbed by iron, chromium, and manganese when heated at a fixed pressure, and on the dissociation pressures. Evidence is found for the formation of a nitride, CrN, in the case of chromium. The compositions of the mixtures of gases, mainly hydrogen and nitrogen, given off when the three metals are heated in a vacuum have been investigated. C. W. Gibby.

Supposed sesquisulphide of molybdenum. V. Montoro (Atti R. Accad. Lincei, 1929, [vi], **9**, 331—337).—An *X*-ray examination has been made of specimens of molybdenite which had been desulphurised by heating in an arc furnace until the sulphur content varied between 0 and 36%. Specimens containing 36—28% of sulphur gave photograms of the molybdenite lines superposed on others less distinct. The relative intensities of these two sets of lines were reversed in photograms of samples containing less than 20% S. The second set of lines disappeared after treating the specimens with dilute aqua regia. The substance to which these lines are due has been identified with a molybdenum carbide (or solid solution of carbon in molybdenum) of composition corresponding with Mo_2C. An analysis of the substance extracted from the roasted molybdenite by aqua regia agrees closely with the composition deduced from the *X*-ray lines. The structure assigned to the substance is that of a hexagonal lattice with $a=2{\cdot}992$ Å. and $c/a=1{\cdot}581$. F. G. Tryhorn.

Amphoteric hydrated oxides, their aqueous solutions and crystalline compounds. VIII. Tungstates, *iso*poly- and heteropoly-tungstic acids. G. Jander, D. Majert, and T. Aden (Z. anorg. Chem., 1929, **180**, 129—149; cf. this vol., 281).—When aqueous solutions of alkali tungstates are gradually acidified, amorphous precipitates of hydrated forms of tungsten trioxide are finally obtained. Before the precipitate is actually formed, however, polymerisation changes occur in the dissolved tungstic acid, and these changes have been investigated by the two methods already used in the case of stannates, viz., by means of measurements of diffusion coefficients and of absorption coefficients of visible and ultra-violet light. The gradual addition of hydrochloric acid to a solution of an alkali tungstate produces first a polymerisation to hexatungstic acid, without the formation of any intermediate acid, as follows: $6WO_4'' + 6H^{\cdot} \rightleftharpoons W_6O_{21}'''''' + 3H_2O$. The salts of hexatungstic acid are identical with the paratungstates of the literature. With the addition of more acid there is a further polymerisation to metatungstic acid, which is probably a diparatungstic acid, and in presence of other acids, such as arsenic or phosphoric acids, heteropolytungstic acids are formed. The changes $H_2WO_4 \longrightarrow H_6[W_6O_{21}] \longrightarrow H_8[As_2(W_2O_7)_6]$ are described in detail. O. J. Walker.

Fluorine and chlorine, an explosive gaseous mixture. K. Fredenhagen and O. T. Krefft (Z. physikal. Chem., 1929, **141**, 221—222).—Since chlorine forms no ions in liquid hydrogen fluoride, it was concluded that there must be considerable affinity between chlorine and fluorine. A mixture of chlorine and fluorine was sparked in a specially constructed tube. On the passage of the spark a yellowish-red flame spread through the tube followed by an explosion. On completely drying the gases and the apparatus no reaction occurred, but on admitting moisture the flame and explosion were once more obtained.

A. J. Mee.

Purification of gases, especially chlorine, by repeated liquefaction. R. Wasmuht.—See B., 1929, 392.

[Reaction between] sulphuric and hydriodic acids. (Miss) F. Bush (J. Physical Chem., 1929, **33**, 613—620).—Qualitative experiments are described and discussed. With a relatively low concentration of hydriodic acid the sulphuric is reduced to sulphurous acid, and with a high concentration to hydrogen sulphide. The relative amounts of sulphurous acid, hydrogen sulphide, and sulphur produced vary considerably with the size of the crystals of potassium iodide dropped into the concentrated sulphuric acid and with the rate of stirring of the solution.

L. S. Theobald.

Action of chlorine on iron oxide. W. Kangro and R. Flügge (Z. Elektrochem., 1929, **35**, 189—194).—Theoretical considerations show that it should be possible for chlorine to react with ferric oxide to form ferric chloride and oxygen at higher temperatures without the use of carbon. Experiments were carried out by passing chlorine through a silica tube, in which a boat containing ferric oxide was inserted at various temperatures, any ferric chloride formed distilling off. One set of experiments, which show the amounts of iron oxide that had been so acted on when subjected to the action of chlorine by passage at a fixed rate for a given time at different temperatures, reveal that whilst little action occurs at temperatures below 700° the amounts of ferric chloride formed increased rapidly with rise of temperature. Iron-bearing minerals, *e.g.*, magnetite, hæmatite, and pyrites, on treatment with chlorine at 900—1000° yielded up nearly all their iron as the volatile chloride. H. T. S. Britton.

Mixed halogen complexes of tervalent iron. F. Krauss and T. von Heidlberg (J. pr. Chem., 1929, [ii], **121**, 364—368).—A series of mixed halogen complex salts of tervalent iron was prepared by the action of ferric chloride or bromide on various alkali halides in solutions strongly acidified with the corresponding hydrogen halide. All these salts are very hygroscopic and undergo fission into their components in aqueous solution. Thus from the appropriate components are obtained the complex *rubidium* salts, $Rb_2[FeBr_3Cl_2,H_2O]$ and $Rb_2[FeCl_3Br_2,H_2O]$, and the two corresponding complex *cæsium* salts, the *triethylammonium* complex salts, $[Et_3NH][FeClBr_3]$, m. p. 39·5° (decomp.), and $[Et_3NH][FeCl_3Br]$, and the complex *pyridinium* salt, $[C_5H_5NH][FeCl_3Br]$, m. p. 84°. J. W. Baker.

Ferrous bromide ennea- and di-hydrate. F. Schimmel (Ber., 1929, **62**, [*B*], 963—966).—The solubility in water of ferrous bromide, prepared by dissolving pure iron in aqueous hydrobromic acid, has been determined over the range −60° to +132°.

The *ennea-* and *di-hydrates* have been isolated. The cryohydric point of the solution lies at −43·6° with 42·25% of ferrous bromide. The transition temperatures of ennea- to hexa-, hexa- to tetra-, and tetra- to di-hydrate are +29·3°, +49·0°, and +83°, respectively. The saturated solution has b. p. 132° and contains 70·2% of ferrous bromide. All the hydrates have a pure green colour; the "red, hygroscopic powder" of commerce owes its colour to ferric salts.

H. Wren.

Chromatocobaltiammines. II. Dichromatotetramminecobaltiates and the maximum co-ordination number of cobalt. S. H. C. Briggs (J.C.S., 1929, 685—690).—Addition of a solution of a diaquotetramminecobaltic salt to a large excess of a concentrated solution of an alkali chromate affords green or brown crystals of the corresponding alkali dichromatotetramminecobaltiate, $M^I[Co,2CrO_4,4NH_3]$. The green form corresponds with the *trans*-configuration and the brown form with the *cis*-configuration of the chromate radicals; the formation of the brown form is favoured by the presence of a large quantity of dichromate in the solution. *Sodium* trans-*dichromatotetramminecobaltiate*, $Na[Co,2CrO_4,4NH_3]$, separates as a green, microcrystalline precipitate, whereas the corresponding cis-*compound* forms greenish-brown crystals with $1H_2O$. *Lithium* cis-*dichromatotetramminecobaltiate,* $2Li[Co,2CrO_4,4NH_3],3H_2O$, and the *potassium trans*-salt, $K[Co,2CrO_4,4NH_3]$, have also been prepared. With magnesium chromate a mixture of brown and green crystals is obtained, the brown crystals being the *compound* $(Mg,2H_2O)[Co,2CrO_4,4NH_3]_2$ and the green crystals the *compound* $(Mg,6H_2O)[Co,4NH_3,2CrO_4,2H_2O]_2$, in which the cobalt atom has the co-ordination number eight. Dehydration of the green salt in a vacuum over sulphuric acid and treatment of the residue with cold water affords the brown *hexahydrate*, $(Mg,6H_2O)[Co,2CrO_4,4NH_3]_2$. Addition of diaquotetramminecobaltic salts to a large excess of neutral sodium chromate affords a dark chocolate *compound*, $Co_2(CrO_4)_3,8NH_3,2{\cdot}5H_2O$, which gives the *monohydrate* in a vacuum desiccator. Using sodium dichromate in this reaction the *compound* $Co_2(Cr_2O_7)_3,9NH_3,4H_2O$ is obtained in brownish-black crystals, whilst ammonium chromate affords the compound $(NH_4)_2CrO_4,[Co,5NH_3,CrO_4]CrO_4$ in dark reddish-brown crystals.

A. R. Powell.

Nickel hydride, NiH_2. T. Weichselfelder [with M. Kossodo] (Ber., 1929, **62**, [*B*], 769—771; cf. A., 1924, ii, 189; 1926, 372).—The assumption that the very unstable nickel diphenyl is formed as an intermediate product in the action of magnesium phenyl bromide on anhydrous nickel chloride and is converted by 2 mols. of hydrogen into nickel hydride and benzene is supported by the following observations. In absence of hydrogen, the products of the change are nickel and diphenyl. If admission of hydrogen follows 4 hrs. after completion of the first action, 70% of the nickel is converted into the hydride but benzene is not produced; if shorter periods elapse before treatment with hydrogen, benzene is formed in amount which increases as the period decreases. If exactly 2 mols. of hydrogen are present from the beginning of the change, the tension of the gas sinks to zero.

Nickel hydride, suspended in ether, can yield a considerable proportion of its hydrogen to an excess of ethylene within a few days at the atmospheric temperature. It is immaterial whether the nickel hydride has nearly the theoretical content of hydrogen or less than half this amount. Complete loss of hydrogen never occurs. The hydride (hydrogen content=80% of theoretical), suspended in ether, causes the union of a mixture of hydrogen and ethylene to ethane within a few hours. When the hydride in ethereal suspension has been treated with alcohol so that it has apparently lost 25% or more of its hydrogen, it causes almost complete union of ethylene with hydrogen in a few minutes. After almost complete decomposition by water, the hydride reacts more slowly but smoothly with the mixture. Nickel, free from hydrogen, does not appear to unite with or adsorb ethylene.

H. Wren.

Double sulphates and their components. IV. Rhodium sulphate and its hydrates. F. Krauss and H. Umbach (Z. anorg. Chem., 1929, **180**, 42—56; cf. this vol., 663).—By dissolving rhodium hydroxide precipitated in the cold in dilute sulphuric acid, evaporating over concentrated acid, and precipitating the alcoholic solution of the residue with ether, a yellow *hydrate* of rhodium sulphate, $Rh_2(SO_4)_3,15H_2O$, is obtained. On isobaric dehydration, the first three molecules of water prove to be zeolitically combined, and then there are indications of hydrates with 12, 9, and 6 mols. of water, the last 6 mols. also being in zeolitic combination. The aqueous solution gives the normal precipitation reactions of rhodium and sulphate ions, but on evaporation yields a red *hydrate,* $Rh_2(SO_4)_3,4H_2O$, the aqueous solutions of which, when freshly prepared, do not react in this way. The whole of the water in this hydrate is held zeolitically.

R. Cuthill.

Cyanogen compounds of the platinum metals. V. Cyanides and thiocyanates of rhodium. F. Krauss and H. Umbach (Z. anorg. Chem., 1929, **179**, 357—368).—The complex ion $Rh(CN)_6'''$ is, contrary to previous reports in the literature, extremely stable. By heating potassium rhodicyanide with concentrated sulphuric acid to above 100° a brown precipitate, which on partial drying has the composition $2Rh(CN)_3,7H_2O$, is formed; complete desiccation is not possible without decomposition; by treatment of the cyanide with concentrated ammonia solution the salt $4Rh(CN)_6,7NH_3,7H_2O$ has been prepared. Rhodium cyanide is insoluble in potassium cyanide solution and is decomposed by concentrated potassium hydroxide solution. The following complex *cyanides* have been prepared: $Cu_3Rh(CN)_6,xH_2O$ (blue), $Cu_3Rh(CN)_6,5NH_3,5H_2O$ (deep blue), $Cu_3Rh(CN)_6,5C_5H_5N,5H_2O$ (deep blue), $Ni_3Rh(CN)_6,xH_2O$ (green), and $Ni_3Rh(CN)_6,4NH_3,10H_2O$ (violet). Solutions of aluminium, ferric, chromic, stannous, lead, palladium, and mercuric salts do not give precipitates with potassium rhodocyanide solution. Attempts to prepare the free acid and salts corresponding with the nitroprussides have been unsuccessful. Rhodium thiocyanate,

$Rh(CNS)_3,xH_2O$, has been prepared by the addition of concentrated sulphuric acid to a cold solution containing rhodium chloride and potassium thiocyanate: on concentration of the solution in a vacuum desiccator an orange precipitate is produced which is soluble in water but precipitated by sulphuric acid solution. Complex rhodium thiocyanates could not be prepared. H. F. Gillbe.

Ultra-violet colorimetry with the aid of fluorescent substances. I. Eisenbrand (Z. angew. Chem., 1929, 42, 445—448).—A simple means for carrying out colorimetric determinations with ultra-violet light consists of a narrow (0·5 cm.) tube containing a solution which is fluorescent in ultra-violet light (*e.g.*, 0·0001*N*-quinine sulphate in 0·1*N*-sulphuric acid) which is immersed perpendicularly in the solution under investigation and projects above the surface. When a parallel beam of ultra-violet light is directed through the solution at right angles to this tube the solution in the latter exhibits unaltered fluorescence if the test solution does not absorb ultra-violet light. If slight absorption occurs, the immersed portion of the fluorescent solution is darker than that projecting above the liquid, becoming quite invisible where strong absorption occurs. For quantitative measurements the method has a maximum error of 33%, and its application to the detection and determination of nitrites and certain alkaloids is described. J. W. Baker.

Critical consideration of some schemes of fractionation. A. A. Sunier (J. Physical Chem., 1929, 33, 577—585).—Four schemes are discussed and it is concluded that (i) a scheme of fractionation should, in general, be carried outwards as far as possible in both directions, (ii) the number of rows worked should be large, and (iii) the more important factors to be considered in any scheme are yield, g. evaporated per g. yield, and quantity of original material needed to produce a required yield. L. S. Theobald.

Influence of shaking on various precipitation reactions. G. Thanheiser and P. Dickens.—See B., 1929, 392.

Differential potentiometric titration. III. Improved apparatus and its application to precision measurements. D. A. MacInnes and M. Dole (J. Amer. Chem. Soc., 1929, 51, 1119—1127).—The retarded electrode (cf. A., 1927, 35) is surrounded by a glass tube having a capillary opening at the bottom and an aperture near the top, a "gas-lift" being sealed mid-way between these openings. When gas is passed down the lift (which is preferably controlled by the burette tap) solution is circulated over the enclosed electrode, whereas this electrode becomes an "isolated" electrode when no gas is passing. The improved apparatus offers several advantages. Ferrous ions may be accurately titrated with potassium dichromate in an atmosphere of carbon dioxide, and chloride ions may be determined with great precision by titration with silver nitrate. An analysis of constant-boiling hydrochloric acid by the improved method gave results agreeing with those of Foulk and Hollingsworth (A., 1923, ii, 482). S. K. Tweedy.

Chart of indicators useful for p_H measurements. C. E. Davis and H. M. Salisbury (Ind. Eng. Chem. [Anal.], 1929, 1, 92).—Fourteen indicators covering the p_H range 1—10 are tabulated together with their optimum concentrations, appropriate solvents, individual ranges of applicability, and a chart illustrating the dependence of colorations on the p_H value. J. S. Carter.

Yatren, a mono-colour, amphoteric indicator. H. W. van Urk (Z. anal. Chem., 1929, 77, 12—14).—Yatren, 7-iodo-8-hydroxyquinoline-5-sulphonic acid, is a mono-colour, amphoteric indicator, the intensity of the yellow coloration of aqueous solutions being dependent on the p_H value. The colour disappears at p_H 8. Determination of the dissociation curve shows that the ions are colourless and that the coloration is due to the neutral ampholyte. J. S. Carter.

Berry-juice indicator. L. Mosendz (Z. anal. Chem., 1929, 77, 37—38).—The colouring matter of the juice of the black mulberry (*Morus nigra*, L.) may be used as an indicator in acidimetry, the colorations in acid and alkaline media being red and green, respectively. The most accurate results are obtained when acids are titrated with alkalis. J. S. Carter.

Determination of the acidity of undissociated acids with dimethylaminoazobenzene as indicator. A. Hantzsch and W. Voigt (Ber., 1929, 62, [*B*], 975—984).—The acidity of acids cannot be calculated from their conductivities in aqueous solution on account of the production of hydroxonium salts, but is deduced chemically from the differing stabilities of their salts. Yellow dimethylaminoazobenzene is a suitable base, since it gives red salts owing to the conversion of the azoid amine into quinonoid salts. The position of the equilibrium $NPh{:}N{\cdot}C_6H_4{\cdot}NMe_2 + HX \rightleftharpoons NHPh{\cdot}N{:}C_6H_4{:}NMeX$ depends primarily on the strength of the acid, secondarily on the nature of the solvent. Only the saturated hydrocarbons and (approximately) their halogeno-derivatives, particularly carbon tetrachloride and to a somewhat smaller extent chloroform, are almost indifferent solvents. All media containing oxygen react chemically with acids in a degree which increases with the strength of the acid. For practical reasons, measurements are made in chloroform and ether. The dimethyl-yellow salts, or equimolar solutions of base and acid, are dissolved in the solvent and diluted until the change of colour shows the practically quantitative fission into the components. The process is less sensitive than the conductivity method, its indefiniteness increasing with the weakness of the acids. As the strength of the latter increases, the method becomes more accurate and is superior to the conductivity process for the strongest carboxylic acids. In dry chloroform, the order of acidity is generally parallel with the dissociation constant, but the acidities increase much more rapidly and markedly than the dissociation constants. The values for the acidity have about ten times as wide a range as those of the dissociation constants, due to the levelling effect of water; this latter influence is obvious in a smaller degree when moist chloroform is used as solvent.

All salts of dimethyl-yellow are completely decomposed by dilution in anhydrous ether much more rapidly than in chloroform, giving dimethyl-yellow and the acid etherate. Addition of water has little influence except that it represses slightly the values for the strongest acids. The salts of the strongest inorganic acids are not completely dissociated in anhydrous chloroform even at very great dilutions. For their investigation, they are dissolved in a little chloroform and the solutions are diluted with ether. The sequence of acidities is $HClO_4 > HBr > HCl > HNO_3$. With a weaker base (dianisylideneacetone), the activities of hydrogen bromide, hydrogen chloride, and trichloroacetic acid can be compared in anhydrous chloroform. By means of these salts, also, it is shown that the halogeno-derivatives of saturated hydrocarbons are less inactivating than benzene or toluene.
H. Wren.

Determination of water by means of difficultly inflammable liquids. F. Friedrichs (Chem.-Ztg., 1929, 53, 287).—The substance is heated with tetrachloroethane in a small flask fitted with a glass stopper carrying a long vertical tube bent over at its upper end to meet a small condenser the lower end of which is connected through a capillary tube with a small burette filled with tetrachloroethane. An overflow tube from the lower end of the burette returns excess of the liquid to the distillation flask. The water vapour condenses as an emulsion with the tetrachloroethane in the condensers and is thus forced into the burette, where the water rises to the surface of the organic liquid and its volume can then be measured.
A. R. Powell.

Microtitration of iodides [alone] and in the presence of large quantities of nitrites. J. F. Reith (Rec. trav. chim., 1929, 48, 386—390).—Details are given of a titration method, using sodium thiosulphate solution, by which from 0·01 to 0·0015 mg. of iodine ion can be determined with an accuracy of from 5 to 2%.

By the application of the sodium azide method 0·005 mg. of iodine ion may be determined with an accuracy of about 2% in the presence of several times that quantity of nitrite.
F. G. Tryhorn.

Absorption of oxygen by dilute alkaline solutions of pyrogallol. T. J. Drakeley and H. Nicol.—See B., 1929, 355.

Determination of gases in metals, particularly of oxygen in steel. W. Hessenbruch.—See B., 1929, 358.

Separation and determination of nitrous acid by esterification. W. M. Fischer and A. Schmidt (Z. anorg. Chem., 1929, 179, 332—338).—Owing to the high esterification velocity of nitrous acid, and to the volatility of the esters, the acid may be readily and quantitatively separated from a mixture by conversion into ethyl or methyl nitrite and removal of the ester in a current of carbon dioxide; after passage of the vapour into potassium iodide solution the liberated iodine may be titrated with sodium thiosulphate solution. Hydrazine, hydroxylamine, aniline salts, and bromates, sulphites, ferrocyanides, and permanganates interfere.
H. F. Gillbe.

Detection of nitrites in the forensic study of gunshot wounds. C. Goroncy (Deut. Z. ges. gerichtl. Med., 1928, 11, 482—486; Chem. Zentr., 1928, ii, 2047).—Lunge's reagent is used, after dissolution with alcoholic potassium hydroxide, for the detection of nitrite from black or smokeless powder.
A. A. Eldridge.

Use of liquid amalgams in volumetric analysis. XI. Determination of phosphoric acid by using zinc or cadmium amalgam. K. Someya (Sci. Rep. Tôhoku Imp. Univ., 1928, 17, 1289—1298).—Molybdic acid is completely reduced to the tervalent state by treatment with zinc or cadmium amalgam in dilute sulphuric acid. Molybdenum can then be determined by titration with potassium permanganate solution. The method is extended to the determination of phosphorus, the usual precipitate of phosphomolybdate being reduced and titrated, assuming 24 mols. of MoO_3 for each mol. of P_2O_5.
C. J. Smithells.

Separation and determination of ortho- and pyro-phosphoric acids. W. Stollenwerk and A. Bäurle (Z. anal. Chem., 1929, 77, 81—111).—Ortho- and pyro-phosphoric acids cannot be quantitatively separated by precipitation of the latter with silver nitrate in the presence of sodium acetate and acetic acid, as an excess of the precipitant results in the gradual conversion of the silver pyrophosphate into orthophosphate; a similar reaction occurs with copper nitrate. Separation of the two acids by precipitation with aluminium, beryllium, magnesium, or lead salts is always incomplete either because of adsorption or owing to the too great solubility of the precipitate. Alkaline-earth salts precipitate completely both acids in the tri- or tetra-basic form respectively. Either acid alone may therefore be determined by titrating its solution with an excess of barium hydroxide in an atmosphere free from carbon dioxide and then determining the total alkalinity of a portion of the filtrate by acidimetric titration or the excess of barium as sulphate gravimetrically; both methods give good results. If both acids are present in the same solution the sum is obtained by the above method and the total P_2O_5 is determined as usual. From these results the proportion of each acid present is readily calculated by the indirect method.
A. R. Powell.

Analytical studies of pyrophosphoric acid. [Determination of pyrophosphate in presence of orthophosphate.] R. Dworzak and W. Reich-Rohrwig (Z. anal. Chem., 1929, 77, 14—37).—The method of Berthelot and André (A., 1897, ii, 158) yields trustworthy results except when orthophosphate is the predominating constituent. Under these latter conditions, however, satisfactory results are obtained by titration with a solution of uranyl acetate, until a permanent precipitate of orthophosphate indicates the completion of the reaction $UO_2(OAc)_2 + 2Na_4P_2O_7 = Na_6[UO_2(P_2O_7)_2] + 2NaOAc$. In accurate work it is desirable to add a trace of ammonia and varying amounts of a solution of uranyl acetate to each of several aliquot parts of the solution to be tested and to keep for several hours. The true titration is the mean of the values which just produce, or do not produce, turbidity. The indirect method of Aoyama (J. Pharm. Soc. Japan, 1925, No. 520, 7), with certain modifications, gives trustworthy results and should be used if metaphosphate is also present.

J. S. Carter.

Volumetric determination of arsenic in organic and inorganic compounds in presence of halogens and heavy metals. P. Villecz (Ber. Ungar. pharm. Ges., 1928, 4, 313—337; Chem. Zentr., 1928, ii, 2173).—The substance is decomposed by heating with concentrated sulphuric acid and 30% hydrogen peroxide; a macro- and a micro-procedure are described. If a brown coloration appears, hydrogen peroxide is again added. Arsenic acid is reduced at the b. p. by hydrazine sulphate in concentrated sulphuric acid, which removes the excess of hydrazine sulphate. The arsenious acid is then titrated with potassium bromate solution. The determination of arsenic in presence of calcium, strontium, barium, iron, lead, mercury, or silver is described.

A. A. Eldridge.

Determination of arsenic by Smith's method. J. Gnessin (Pharm. J. Russia, 1928, 89, 442—444; Chem. Zentr., 1929, ii, 2269).—Gadamer's method (Lehrb. d. Chem. Tox., 1924, 166) is modified, the arsenic hydride being produced in a Marsh–Lockemann apparatus and then passed into the solution containing mercuric chloride, potassium iodide, and sodium hydrogen carbonate. A. A. Eldridge.

Test for boric acid and borates. A. S. Dodd (Analyst, 1929, 54, 282—285).—To about 10 c.c. of an acid aqueous solution of the substance to be tested are added methyl-red or Sofnol indicator 1, and the solution is neutralised with sodium hydroxide. After boiling (filtering if necessary), the liquid is acidified with dilute sulphuric acid and just neutralised with 0·1*N*-sodium hydroxide solution, when 0·5 g. of mannitol is added. If on shaking a reddish-pink colour appears, borates are present. Small quantities of carbon dioxide do not interfere if 0·01 g. of boric acid is present. A reaction is given with 0·2 mg. of boric acid and a very distinct one with 0·3 mg. The following substances gave negative results with the test and did not interfere when present with borates: Metallic radicals: aluminium, ammonium, antimony, barium, bismuth, cadmium, calcium, cobalt, copper, iron, lead, lithium, magnesium, manganese, mercury, molybdenum, nickel, potassium, silver, sodium, strontium, tin, titanium, and zinc. Acid radicals: acetates, benzoates, bromates, bromides, chlorates, chlorides, citrates, formates, iodates, iodides, lactates, molybdates, nitrates, nitrites, oxalates, salicylates, sulphates, sulphides, sulphites, tartrates, and tannates. Tungstates gave a colour similar to that produced by boric acid. D. G. Hewer.

Detection of alkali metals in mixtures of salts and in silicates. N. A. Tananaev (Z. anorg. Chem., 1929, 180, 75—82).—If a mixture of chlorides and nitrates is converted into oxides, carbonates, and free metals by ignition with oxalic acid, then treated with ammonium carbonate to change any calcium oxide into carbonate, the aqueous extract of the residue can contain only alkali metals and a little magnesium carbonate, so that if the latter is decomposed by evaporating the solution and igniting, an alkaline reaction in the aqueous extract of the residue proves the presence of alkali metals. If, however, the original mixture contained arsenite or arsenate, this solution will contain arsenite, which must be precipitated as sulphide by addition of ammonium sulphide and oxalic acid, the residue left on evaporation of the filtrate being ignited, and then dissolved in water and its alkalinity examined. Any sulphate present in the mixture is converted into chloride by addition of excess of barium chloride before ignition with oxalic acid, whilst silicates require a preliminary treatment with hydrofluoric acid, the fluorides then reacting with oxalic acid in the same way as chlorides.

R. Cuthill.

Determination of metals as sulphates using silica crucibles. A. A. Guntz and J. Barbier (Chim. et Ind., 1929, 21, 711—712).—The determination of various metals as sulphates using vitreosil crucibles in an electric furnace with temperature control was investigated, with results as follows. Sodium: the method is accurate between 700° and 950° (m. p. of sodium sulphate, 880°). Magnesium: accurate between 600° and 850°. Lithium: accurate from 500° to 950° (m. p. of lithium sulphate, 580°). Cadmium: accurate between 450° and 800°. It is impracticable to heat further and determine as oxide. Lead and manganese can be determined between limits 450° and 800° and 400° and 750°, respectively. Zinc requires close temperature control as the limits are 400° and 600°; by heating to above 900° in a closed crucible it may be weighed as oxide. Cobalt and nickel: the method is unsuitable. C. Irwin.

Zirconium. III. Influence of lithium, rubidium, cæsium, and magnesium on the detection of potassium by zirconium sulphate. R. D. Reed and J. R. Withrow (J. Amer. Chem. Soc., 1929, 51, 1062—1065; cf. A., 1928, 858).—Zirconium sulphate will detect 1·0 mg. or more of potassium in 2 c.c. of solution containing 50 mg. of lithium sulphate, 16·6 mg. of rubidium sulphate, or 11·6 mg. of cæsium sulphate. It will also detect 0·5 mg. or more of potassium in 2 c.c. of a solution which are free from interfering ions or contain 50 mg. of magnesium sulphate. S. K. Tweedy.

Determination of small quantities of beryllium in rocks. B. E. Dixon (Analyst, 1929, 54, 268—274).—The determination of beryllium present in silicate rocks has been hampered by lack of a suitable way of separating from titanium. This may be brought about by precipitating the weak hydroxide of titanium with *p*-chloroaniline, and subsequently the beryllium with ammonia. The hydroxides of iron, aluminium, etc. are separated from the solution of chlorides by two precipitations with boiling ammonia, with evaporation of the filtrate to recover any unprecipitated traces. The precipitates are dried and ignited with the residue from the silica determination, ground and mixed with 5 g. of sodium carbonate, and heated for 2·5—3 hrs., first in the molten condition. The mass is digested with water, filtered, and washed with sodium carbonate solution. Any chromium can be determined colorimetrically in the filtrate. The solution is then acidified with 15 c.c.

of hydrochloric acid, evaporated to dryness, a few c.c. of hydrochloric acid are added, then 100 c.c. of hot water, and the liquid is filtered. The precipitate is ignited and weighed, and the weight of silica determined by loss in weight on evaporation with hydrofluoric and sulphuric acids. Aluminium can be determined in the filtrate and a correction made for any chromium and phosphorus which are also precipitated. Ten c.c. of hydrochloric acid are put into the sodium carbonate fusion crucible, and the extract is used to dissolve the precipitate of iron, titanium, and beryllium on the filter paper. The paper is ashed and any residue is dissolved in hydrochloric acid and added to the main solution, which is neutralised with ammonia and 10 g. of solid sodium hydrogen carbonate are added per 100 c.c., the solution is boiled for 1 min., cooled, filtered, the residue washed with 50 c.c. of hot 10% sodium hydrogen carbonate solution, redissolved in hydrochloric acid, neutralised, and the precipitation repeated. The final precipitate of ferric and titanic hydroxides is ignited. The united filtrates are acidified with 30 c.c. of hydrochloric acid, the solution is boiled, and a preliminary separation of beryllium and titanium hydroxides made by dissolving in hydrochloric acid, treating with ammonia until a turbidity but not flocculation is present. *p*-Chloroaniline (1—1·5 g.) is then added, the solution is boiled for 3 min. and filtered, and the precipitate redissolved and reprecipitated, ignited, and weighed. A slight excess of ammonia is added to the filtrate, the solution boiled and filtered after uniting with the filtrate from the final separation, and the beryllium hydroxide washed free from chlorides, ignited, and weighed.

D. G. Hewer.

Detection of magnesium in silicates. H. Leitmeier and F. Feigl (Tsch. Min. Petr. Mitt., 1928, 29, 323).—The test by fusing with cobalt nitrate is unsatisfactory and a quick test for magnesium is wanting. Silicates are treated with hydrofluoric acid, or with potassium hydrogen fluoride and sulphuric acid, and the solution is heated with an alkaline alcoholic solution of diphenylcarbazide. In the presence of magnesium a bluish-violet colour results (cf. A., 1928, 1108). L. J. Spencer.

Rapid electrolytic determination of lead as peroxide. H. Töpelmann (J. pr. Chem., 1929, [ii], **121**, 289—319).—Various physico-chemical factors affecting the electrolytic determination of lead have been investigated and on the basis of the results the following procedure is recommended. The solution of lead nitrate (100 c.c.) containing 0·3—0·5 g. of lead, 8—10 c.c. of nitric acid, *d* 1·4, and 1—2 g. of copper nitrate is electrolysed at the ordinary temperature with a platinum gauze anode and a rotating platinum cathode for 1—2 min. with a current of 0·5 amp., the current strength then being increased to 2 amp. in the course of 0·25 hr. After a further 0·25 hr. the anode is washed with distilled water before interrupting the current and dried under conditions elaborated below. Complete precipitation of the lead is affected by the evolution of oxygen, which sets in towards the end of the electrolysis and by the solvent action of the nitrous acid produced, but with the above procedure these errors amount to less than 0·1 mg. The varying factors recorded for conversion of the weight of dried lead peroxide into lead (usually more than 1% below the theoretical value) are shown to be due, not to the presence of higher oxides, nor, entirely, to the presence of nitrate (which never exceeds 1%), but to occlusion of varying amounts of water depending on the method of drying and on the physical state of the deposit, the latter, in turn, depending on the temperature of electrolysis and current density. The best results are obtained by drying in a described apparatus at 260° for 2 hrs., for which a constant conversion factor (independent of the quantity of lead) 0·8628 is found. Constant conversion factors are also obtained by drying for 0·5 hr. (0·8580) or 1 hr. (0·8589) at 230°, but previous washing with alcohol and ether is not to be recommended. Thermal dissociation of lead peroxide occurs slowly at 320—350°, but is not appreciably accelerated by diminution of the partial pressure of the oxygen. Contrary to some results of earlier investigators, the presence of ammonium or alkali nitrates (in concentration 0·32*N*) does not affect the electrolytic determination of lead, but by altering the anode and cathode potentials small concentrations (0·00455*N*) of chloride ion have a relatively large effect and must be avoided. The adaptation of the method to the micro-determination of lead is described. J. W. Baker.

Volumetric determination of thallous salts using potassium permanganate in a medium containing hydrochloric acid. A. Jílek and J. Lukas (Chem. Listy, 1929, 23, 124—129).—The accuracy of the following gravimetric methods for the determination of thallium salts is examined. The experimental errors of Werther and Willm's method (Z. anal. Chem., 1865, 4, 432) are from −10 to +3%, of Browning and Palmer's method (A., 1909, ii, 620) about +2%, of Browning's method (A., 1900, ii, 247) from −20 to +2%, of Werther's method (Z. anal. Chem., 1864, 3, 2) only +0·1%, of Willm's method (Z. anal. Chem., 1865, 4, 432) −0·3%, of Crookes' method (Chem. News, 1863, 8, 255) +3%, and of Carstenjen's method (Z. anal. Chem., 1867, 8, 73) from −3 to +7%. Willm's volumetric method (Bull. Soc. chim., 1863, 5, 532) gives fairly accurate results (99·5—102·4%), using 0·02*N*-solutions of thallous salts and of potassium permanganate, and in the presence of potassium chloride, 1 c.c. of permanganate being equivalent to 2·078 mg. of thallium.

R. Truszkowski.

Cupric oxide as a standard in iodometry. T. F. Buehrer and C. M. Mason (Ind. Eng. Chem. [Anal.], 1929, **1**, 68—70).—Since impurities in metallic copper are unevenly distributed, the use of copper oxide as an iodometric standard is recommended. After a copper compound has been evaporated to dryness with sulphuric acid it is unnecessary to neutralise with ammonia and re-acidify with acetic acid before adding potassium iodide. J. S. Carter.

Determination of copper. H. F. Bradley.—See B., 1929, 359.

Ceric sulphate in volumetric analysis. V. Potentiometric study of the reaction between

ferrocyanide and ceric ions. N. H. Furman and O. M. Evans (J. Amer. Chem. Soc., 1929, 51, 1128—1133).—Ferrocyanide ions may be accurately titrated potentiometrically with ceric sulphate. If a small quantity of ferric iron is present in the ceric solution there is produced a green coloration of ferric ferrocyanide which disappears at a point which practically coincides with the potentiometric end-point. The reverse titration is accurate only if most of the ferrocyanide is added very rapidly. S. K. Tweedy.

Confirmatory test for aluminium. R. Gemmill, R. Brackett, and C. R. McCrosky (J. Amer. Chem. Soc., 1929, 51, 1165).—An asbestos wad looped in platinum wire is dipped in 0·05*N*-cobalt nitrate solution, ignited, dipped in the aluminium nitrate solution, and again ignited (cf. Pañganiban and Soliven, A., 1928, 1206). The test is sensitive to 0·2 mg. of aluminium; sodium salts do not interfere. 0·5 Mg. of zinc may be readily detected in a similar manner. S. K. Tweedy.

Behaviour of certain zeolites. G. Grassi-Cristaldi and F. Scafile (Annali Chim. Appl., 1929, 19, 136—140).—Besides in the ordinary mineral acids, the two zeolites, analcime and mesolite, are soluble, with decomposition, in certain organic acids. Thus, aqueous 5% oxalic acid dissolves analcime when hot and mesolite when cold, and the oxalic acid solutions may be employed for the separation and determination of the constituents. T. H. Pope.

Determination and separation of rare from other metals. XV. Determination of gallium. II. L. Moser and A. Brukl (Monatsh., 1929, 51, 325—333; cf. A., 1928, 1347).—Gallium may be determined and quantitatively separated from aluminium, chromium, indium, uranium, and cerium by means of its compound with "cupferron." The neutralised solution (containing 0·01—0·3 g. of gallium) is diluted to 200—300 c.c. with 2*N*-sulphuric acid (the precipitate is somewhat soluble in more concentrated acid) and treated with a 6% aqueous cupferron solution at the ordinary temperature (only 0·1 g. of cupferron for each 0·1 g. of gallium). The precipitate is washed free from chloride ion (gallium oxide being volatile in the presence of ammonium chloride) and ignited to gallium oxide. The filtrate, after addition of hydrogen peroxide, is evaporated to fuming and redissolved in water, and the other metal determined in the usual manner. In the separation from indium a little cupferron solution is added to the 2*N*-sulphuric acid used in washing the precipitate, great care being required in this operation, whilst in the separation from uranium any reduction must be avoided, since quadrivalent uranium is quantitatively precipitated by cupferron. In the quantitative separation of gallium from iron three cases are considered: (1) a small quantity of gallium with much iron, (2) a small quantity of each, (3) much gallium in the presence of a small amount of iron. In (1) the neutralised solution (free from ammonium salts) is treated in the cold with sodium thiosulphate solution until the violet colour of the ferric salt is destroyed, heated to boiling for 0·25 hr., and 10 c.c. of aniline are added at 5 min. intervals to the boiling solution. The precipitated gallium hydroxide is filtered hot, washed free from sodium with hot water, and ignited to gallium oxide. The latter contains a little ferric oxide and is fused with potassium pyrosulphate, the mass dissolved in very dilute sulphuric acid, and the gallium determined by method (2) or (3). In (2) the solution is treated with sulphosalicylic acid followed by sufficient ammonia to yield a clear red solution and the iron is separated as ferrous sulphide by passing hydrogen sulphide into the hot solution. The filtrate is acidified with acetic acid, boiled to expel hydrogen sulphide, ammonium acetate added, and the gallium precipitated with tannin (*loc. cit.*). In (3), the neutral solution is poured slowly with stirring into a hot solution of ammonia and the precipitated ferric hydroxide, which adsorbs some gallium, washed with hot water, and treated as in (2). Gallium is determined in the united filtrates by the tannin method. J. W. Baker.

Two reversible oxidimetric indicators and the manganometric determination of hydroferrocyanic acid. J. Knop (Z. anal. Chem., 1929, 77, 111—125).—The triphenylmethane dyes, erioglaucin A and erio-green B, are completely reversible indicators in titrations with permanganate but not with dichromate. The former in acid solution gives a green colour which becomes bluish-red on addition of a slight excess of permanganate; as these colours are almost complementary, the end-point in a titration is characterised by a change from green to a pale grey or almost colourless. Erio-green B gives a yellow colour to acid solutions which becomes deep orange-yellow on the addition of a drop of permanganate. In both cases the colour changes are more sensitive than the pink colour which permanganate imparts to water. For the titration of ferrocyanide with permanganate 1 g. is dissolved in 400 c.c. of water and 20 c.c. of 8*N*-sulphuric acid, 1 c.c. of erioglaucin or 2 c.c. of erio-green (0·1% solution) are added, and the solution is titrated with 0·05*N*-permanganate until the colour changes from yellowish-green to brownish-orange in the first case or from deep yellow to orange-yellow in the second case. The results are correct to within 0·02 c.c. A. R. Powell.

Permanganate titration of iron with erioglaucin A or erio-green B as indicator. J. Knop and O. Kubelkova (Z. anal. Chem., 1929, 77, 125—130).—Ferrous salts may be determined accurately by macro- or by micro-titration with permanganate, using erioglaucin A or erio-green B as indicator (cf. preceding abstract). For the micro-titration 2 c.c. of the iron solution are treated with 0·5 c.c. of 1 : 4 sulphuric acid and 0·1 c.c. of indicator solution and titrated with 0·005*N*-permanganate; the results are correct to within 0·5% of the iron present. A. R. Powell.

Prussian-blue and Turnbull's blue reactions. H. W. van Urk (Z. anal. Chem., 1929, 77, 39—41; cf. Szebellédy, A., 1928, 1347).—The influence of ammonium fluoride in repressing the Prussian-blue and Turnbull's blue reactions is due to the depression of the hydrogen-ion concentration below that necessary for their occurrence. J. S. Carter.

Iodometric determination of chromic oxide in potassium chromium alum. J. E. S. Han.—See B., 1929, 391.

Separation of thorium from uranium by means of ether. P. Misciattelli (Phil. Mag., 1929, [vii], 7, 670—674).—The anhydrous ternary system uranyl nitrate–thorium nitrate–ether has been examined. It is shown that thorium nitrate is undissolved only in ether solutions saturated with the uranyl salt at temperatures above 20°. The results are important in connexion with the analytical separation of thorium from uranium by extraction of the mixed nitrates with ether. A. E. Mitchell.

Determination of tin by rapid electrolysis. J. Švéda and R. Uzel (Coll. Czech. Chem. Comm., 1929, 4, 203—222).—The most suitable conditions for the electrolytic determination of tin in stannous or stannic salt solutions are obtained by the addition of ammonium oxalate, oxalic acid, and hydroxylamine hydrochloride to the solution and electrolysing for 25 min. (5 amp. at 2·5—3·5 volts) at 60—70° while the solution is rapidly stirred. For solutions of ammonium thiostannate, sodium sulphite and the ammonium salt of a strong acid must be added. The method is not applicable to sodium thio-salt solutions. A. I. Vogel.

Titration of tin with "chloramine." E. Rupp and F. Lewy (Z. anal. Chem., 1929, 77, 1—3; cf. A., 1928, 387).—Reduction of stannic to stannous salts in acid media is conveniently effected by electrolytic iron foil. Oxidation during manipulations is avoided by allowing a solution of sodium hydrogen carbonate to drip into the reduction flask. J. S. Carter.

Determination of bismuth in bismuth hydroxy-iodide. G. Bümming and K. Ferrein.—See B., 1929, 355.

Separation of niobium and tantalum by electrolytic hydrolysis. L. F. Yntema (Amer. Electrochem. Soc., May 1929. Advance copy, 3 pp.).—The niobate–tantalate mixture obtained by fusing tantalite with potassium hydroxide was dissolved in water and enough sulphuric acid added to cause a slight turbidity. Electrolysis in a diaphragm cell with 0·07 amp./cm.^{2} at the platinum anode yielded a granular precipitate around the anode. Analysis of successive portions of this precipitate showed an excess of niobium in the earlier fractions, and it is concluded that the method could be used for concentrating either niobium or tantalum, although it does not lead to a complete separation. H. J. T. Ellingham.

Separation of ruthenium and osmium, and the use of benzene in the iodometric titration of osmium. S. Saitō (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 164—179).—The separation of osmium and ruthenium under various conditions is described. Osmium can be completely removed by distillation with nitric acid of concentration greater than 6*N*, if it is present in a soluble form. Ruthenium obtained by evaporation of an aqua regia solution of the sulphide does not distil; it distils slightly if present as the oxide RuO_4, whilst the product obtained by fusion with sodium peroxide is almost completely distilled. Osmium distils completely, but ruthenium not at all, on boiling with *N*-hydrochloric acid solution. The residual ruthenium in both cases can be completely distilled as RuO_4 by making the acid solution strongly alkaline with sodium hydroxide, passing in chlorine, and heating the solution. Small quantities of osmium are most accurately determined from the colour of the sodium hydroxide solution in the receiver on distilling with hydrochloric acid. Benzene is a suitable indicator of the end-point in the iodometric titration of osmium. C. J. Smithells.

***X*-Ray tube with detachable ends and electrodes for *X*-ray spectroscopy.** W. Band and A. J. Maddock (J. Sci. Instr., 1929, 6, 160—161).—Detailed directions are given for the construction of an *X*-ray tube. The ends are made of brass, with soldered joints, and are clamped to the porcelain tube which forms the body by plates fitting on rubber washers. C. W. Gibby.

Optical method for analysing photographs of α-ray tracks. J. M. Nuttall and E. J. Williams (Nature, 1929, 123, 799).—A method similar to that of Curtiss (this vol., 534) has already been used for the study of β-ray tracks. A. A. Eldridge.

Calibration of sixty-five 35-yellow Lovibond glasses. I. G. Priest, D. B. Judd, K. S. Gibson, and G. K. Walker (Bur. Stand. J. Res., 1929, 2, 793—819).—The glasses are used as precision colour standards, but it is shown that in the sixty-five specimens examined there are many imperfections which make them unsuitable for this work. Accurate calibration would therefore serve no useful purpose. The data reported include for each glass: (1) the equivalent in terms of standard Lovibond yellow and red, and (2) the sunlight transmission. Directions are given for using the equivalents in practice. Special comments are made on seven glasses which have strikingly abnormal transmissions or badly marred surfaces. The application of the results to the colour-grading of oils and the conditions of observation necessary for the highest obtainable accuracy are given. The sources of discrepancies in the colour grading of oil may be traced to: (1) unstandardised, non-uniform, and insensitive methods of comparing the oil samples with the glasses, (2) the grading of oils by observers having abnormal colour sense or low power of hue discrimination, and (3) errors in the red glasses. A. J. Mee.

Device for identifying colours. W. C. Holmes (Chemicals, 1928, 30, No. 21, 31).—The spectrophotometer gives better results than the colorimeter. The former is applied to the examination of dyes and gases, and to the determination of p_H and dissociation constants of indicators. Chemical Abstracts.

Simple interferometer for the measurement of small thicknesses. H. Fromherz and W. Menschick (Z. physikal. Chem., 1929, B, 2, 399—404).—A simple interferometric method is described for the measurement of thicknesses of 200—1 μ. The optical arrangement is described in detail. The method is of use in the determination of the absorption of light by strongly absorbing solutions where only very thin layers can be used. A. J. Mee.

Sensitive micromanometer. J. L. Hodgson (J. Sci. Instr., 1929, 6, 153—156).—Differences in pressure cause the movement of an oil meniscus in a tube inclined at a small angle. The meniscus is brought back to zero by raising or lowering a plunger actuated by a screw with a graduated head and vernier. Pressure differences of 10^{-5} in. of water can be measured. C. W. Gibby.

Measurement of small pressures with an external indicator. A. Simon and F. Fehér (Z. Elektrochem., 1929, 35, 162—165).—A method has been devised by which small pressures may be measured at a distance from the reaction vessel; it is particularly useful for reactions that are apt to be explosive, *e.g.*, in the measurement of the dissociation pressure of manganese heptoxide. The gas is led into one limb of a U-tube tensimeter containing mercury, whilst within the other limb and very close to, and above, the mercury level is fixed a glass rod, thus confining the movement of the mercury to the space between the glass wall and the central glass obstruction. Outside the manometer tube at this point a sheet of tin-foil is folded, so that, in effect, a condenser is formed between the mercury in the manometer and the tin-foil. An increase in gas pressure causes the mercury to rise inside the space surrounded by the tin-foil sheath and thereby alters the capacity of the condenser. This is included in a system containing two valves, oscillating in resonance, and a milliammeter in the plate circuit, so that any change in the capacity disturbs the state of the valves, which after readjustment enables a current to be measured which can be calibrated in terms of pressure. The glass-blowing technique involved is difficult. Pressures of the order of 0·05 mm. of mercury may thus be measured. A less sensitive modification of the manometer device is also described, in which a glass rod, around which is wound a constantan wire of 16 ohms resistance, is placed in the central portion of the remote arm immediately above the mercury level. An increase in pressure causes the mercury to rise over a portion of the wire and so reduces the resistance of the wire, which is registered by means of a milliammeter in the anode circuit of a valve in the filament circuit of which the resistance is connected. By using wire of greater resistance, 160 ohms, the use of a valve was unnecessary. H. T. S. Britton.

Gravitometer for recording rapid changes of density in gases. A. Blackie and B. H. Williams (J. Sci. Instr., 1929, 6, 157—160).—A Ranarex carbon dioxide recorder has been adapted to measure small differences in the densities of gases considerably lighter than air. The standard gas and that under test are driven through two similar cylinders by two fans rotating at identical speeds, and the torques produced on two free fans at the other ends of the cylinders are balanced against one another by a connexion which actuates a pointer. The pressures of the gases on the entry sides must be kept the same. The sensitivity varies with the density of the gas used. C. W. Gibby.

Extraction apparatus and "perforators" for liquid extraction. P. H. Prausnitz (Oesterr. Chem.-Ztg., 1929, 32, 71—73).—Descriptions of various modifications of Soxhlet's extractor and "perforators" are given. A. J. Mee.

Apparatus for electrolytic analysis. H. J. S. Sand (Analyst, 1929, 54, 275—282).—The apparatus described is based in general purpose and design on that used previously (J.C.S., 1907, 91, 374). The new designs of electrodes achieve reduction in the weight of platinum required. A rotating anode to be used in conjunction with a revolving partition (a parchment-paper thimble) when the anode and electrolyte must not come in contact is also described. A special mounting of the electrodes on a rubber and glass frame is useful for zinc and similar determinations. D. G. Hewer.

Air separator for the laboratory. R. E. Zinn (Ind. Eng. Chem. [Anal.], 1929, 1, 112).—The powder to be separated is carried by an air stream into the annular space between two cylindrical containers, where the velocity is depressed sufficiently to cause deposition of coarser particles. The air then enters the inner container, where finer particles are deposited. Escaping dust is arrested by a muslin etc. filter. J. S. Carter.

Receiver for vacuum distillation. E. J. Poth (Ind. Eng. Chem. [Anal.], 1929, 1, 111—112).—By using float check valves sealed against mercury and suitably coupling these with levelling bulbs the use of stopcocks is avoided. J. S. Carter.

Continuous still for conductivity water. C. C. De Witt and G. G. Brown (Ind. Eng. Chem. [Anal.], 1929, 1, 109—111).—Vapour from the first still, which contains a permanganate solution, passes up a packed column and reflux condenser into the column of a second still. The second still is charged with pure distilled water. The final product is drawn from the base of the second column. All parts are made of tin and heating is effected by steam coils. J. S. Carter.

Containers for caustic solutions. B. A. Soule (Ind. Eng. Chem. [Anal.], 1929, 1, 109).—Solutions of sodium hydroxide may be stored safely over reasonably long periods in bottles coated with rubber paint. The use of such paint as a protection for glass against hydrofluoric acid is unsatisfactory. J. S. Carter.

Heavy-duty thermostat. D. F. Othmer (Ind. Eng. Chem. [Anal.], 1929, 1, 97).—A single heating circuit thermostatic system used to maintain the temperature of a small boiler constant to 0·02° is described. J. S. Carter.

Utility shaking machine. W. M. Shaw (Ind. Eng. Chem. [Anal.], 1929, 1, 93).—The shaker consists of a system of trays, each accommodating six containers, and overhead clamps arranged radially every 60° about the centre shaft. J. S. Carter.

Electrically-heated thermocirculator for hot leaching and digesting. M. G. Raeder (Ind. Eng. Chem. [Anal.], 1929, 1, 88).—The apparatus consists of a glass bulb connected with a reflux condenser at the top and a circulation tube, with an electrically-heated portion, between the bottom and the upper portion. Circulation is not continuous but pulsating, and material being leached is brought into vigorous circulation. J. S. Carter.

Coated spiral fractionating columns. T. Midgley, jun. (Ind. Eng. Chem. [Anal.], 1929, 1, 86—88).—Improved fractionation is effected by coating spirals, Hempel columns, etc. with carborundum. Obvious precautions must be taken in choosing a suitable binding material. Shellac is a satisfactory binding material for use with hydrocarbons etc. J. S. Carter.

Automatic pipette. L. N. Markwood (Ind. Eng. Chem. [Anal.], 1929, 1, 82).—The apparatus consists of a bulb with overflow arrangement and a valve rod passing down the pipette and ground in at the exit orifice to make a liquid-tight seal. J. S. Carter.

Self-regulating gas flow-meter. L. Chalkley, jun. (Ind. Eng. Chem. [Anal.], 1929, 1, 74—75).—The arrangement consists essentially of an electrically-operated gas valve, a capillary tube flow-meter with a mercury manometer connected across it, and suitable connexions for operating the valve by changes in the manometer level. J. S. Carter.

Glass electrode. D. A. MacInnes and M. Dole (Ind. Eng. Chem. [Anal.], 1929, 1, 57—59).—The usual bulb electrode is replaced by a glass tube, to the bottom of which is fused a very thin (0·001 mm.) glass diaphragm. The inner electrolyte is 0·1*N*-hydrochloric acid and the inside electrode Ag|AgCl. Using two such electrodes it is possible to perform titrations by the differential method (A., 1927, 35) with considerable accuracy. Glass electrodes respond to changes in hydrogen-ion concentration only and are independent of oxidation–reduction potentials existing in the solution. J. S. Carter.

Intermittent extraction apparatus. C. W. Eddy (Chemist-Analyst, 1929, 18, 15—16).

Thermostat. V. Čupr (Pub. Facs. Sci. Univ. Masaryk, No. 108, 1929, 8 pp.).—See A., 1928, 1348.

Geochemistry.

Determination of nitrides in Etna projections. D. Grassi-Cristaldi and A. Giammona (Annali Chim. Appl., 1929, 19, 128—135).—When hydrolysed, the nitrides present in Etna lava yield ammonia, which may be determined by means of Nessler's solution. Decomposition of the material with potassium hydroxide does not always give trustworthy results and the disgregation is best effected by sulphuric acid and potassium fluoride, which, unlike hydrofluoric acid, is always free from ammonia. The percentages of ammonia obtained from the upper, central, and lower (in contact with the soil) portions of the lava from the eruption of 1669 are 0·0738, 0·0403, and 0·0252, respectively. T. H. Pope.

Paragenetic classification of the minerals of Franklin, New Jersey. C. Palache (Amer. Min., 1929, 14, 1—18).

Phosphorescence and fluorescence of Franklin minerals. C. Palache (Amer. Min., 1928, 13, 330—333).

Seligmanite from Bingham, Utah. C. Palache (Amer. Min., 1928, 13, 402—405).—Crystallographic data are recorded. Chemical Abstracts.

Beryllonite and other phosphates from Newry, Maine. C. Palache and E. V. Shannon (Amer. Min., 1928, 13, 392—396).—The composition and optical characters of beryllonite (*d* 2·806), herderite, and eosphorite are recorded. Chemical Abstracts.

Rosy muscovite from Suizawa and a dark grey muscovite from Doi. S. Iimori and J. Yoshimura (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, 10, 221—223).—Analyses are given of a rosy muscovite from Suizawa, the colour of which is probably due to colloidal copper, and of a dark grey muscovite from Doi. C. W. Gibby.

Radioactive constituents of hokutolites and other minerals of Japan. J. Yoshimura (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 223—227, and Bull. Chem. Soc. Japan, 1929, 4, 91—96).—The radium and thorium contents of four Japanese minerals were found to be as follows: hokutolite from Hokuto 1·73 × 10^{-7}% Ra, 0·02% ThO_2; hokutolite from Shibukuro 1·22 × 10^{-7}% Ra, 0·01% ThO_2; allanite from Kyoto 4·87 × 10^{-9}% Ra, 1·05% ThO_2, 0·017% U_3O_8; xenotime from Ishikawa 6·98 × 10^{-7}% Ra and 2·42% U_3O_8. The uranium content was calculated from the radium content. C. J. Smithells.

Quartz-porphyry and granite-porphyry from Teplitz, Bohemia. J. E. Hibsch (Tsch. Min. Petr. Mitt., 1928, 39, 320—322).—New analyses of the fresh rocks differ appreciably from earlier analyses. L. J. Spencer.

Makite and hanksite. R. Wegscheider (Tsch. Min. Petr. Mitt., 1928, 39, 316—319).—The formula of hanksite has been variously given as $4Na_2SO_4,Na_2CO_3$ and $9Na_2SO_4,2Na_2CO_3,KCl$. The chloride is no doubt present as an impurity, and perhaps also some of the sulphate. The suggestion is made that hanksite is identical with the artificial double salt, $2Na_2SO_4,Na_2CO_3$ (A., 1926, 664), or with the double sulphate and carbonate of sodium from salt lakes of Armenia, described under the name makite by Abich in 1846. The formula of the latter is then deduced as $4Na_2SO_4,Na_2CO_3$ with some admixed Na_2CO_3,H_2O (thermonatrite). L. J. Spencer.

Rocks from the Stubalp, Styria. F. Angel and A. Rusch (Tsch. Min. Petr. Mitt., 1928, 39, 254—303).—Nine analyses of gneisses of different types show a range in silica from 44·15 to 73·30%. L. J. Spencer.

Spinels. L. Passerini (Atti R. Accad. Lincei, 1929, [vi], 9, 338—343).—An *X*-ray examination of seven spinels has been made by the powder method, and the results for two, magnesium chromite, $MgCr_2O_4$, and nickel ferrite, $NiFe_2O_4$, are detailed. A more accurate examination is promised of the others, which have previously been examined by Holgersson (Lunds Univ. Årsskrift, 1927, [ii], (2), **23**, 9). The two spinels mentioned above were prepared by calcination at about 800° of the mixed nitrates in the case of magnesium chromite and of the mixed hydroxides in the case of nickel ferrite. Both substances form cubic crystals with the typical spinel lattice, a fact confirmed by the agreement of the observed intensities of the X-ray lines with those calculated from the postulated structure. For $MgCr_2O_4$ and $NiFe_2O_4$ the width and volume of the unit cell, and the calculated d, were, respectively: $a=8{\cdot}290\pm0{\cdot}005$, $8{\cdot}340\pm0{\cdot}005$ Å.; $569{\cdot}72\times10^{-24}$, $580{\cdot}09\times10^{-24}$ c.c.; d 4·49, 5·268.

F. G. TRYHORN.

Thucholite. H. V. ELLSWORTH (Amer. Min., 1928, **13**, 419—439).—Thucholite, a black, lustrous mineral from Parry Sound, Ont., has H 3·5—4, $d^{17{\cdot}74}$ 1·777, and is of variable composition, containing about 50% C, 13% H_2O, and 28% of ash, of which half is thorium dioxide. The radioactivity of the ash and the gas content are high.

CHEMICAL ABSTRACTS.

Heulandite of Monastir. G. MARTINEZ (Atti R. Accad. Lincei, 1929, [vi], **9**, 428—433).—Microscopical, chemical, and crystallographic analyses have been made of specimens of heulandite obtained from the basaltic and trachitic regions of Monastir. The presence of the following minerals was recognised: plagioclase, olivine, monoclinic pyroxene, serpentine amphibole, basaltic hornblende, serpentine, muscovite, epidote, chlorite, and iron oxide. The excess of iron oxide was the cause of the red colour of the heulandite.

Chemical analysis gave the following results: SiO_2 47·77, TiO_2 0·57, Al_2O_3 19·01, Fe_2O_3 8·88, FeO 2·0, MnO 0·01, MgO 4·23, CaO 8·70, Na_2O 3·00, K_2O 1·59, H_2O 3·97, total 99·72%. The Löwinson-Lessing magmatic formula is RO 1·46, R_2O_3 1, SiO_2 3·23, $\alpha=1{\cdot}60$, $\beta=76$, $R_2O:RO=1:4{\cdot}27$, $K_2O:Na_2O=1:2{\cdot}5$. The triangular representation of Osann is given by $S=62{\cdot}64$, $A=5{\cdot}24$, $C=9{\cdot}56$, $F=22{\cdot}26$, $a=4{\cdot}25$, $c=7{\cdot}75$, $f=18{\cdot}00$, $n=7{\cdot}14$, and the tetrahedral representation of Niggli by $al=28{\cdot}26$, $fm=37{\cdot}56$, $c=23{\cdot}76$, $alk=10{\cdot}10$, $si=120{\cdot}26$, $k=0{\cdot}28$, $mg=0{\cdot}43$, $c/fm=0{\cdot}63$. The forms $b\{010\}$, $c\{010\}$, $t\{201\}$, $s\{201\}$, $m\{110\}$, and $u\{\bar{1}11\}$ were recognised among the monoclinic crystals of heulandite.

Analysis of the purest crystals (d 2·19) gave SiO_2 57·40, Al_2O_3 17·10, CaO 7·80, H_2O 17·67.

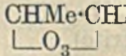
F. G. TRYHORN.

Minerals. IX, X, XI, XII. H. COLLINS (Chem. News, 1929, **138**, 82—84, 184—186, 273—275, 369—371.)

Organic Chemistry.

Condensation of ethylene with sulphuric acid in presence of mercurous and copper sulphates. J. BÖESEKEN and N. MAX (Rec. trav. chim., 1929, **48**, 486—488; cf. Ormandy and Craven, B., 1929, 462).—When ethylene is passed into 93—95% sulphuric acid containing 5% of anhydrous copper sulphate and 2% of mercurous sulphate, saturated and unsaturated hydrocarbons are produced. The saturated hydrocarbons of low b. p. appear to be paraffins, whilst the mixture of unsaturated substances contains a fraction, b. p. 184—196°, resembling dipentene.

H. BURTON.

Ozonisation of gaseous unsaturated hydrocarbons. III. Butenes, aldehydes, and acetone. E. BRINER and R. MEIER (Helv. Chim. Acta, 1929, **12**, 529—553).—When Δ^{β}-butene dissolved in methyl chloride is treated with ozone at −80°, the liquid ozonide, d^{21} 1·081, n_D^{21} 1·4120, obtained contains only traces of hydrogen peroxide. Decomposition with water at 70—75° gives, in addition to acetaldehyde and acetic acid, methane, formic acid, and small amounts of oxides of carbon. The following side-reaction presumably occurs:  $\underbrace{\text{CHMe}\cdot\text{CHMe}}_{O_3}+H_2O=Me\cdot CO_2H+H\cdot CO_2H+CH_4$. Decomposition of the ozonide with cold water is slow: a small amount of formic acid is again produced. The ozonide from a Δ^{α}-butene containing 20% of the Δ^{β}-isomeride gives hydrogen on hydrolysis. This is formed by decomposition of the intermediate hydroxymethyl-α-hydroxypropyl peroxide (cf. Briner and Schnorf, this vol., 290). The ozonide, d^{20} 1·05, n_D^{20} 1·4081, from *iso*butene decomposes rapidly even in absence of water, yielding acetone peroxide and formaldehyde. With water at 70° these products, together with acetone, formic acid, hydrogen, and oxides of carbon, are produced. Propene ozonide also gives hydrogen, methane, and oxides of carbon. In all the above cases the amount of acid products formed during decomposition of the ozonides by water exceeds that of aldehydes. Ozonisation of the isomeric butenes has also been carried out in the gaseous state by the method previously described (*loc. cit.*). An excess of acid products is again formed: hydrogen and formaldehyde are also obtained in varying amounts. Application of this method to a mixture of butenes obtained by "cracking" gives results similar to those obtained with the individual hydrocarbons. Ozone reacts only slowly with formaldehyde, yielding traces of formic acid and carbon monoxide. Acetaldehyde furnishes formaldehyde, formic acid, and carbon monoxide in varying amounts. Propaldehyde yields carbon monoxide, formic acid, acetaldehyde, and a trace of formaldehyde. Formaldehyde and formic acid are also obtained by the action of ozone on acetone.

H. BURTON.

Natural and synthetic rubber. II. Reduction of isoprene by Na–NH_3. III. Dimethyloctadiene. T. MIDGLEY, jun., and A. L. HENNE (J. Amer. Chem. Soc., 1929, **51**, 1293—1294, 1294—1296).—The volatile product obtained by adding isoprene to sodium dissolved in liquid ammonia consists entirely of β-methyl-Δ^{β}-butene (60% of the theoretical) which is not reduced to *iso*pentane by excess of the reagent.

Isoprene is reduced and polymerised by potassium and ethyl alcohol to a mixture, b. p. 163—167°, d_{20}^{20} 0·769, n_D^{20} 1·4457, of βζ-, βη-, and γζ-dimethyl-$\Delta^{\beta\zeta}$-octadienes, identified by hydrogenation to a mixture of the corresponding dimethyloctanes and by oxidation with chromic and acetic acids to acetone, hexane-βε-dione, and lævulic and succinic acids.

H. E. F. Notton.

Low-temperature oxidation of hydrocarbons. I. Pressure–temperature curves of amylene–oxygen mixtures. J. S. Lewis.—See this vol., 655.

Preparation of acetylenic hydrocarbons from epidibromohydrins. R. Lespieau and Wiemann (Compt. rend., 1929, **188**, 998—1000).—When treated with magnesium methyl bromide epidibromohydrin yields mainly *γ-bromo-Δ^{γ}-hexene*, b. p. 34°/16 mm., d^{21} 1·197, n^{21} 1·459, converted by bromine into *γγδ-tribromohexane*, b. p. 105—106°/9 mm., d^{20} 1·9434, n^{20} 1·5508, yielding with alcoholic sodium hydroxide *γδ-dibromo-Δ^{γ}-hexene*, b. p. 60—61°/9 mm., d^{20} 1·6128, n^{20} 1·514. With zinc dust and alcohol the latter yields mainly *Δ^{γ}-hexinene*, m. p. —51°, b. p. 79—80°/770 mm., d^{20} 0·724, n^{20} 1·4115, together with a very little γ-methyl-Δ^{α}-pentinene, b. p. 65—70°/770 mm. The epidibromohydrin accordingly probably possesses the structure $CH_2Br{\cdot}CBr{\vdots}CHEt$ and not $CH_2{\vdots}CBr{\cdot}CHEtBr$, as Bouis suggests from considerations of b. p. The b. p. of Δ^{γ}-hexinene lies between that of the Δ^{α}- and Δ^{β}-isomerides.

R. Brightman.

Action of acetylene on selenium. F. P. Mazza and L. Solazzo.—In the abstract under this title (this vol., 290) the b. p. of selenophen should be 113—114°. The b. p. 207—209° given is that of selenonaphthen, m. p. 53—54°.

Law of periodicity. P. Petrenko-Kritschenko (Ukraine Chem. J., 1928, **3** [Sci.], 445—455).—See A., 1927, 713; 1928, 614.

Law of periodicity. P. Petrenko-Kritschenko [with A. Ravikovitsch, V. Opotzki, E. Putjata, and M. Diakova] (J. Russ. Phys. Chem. Soc., 1929, **61**, 29—40).—See A., 1928, 614.

Ferric ethoxide (preparation and properties). P. A. Thiessen and O. Koerner (Z. anorg. Chem., 1929, **180**, 65—74).—From a mixed solution of ferric chloride and sodium ethoxide in absolute alcohol ferric ethoxide separates in dark brown crystals which do not contain alcohol of crystallisation. The solubility in alcohol has been measured between 11° and 58°, the mol. wt. of the solute, as determined from the b.-p. elevation, corresponding with the formula $Fe(OEt)_3$.

R. Cuthill.

Action of Grignard reagent on highly branched carbonyl compounds. J. B. Conant and A. H. Blatt (J. Amer. Chem. Soc., 1929, **51**, 1227—1236).—The yields of *sec*.- and *tert*.-alcohols obtainable from aliphatic aldehydes and ketones, respectively, by the Grignard reaction are decreased by the introduction of branched or lengthy alkyl radicals into either reagent, whilst products formed by concurrent reactions such as reduction, enolisation, and intermolecular condensation of the carbonyl compound appear to a greater extent. Attempts to prepare *tert*.-carbinols containing more than two *sec*.- or *tert*.-alkyl radicals were unsuccessful. Thus, under standard conditions using excess of Grignard reagent, magnesium *tert*.-butyl chloride gives with acetaldehyde methyl*tert*.-butylcarbinol (80% of the theoretical); with *iso*butaldehyde, *iso*butyl alcohol (20%) and *iso*propyl-*tert*.-butylcarbinol (44%), but no ββδ-trimethylpentane-αγ-diol (cf. Favorski. A., 1913, i, 1146); with diethyl ketone, no definite products; with methyl *tert*.-butyl ketone, a small yield of condensation products of high b. p.; with di*iso*propyl ketone, di*iso*propylcarbinol (80%); with *iso*propyl *tert*.-butyl ketone, *iso*propyl*tert*.-butylcarbinol (90%); with di-*tert*.-butyl ketone, di*tert*.-butylcarbinol (69%), and with ethyl trimethylacetate, no reaction. Magnesium *iso*propyl bromide gives with *iso*butaldehyde di*iso*propylcarbinol (78%); with methyl *tert*.-butyl ketone, condensation products of high b. p. ; with di*iso*propyl ketone, di*iso*propylcarbinol (78%); with *iso*propyl *tert*.-butyl ketone, *iso*propyl*tert*.-butylcarbinol (88%), and with ethyl phenylacetate, ethyl αγ-diphenylacetoacetate (94%). Magnesium *n*-butyl bromide yields with diethyl ketone *diethyl*-n-*butylcarbinol* (60%), b. p. 116—118°/105 mm., d_4^{20} 0·8409, n_D^{20} 1·4360, but no diethylcarbinol (3 : 5-*dinitrobenzoate*, m. p. 101°); with methyl *tert*.-butyl ketone, *methyl*-n-*butyl*-tert.-*butylcarbinol* (25%), b. p. 84—87°/13 mm., d_4^{20} 0·8487, n_D^{20} 1·4409, and methyl*tert*.-butylcarbinol (30%), and with di*iso*propyl ketone, *diisopropyl*-n-*butylcarbinol* (40%), b. p. 115—118°/45 mm., d_4^{20} 0·8487, n_D^{20} 1·4435, and di*iso*propylcarbinol (13%). Magnesium methyl iodide gives with *iso*propyl *tert*.-butyl ketone *methylisopropyl*tert.-*butylcarbinol* (60%), b. p. 56—57°/6 mm., d_4^{20} 0·8564, n_D^{20} 1·4430, and with di*tert*.-butyl ketone, *methylditert*.-*butylcarbinol* (78%), m. p. 39—41°, b. p. 184—191°. Magnesium *iso*propyl chloride and this ketone give a small yield of di*tert*.-butylcarbinol.

H. E. F. Notton.

Isomerisation of acetylenic carbinols to ethylenic ketones. A. Willemart (Compt. rend., 1929, **188**, 1172—1174).—The conversion of various acetylenic carbinols $CR^1R^2(OH){\cdot}C{\vdots}CR^3$ into the ethylenic ketones $CR^1R^2{:}CH{\cdot}COR^3$ is effected by heating with alcoholic sulphuric acid, whilst the corresponding chloro-compounds, $CR^1R^2Cl{\cdot}C{\vdots}CR^3$, are similarly converted by heating with alcohol alone. Thus the following: *diphenylheptinylcarbinol*, b. p. 179—180°/1 mm.; *diphenyl*-β-p-*tolylethinylcarbinol*, m. p. 68—69°; *phenyl-α-naphthyl-β-phenylethinylcarbinol*, m. p. 137—138° (only through its chloro-compound); *di-α-naphthyl-β-phenylethinylcarbinol*, m. p. 70—71°; *diphenyl-β-naphthylethinylcarbinol*, m. p. 99—100°, are converted, respectively, into β-*phenylstyryl* n-*amyl ketone*, m. p. 7—8°, b. p. 173°/1 mm.; p-*tolyl-β-phenylstyryl* n-*amyl ketone*, m. p. 74—75°; *phenyl* β-(1-*naphthyl*)*styryl ketone*, m. p. 107—108°; *phenyl* ββ-*di*-(1-*naphthyl*)*vinyl ketone*, m. p. 170—171°; and 2-*naphthyl* β-*phenylstyryl ketone*, m. p. 168—169°.

J. W. Baker.

Electronic conception in organic chemistry. II. Interpretation of the rearrangements of trisubstituted α-glycols. M. Migita (Bull. Chem. Soc. Japan, 1929, **4**, 57—65).—An explanation in terms of the electronic theory of the rearrangements following the dehydration of trisubstituted α-glycols by dilute or concentrated sulphuric acid is given. It is assumed that the dilute acid acts catalytically, the concentrated acid substitutively. Semihydrobenzoin rearrangement takes place, when dilute acid is used, if the tertiary hydroxyl group has negative polarity and the hydrogen of the secondary hydroxyl group is induced (by the presence of a negative group) more positive than that bound to the secondary carbon atom : $\mathrm{CRR'(OH){\cdot}CHAr{\cdot}OH} \longrightarrow \mathrm{CRR'{\cdot}CHAr(O{\cdot})} \longrightarrow \mathrm{CRR'Ar{\cdot}CHO}$. Vinyl dehydration results either with the dilute acid when the tertiary hydroxyl has negative polarity and the hydrogen attached to the secondary carbon atom is induced (by the presence of a positive group) more positive than that of the secondary hydroxyl group : $\mathrm{CRR'(OH){\cdot}CHR''{\cdot}OH} \longrightarrow \mathrm{CRR'{:}CR''{\cdot}OH} \longrightarrow \mathrm{CHRR'{\cdot}CO{\cdot}R''}$, or with concentrated acid when the tertiary hydroxyl group is markedly negative : $\mathrm{CRR'(OH){\cdot}CHR''{\cdot}OH} \longrightarrow \mathrm{CRR'(SO_4H){\cdot}CHR''{\cdot}OH} \longrightarrow \mathrm{CRR'{:}CR''{\cdot}OH} \longrightarrow \mathrm{CHRR'{\cdot}CO{\cdot}R''}$. Semipinacolin rearrangement results, using dilute or concentrated acid, in the few cases of glycols having a negatively polarised secondary hydroxyl group : $\mathrm{CRR'(OH){\cdot}CHR''{\cdot}OH} \longrightarrow \mathrm{CRR'(O{\cdot}){\cdot}CHR''} \longrightarrow \mathrm{R{\cdot}CO{\cdot}CHR'R''}$, and also by action of the concentrated acid on glycols with feebly negative tertiary hydroxyl groups, as steric hindrance here plays a part. B. W. Anderson.

Affinity of hydrocarbon radicals for oxygen. I. R. Lydén (Finska Kemistsamf. Medd., 1928, **37**, 53—75; Chem. Zentr., 1928, ii, 2133).—Ethereal components of a reaction system may exercise a mutual influence which can result in a marked diminution of reactivity; this is especially so when the system contains a simple aliphatic ether and an aromatic ether containing an aliphatic group differing from that of the simple aliphatic ether. As the carbon content of the alkyl groups is increased the activity of the aromatic aliphatic ether component is diminished. If the system consists of a mixed aliphatic ether and an aromatic aliphatic ether containing a common alkyl group, the reactivity of the aromatic aliphatic ether has an intermediate value. By heating the components with acetyl bromide in a sealed tube and submitting the products to fractional distillation, the following molecular reactivities were obtained : ethyl ether–phenyl *iso*amyl ether, 1 : 0·0113; *iso*amyl ether–phenyl *iso*amyl ether, 1 : 0·528; phenetole–phenyl *iso*amyl ether, 1 : 0·335; ethyl *iso*amyl ether–phenyl *iso*amyl ether, 1 : 1·58; ethyl *iso*amyl ether–phenetole, 1 : 0·852; *n*-propyl ether–phenyl *n*-propyl ether, 1 : 0·753; *n*-butyl ether–phenyl *n*-butyl ether, 1 : 0·528. A. A. Eldridge.

Organic cyclic polysulphides. Condensation of ethyl mercaptan with di- and tri-chloroacetic acids. G. C. Chakravarti and J. M. Saha (J. Indian Inst. Sci., 1928, **11A**, 226—230).—See A., 1928, 1214.

Octa- [and hexa-]decoic acids and their bactericidal action towards *B. leprae*. XV. W. M. Stanley, M. S. Jay, and R. Adams (J. Amer. Chem. Soc., 1929, **51**, 1261—1266; cf. A., 1928, 754, 990, 1003).—The bactericidal activity of the series of acids obtained by introducing a carboxyl group successively into each position in the pentadecane and heptadecane molecules shows that the effect is not connected with the presence of a ring. The first member of each series (palmitic and stearic acids) is much less active than the others, and, of the two acids with a common alkyl radical, the pentadecane is more active than the heptadecane derivative. A general review of the acids tested suggests that the physical properties and not the chemical constitutions of the individual acids are primarily responsible for their bactericidal power. The effect of six of the acids on *B. tuberculosis* is similar to, but considerably less than, that on *B. leprae*. The toxicity of two natural, and three synthetic acids towards eight different strains of *B. leprae* is tabulated. The following are described, b. p., d_4^{25}, and n_D^{25} being given in that order : *ethyl dialkylmalonates* : *methylpentadecyl-*, 179—183°/5 mm., 0·9119, 1·4453; *ethyltetradecyl-*, 172—177°/3 mm., 0·9163, 1·4461; *propyltridecyl-*, 183—187°/5 mm., 0·9048, 1·4475; *butyldodecyl-*, 175—180°/3·5 mm., 0·9104, 1·4473; *amylundecyl-*, 180—185°/5 mm., 0·9124, 1·4509; *hexyldecyl-*, 185—188°/2·5 mm., 0·9118, 1·4476; *heptylnonyl-*, 193—197°/5 mm., 0·9118, 1·4471; *dioctyl-*, 192—195°/3 mm., 0·9135, 1·4471; iso*propyltridecyl-*, 179—183°/5 mm., 0·9144, 1·4491; iso*butyldodecyl-*, 180—185°/5 mm., 0·9115, 1·4481; sec.-*butyldodecyl-*, 180—184°/5 mm., 0·9163, 1·4501; sec.-*amylundecyl-*, 175—178°/4 mm., 0·9155, 1·4509; *methyltridecyl-*, 167—170°/3 mm., 0·9181, 1·4418; *ethyldodecyl-*, 181—183°/4 mm., 0·9249, 1·4422; *propylundecyl-*, 178—179°/4 mm., 0·9186, 1·4422; *butyldecyl-*, 181—183°/4 mm., 0·9220, 1·4424; *amylnonyl-*, 185—186°/5 mm., 0·9282, 1·4462; *hexyloctyl-*, 175—178°/4 mm., 0·9168, 1·4458; *diheptyl-*, 178—180°/3 mm., 0·9169, 1·4459; iso*butyldecyl-*, 160—162°/2 mm., 0·9207, 1·4428; sec.-*butyldecyl-*, 196—198°/10 mm., 0·9253, 1·4454; and *dialkylacetic acids* : methylpentadecyl (m. p. 34—35°), 179—183°/5 mm.; *ethyltetradecyl-* (m. p. 23—24°), 167—170°/2·5 mm., 0·8767, 1·4531; *propyltridecyl-* (m. p. 31—32°), 179—183°/5 mm.; *butyldodecyl-* (m. p. 23—24°), 180—184°/4 mm., 0·8743, 1·4528; *amylundecyl-*, 180—185°/4 mm., 0·8829, 1·4519; *hexyldecyl-*, 182—184°/5 mm., 0·8741, 1·4527; *heptylnonyl-*, 180—183°/5 mm., 0·8747, 1·4528; dioctyl- (m. p. 35—36°), 183—185°/5 mm.; iso*propyltridecyl-* (m. p. 58—59°), 178—182°/5 mm.; iso*butyldodecyl-* (m. p. 26—27°), 175—180°/4 mm.; sec.-*butyldodecyl-* (m. p. 38—39°), 178—183°/6 mm.; sec.-*amylundecyl-*, (m. p. 37—38°), 175—178°/5 mm.; methyltridecyl- (m. p. 24°), 172—173°/2·5 mm., 0·8765, 1·4453; *ethyldodecyl-* (m. p. 23°), 178—179°/3 mm., 0·8808, 1·4460; *propylundecyl-* (m. p. 16·5—17°), 178—179°/3 mm., 0·8808, 1·4460; *butyldecyl-* (m. p. 13—14°), 175—176°/3 mm., 0·8789, 1·4458; *amylnonyl-* (m. p. 9—10°), 178—179°/3 mm., 0·8887, 1·4518; *hexyloctyl-*, 165—168°/2 mm., 0·8768, 1·4495; diheptyl- (m. p. 26—27°), 187—189°/4 mm., 0·8771, 1·4497; iso*butyldecyl-*, (m. p. 17·5—18°), 187—188°/9 mm., 0·8763, 1·4448; and sec.-*butyldecyl-* (m. p. 38—39°), 185—186°/9 mm. (cf. Morgan and Holmes, A., 1927, 539; Guthzeit, A., 1880, 871; Jourdan, A., 1880, 313). H. E. F. Notton.

Acid sodium palmitates. P. Ekwall and W. Mylius (Ber., 1929, **62**, [*B*], 1080—1084).—By crystallisation of suitable mixtures of the components from ethyl alcohol the following *acid sodium palmitates* have been isolated: $2C_{16}H_{31}O_2Na,C_{16}H_{32}O_2$, m. p. 115—117°; $C_{16}H_{31}O_2Na,C_{16}H_{32}O_2$, m. p. 97—98°; $C_{16}H_{31}O_2Na,2C_{16}H_{32}O_2$, m. p. 81—82°. The individuality of the substances is confirmed by microscopical examination and determinations of mol. wt. in camphor. H. WREN.

Use of methyl-alcoholic barium hydroxide. C. NEUBERG (Helv. Chim. Acta, 1929, **12**, 304).—A claim of priority (Neuberg and Behrens, A., 1926, 542) against Escher (this vol., 294). J. W. BAKER.

Action of hydrazine on some unsaturated acids, $C_nH_{2n-2}O_2$, $C_nH_{2n-4}O_2$, $C_nH_{2n-6}O_2$. J. HANUŠ and J. VOŘIŠEK (Coll. Czech. Chem. Comm., 1929, **4**, 223—227).—The interaction between hydrazine hydrate and oleic acid in the cold affords the *hydrazide* of oleic acid as a gelatinous mass which after several days at the ordinary temperature yields a solid mass, from which a 50% yield of stearic acid, m. p. 69—69·5°, is obtained on decomposition with dilute sulphuric acid. Interaction at 100° gives the *hydrazide* of stearic acid (I), m. p. 114°, whilst the reaction between potassium oleate and hydrazine hydrate at 100° yields stearic acid mixed with a little of its hydrazide. Elaidic acid and hydrazine hydrate at 100° similarly give the hydrazide of stearic acid (*acetyl* derivative, m. p. 138·7°); under similar conditions the mixture of linoleic and linolenic acids isolated from linseed oil gives a 50% yield of I. A. I. VOGEL.

Removal of halogen from halogenated elæostearic acid. D. HOLDE, W. BLEYBERG, and M. A. AZIZ (Z. angew. Chem., 1929, **42**, 283—284).—The ease with which hydrogen halide is removed from halogenated elæostearic acid suggests the possibility of the formation of an *o*-disubstituted aromatic compound which should yield phthalic acid on oxidation; none could be found, however, on carrying out a test. The fluorescein test for phthalic acid is not specific unless the condensation with resorcinol is conducted at 205—210° without sulphuric acid; in the presence of the latter many other compounds give fluorescent condensation products. A. R. POWELL.

Determination of lactic acid. T. E. FRIEDEMANN and A. I. KENDALL (J. Biol. Chem., 1929, **82**, 23—43).—The yield of acetaldehyde obtainable from lactic acid by oxidation with potassium permanganate or with manganese dioxide is increased by diluting the oxidising agent and by working in the presence of large amounts of manganese sulphate and at a low acidity (about 0·1*M*-phosphoric acid). A modification of the method of Friedemann, Cotonio, and Shaffer (A., 1927, 800) is described which is based on a consideration of the factors mentioned and by which a yield of 97—99% of acetaldehyde is obtainable from pure solutions of lactic acid. The determination of lactic acid in various biological fluids is discussed.

C. R. HARINGTON.

Determination of pyruvic acid. B. H. R. KRISHNA and M. SREENIVASAYA (J. Indian Inst. Sci., 1929, **12A**, 41—51).—A method, applicable to quantities of pyruvic acid between 0·5 and 15 mg. in solutions of concentration 0·1—0·05%, is based on determination of acetaldehyde formed by permanganate oxidation of lactic acid produced by reduction of pyruvic acid by the zinc–copper couple in sulphuric acid solution. The probable error of a single determination is about 1·1%. The method may be used for biological fluids, provided that proteins be first removed by precipitation and all preformed acetone, acetaldehyde, etc. driven off by distillation in a vacuum. Pyruvic acid is then extracted from the nearly dry residue with sodium hydrogen sulphite solution and determined. R. J. W. LE FÈVRE.

Hydroxypolymethylenecarboxylic acids with eight to twenty-one carbon atoms. P. CHUIT and J. HAUSSER (Helv. Chim. Acta, 1929, **12**, 463—492).—ω-Hydroxyaliphatic acids, $OH\cdot[CH_2]_n\cdot CO_2H$ ($n=7$—20), have been prepared by reduction of alkyl or alkyl hydrogen polymethylenedicarboxylates, oxidation of polymethylene glycol monoacetates or bromides (with subsequent replacement of bromine by hydroxyl), from bromohydrins by treatment with potassium cyanide and subsequent hydrolysis, and by oxidative fission of unsaturated alcohol acetates. Thus, reduction of potassium ethyl suberate with sodium and alcohol and subsequent treatment with a mixture of acetic and hydrochloric acids give *η-acetoxyoctoic acid*, b. p. 155—158°/1·5 mm., m. p. 9—10°, d^{20} 1·042, hydrolysed to *η-hydroxyoctoic acid*, m. p. 58° (*methyl* ester, b. p. 137—138°/8 mm., d^{20} 0·992). Treatment of this with an acetic acid solution of hydrogen bromide yields *η-bromo-octoic acid*, b. p. 147—150°/2 mm., m. p. 38·5—39°. Similar reduction and treatment of potassium ethyl azelate affords the acetyl derivative, b. p. 192—193°/10 mm., m. p. 1°, d^{20} 1·025, of θ-hydroxynonoic acid (I), m. p. 51—51·5° (methyl ester, b. p. 147—150°/13 mm., d^{20} 0·978), also obtained in 8% yield by reduction of ethyl azelate. Oxidation of *ι-bromononan-α-ol*, b. p. 125—126°/2 mm., m. p. 33·5°, with potassium dichromate and sulphuric acid in presence of benzene yields θ-*bromononoic acid* (II), b. p. 160—161°/2 mm., m. p. 36—36·5°, together with *ι-bromononyl* θ-*bromononoate* (III), b. p. 228—232°/2 mm., m. p. 5°, d^{15} 1·237. Treatment of II with potassium acetate at 200° and subsequent hydrolysis furnishes I: during this reaction the *substance* (IV), $OAc\cdot[CH_2]_8\cdot CO_2\cdot[CH_2]_8\cdot CO_2H$, m. p. 40°, is also produced. Similar treatment of III gives a *diacetate*, b. p. 222—223°/1 mm., d^{20} 0·988, hydrolysed by alcoholic potassium hydroxide to I and nonane-αι-diol. When θ-acetoxynonoic acid is heated with a small amount of potassium acetate at 200—210°, IV results: this is also hydrolysed to I. Oxidation of nonane-αι-diol monoacetate, b. p. 159—161°/10 mm., d^{20} 0·955, with chromic and acetic acids, and subsequent hydrolysis gives I. The dimeric intermolecular *acid*, $OH\cdot[CH_2]_8\cdot CO_2\cdot[CH_2]_8\cdot CO_2H$, m. p. 60—61°, is obtained when I is heated at 100°/vac.; at 200°/vac. the *substance* $CO_2H\cdot[CH_2]_8\cdot\{CO_2\cdot[CH_2]_8\}_3\cdot OH$, m. p. 71—72°, results. When the methyl ester of ι-hydroxydecoic acid (Grün and Wirth, A., 1922, i, 804; Chuit and others, A., 1927, 40) (*ι-bromo-acid*, b. p. 163—165°/2 mm., m. p. 42—42·5°) is heated at 220—230°, methyl alcohol is eliminated and the dimeric *methyl* ester, $OH\cdot[CH_2]_9\cdot CO_2\cdot[CH_2]_9\cdot CO_2Me$, m. p. 56—56·5°, is formed. The acid itself gives small amounts of complex condensation products. κ-Hydroxyundecoic acid (Walker and Lumsden, J.C.S., 1901, **79**, 1193) (*acetyl* derivative, b. p. 184—185°/2 mm., m. p. 34°; *methyl* ester, b. p. 168—169°/8 mm., m. p. 27—27·5°), is obtained by hydrolysis of the corresponding *nitrile*, b. p. 186—187°/13 mm., m. p. 12—13°, d^{20} 0·910, or by condensing ι-bromononan-α-ol and ethyl sodiomalonate, with subsequent thermal decomposition of the intermediate dicarboxylic acid.

[With G. Malet.]—λ-Hydroxydodecoic acid [sabinic acid] (Bougault and Bourdier, A., 1909, i, 82; Lycan and Adams, this vol., 423) (methyl ester, m. p. 34—34·5°) is obtained by the malonic ester method from κ-bromodecan-α-ol, and by the hydrolysis of λ-acetoxydodecoic acid, m. p. 45°, formed together with λ-*acetoxydodecaldehyde*, b. p. 143—145°/0·5 mm., m. p. 8—9°, d^{15} 0·9436 (*semicarbazone*, m. p. 85—86°), by the action of ozone on tridecenyl acetate (Chuit and others, A., 1927, 445). λ-*Bromododecoic acid* has m. p. 52—52·2°. Hydrolysis of the waxy residue obtained during the reduction of ethyl brassylate (cf. A., 1926, 499) with aqueous-alcoholic sodium hydroxide gives an insoluble *sodium* salt of μ-hydroxytridecoic acid (V) (*acetyl* derivative, b. p. 202—205°/1·5 mm., m. p. 49—49·2°; *methyl* ester, b. p. 192—193°/10 mm., m. p. 44·5°). μ-*Bromotridecoic acid*, m. p. 59—59·2°, is prepared by the action of hydrobromic acid on V, or by oxidation of ν-*bromotridecan-α-ol*, m. p. 59°. ν-*Bromotridecanyl* μ-*bromotridecoate* has m. p. 38—39°. ν-Hydroxytetradecoic acid, m. p. 91—91·5° (*acetyl* derivative, b. p. 215°/3 mm., m. p. 54—54·5°; *methyl* ester, b. p. 196—198°/10 mm., m. p. 47°; ν-*bromo-acid*, m. p. 61·8—62°), is formed by hydrolysis of the corresponding *nitrile*, b. p. 205°/4 mm., m. p. 53°, by reduction of methyl dodecane-αμ-dicarboxylate, and by the malonic ester method from μ-bromodecan-α-ol. By methods similar to the last two ξ-hydroxypentadecoic acid, m. p. 84·8—85·2° (lit. 82—82·5°; *acetyl* derivative, b. p. 219—221°/2 mm., m. p. 59·4—59·6°; *methyl* ester, b. p. 180—182°/2 mm., m. p. 52—52·5°; ξ-*bromo-acid*, m. p. 65·2—65·5°), is prepared. Oxidation of *hexadecane-απ-diol monoacetate*, b. p. 217—218°/8 mm., m. p. 54—54·5° (*diacetate*, b. p. 193—194°/1·5 mm., m. p. 47°), with chromic and acetic acids gives ο-*acetoxyhexadecoic acid*, m. p. 62°, hydrolysed to ο-hydroxyhexadecoic acid (VI) [juniperic acid] (*methyl* ester, b. p. 194—196°/2 mm., m. p. 55—55·5°; ο-*bromo-acid*, m. p. 70—70·5°), prepared also by reduction of methyl tetradecane-αξ-dicarboxylate. When VI is heated at 125°/vac. a tetrameric intermolecular *acid*, $C_{64}H_{122}O_9$, m. p. 87·5—88°, results. π-Hydroxyheptadecoic acid, m. p. 87·5—88° (lit. 84—85°; *acetyl* derivative, b. p. 223—225°/1 mm., m. p. 67·6—68°; *methyl* ester, b. p. 210°/3 mm., m. p. 58·6—59°; π-*bromo-acid*, b. p. 219—220°/1 mm., m. p. 70·5—71°), ρ-*hydroxyoctadecoic acid*, m. p. 96·6—97·2° (*acetyl* derivative, b. p. 228—231°/1·5 mm., m. p. 70—70·5°; *methyl* ester, m. p. 61·5—62°; ρ-*bromo-acid*, b. p. 240—241°/4 mm., m. p. 75·2—75·8°), σ-*hydroxynonadecoic acid*, m. p. 91—91·5° (*acetyl* derivative, b. p. 225—229°/2·5 mm., m. p. 70—70·2°; *methyl* ester, m. p. 65·6—66°; σ-*bromo-acid*, b. p. 225—228°/2·5 mm., m. p. 73—74°), τ-*hydroxyeicosoic acid*, m. p. 97·4—97·8° (*acetyl* derivative, b. p. 235—240°/3 mm., m. p. 77°; *methyl* ester, m. p. 68—68·5°; τ-*bromo-acid*, b. p. 245—247°/3 mm., m. p. 77—78°), and υ-*hydroxydocosoic acid*, m. p. 92·5—93° (*acetyl* derivative, b. p. 239—242°/3 mm., m. p. 73·8—74·2°; *methyl* ester, m. p. 70—71°; υ-*bromo-acid*, m. p. 75—76°), are prepared by reduction of the requisite polymethylenedicarboxylate.

The m. p. of the hydroxy-acids alternate, the even-numbered series being the less fusible. The m. p. of the methyl esters approximate to a curve which ascends with increasing number of carbon atoms. There is no simple relationship between m. p. and number of carbon atoms in the acetoxy- and bromo-derivatives.

H. Burton.

Complex oxalates of quadrivalent molybdenum. H. M. Spittle and W. Wardlaw (J.C.S., 1929, 792—799).—When molybdenum trihydroxide, carefully freed from ammonia and ammonium salts, is treated with oxalic acid and then evaporated rapidly in absence of air, a deep brown solution is obtained, which is oxidised by ammonia-free air, giving a bright red solution (*A*) of molybdenyl oxalate. Addition of a large amount of alcohol to this and treatment with the appropriate base affords amorphous, bluish-pink, *dipyridinium*, *dipotassium*, and *diammonium trimolybdenumtetroxytrioxalates*, $B_2[Mo_3O_4(C_2O_4)_3,5H_2O]$ ($B=C_5H_5N$, K, and NH_4, respectively). These salts dissolve readily in water, giving bright red solutions, in which the oxalate ion cannot be detected. Addition of alkali in the cold does not give an immediate precipitate of molybdenum hydroxide, and the solutions possess marked reducing properties. When *A* is concentrated on the water-bath and then treated with alcohol and solid ammonium oxalate the purplish-red *salt*, $(NH_4)_2[Mo_3O_4(C_2O_4)_3,5H_2O],1\cdot5EtOH$, is obtained. Molybdenyl oxalate, $MoO(C_2O_4),3H_2O$, is best formulated as the compound $H_2[Mo_3O_4(C_2O_4)_3,xH_2O]$, containing a polynuclear complex of three molybdenum atoms, and not as $H_2[MoO_2(C_2O_4),2H_2O]$. This is supported by molecular conductivity measurements at 0° of the above dipyridinium and ammonium salts, which indicate that they are ternary electrolytes. When *A* is concentrated by boiling and then treated with acetone *pentamolybdenum hexaoxytetroxalate*, $Mo_5O_6(C_2O_4)_4$ (purple), is precipitated. Extraction of this with aqueous alcohol at the ordinary temperature gives *tetramolybdenum pentaoxytrioxalate*, $Mo_4O_5(C_2H_4)_3,10H_2O$ (brown), also obtained by atmospheric oxidation of a suspension of molybdenum oxyoxalate (A., 1925, i, 893) in water or aqueous oxalic acid. Both these complex salts are converted by treatment with appropriate concentrations of oxalic acid into molybdenyl oxalate. H. Burton.

Stability of complex metallic salts. F. G. Mann (J.C.S., 1929, 651—658).—The stability of complex metallic salts is usually considered to be dependent on the electronic structure of the co-ordinated metal, since during co-ordination the metal endeavours to increase the number of its electrons to that of the next inert gas. This explains the great stability of the complex tervalent cobalt salts (inert gas configuration), and accounts for the instability of potassium ferricyanide (electron deficiency) when compared with the ferrocyanide. Where two types of salts are obtained, *e.g.*, nickel tetrammino- and hexammino-series, the excess of electrons in the latter series causes a greater instability. A second factor is now considered, namely, the ease with which a polyamine molecule can arrange itself around a complex (square, tetrahedron, octahedron, or cube, according to the co-ordination number). Thus, αβγ-triaminopropane (I) =[ptn], when treated with zinc nitrate and potassium iodide gives the very stable *bistriaminopropanezinc iodide* $[Zn\,ptn_2]I_2$, decomp. 255—270°, where the metal has a co-ordination number of 6 (cf. Mann and Pope, A., 1925, i, 373; 1926, 1233; Mann, A., 1928, 622), and an excess of 4 electrons over the inert gas configuration. Bivalent palladium also adopts the abnormal co-ordination number 6 (cf. Mann, *loc. cit.*) in order to provide the necessary octahedron for maximum stability. Thus, the reaction product from ammonium chloropalladite and I, when treated with potassium iodide, yields *bistriaminopropanepalladous iodide*, m. p. 230° (decomp.), where the metal has an excess of 2 electrons. If the above reaction product is treated with potassium thiocyanate and acetic acid *bis(triaminopropanemonothiocyanate)palladous dithiocyanate*, m. p. 166—168° (decomp.), is obtained; here the metal shows the normal co-ordination number of 4. The same co-ordination number is shown by cadmium in all its complex salts with I. *Tetrakistriaminopropanetriscadmium hexaiodide*, $[Cd_3ptn_4]I_6$ (*hexabromide* $+3H_2O$), is converted by boiling with water into *monoiodotriaminopropanecadmium monoiodide*, m. p. 210—213°. *Monobromotriaminopropanecadmium monobromide*, m. p. 221—223° (decomp.), is obtained similarly. *Dithiocyanato(triaminopropane-monohydrochloride)-cadmium*, m. p. 150—154° (decomp.), when exposed to air loses hydrogen chloride yielding *monothiocyanatotriaminopropanecadmium monothiocyanate*, [SCN ptn Cd]SCN, m. p. 201—202° (decomp.).

H. BURTON.

Preparation of maleic acid by catalytic oxidation of benzene. T. YABUTA and R. SIMOSE (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 197—205).—The method of preparation of the catalyst, the effect of acid oxides on the vanadium oxide (catalyst ?), and the influence of the diluent gas in the reaction mixture of benzene and air have been studied. H. BURTON.

Supposed αββ-trimethylglutaric acid of Noyes and Skinner. F. E. RAY (J. Amer. Chem. Soc., 1929, **51**, 930—932).—Prolonged hydrolysis of ethyl α-cyano-αββ-trimethylglutarate (Perkin and Thorpe, J.C.S., 1899, **75**, 65) with boiling aqueous 50% potassium hydroxide affords *α-carboxy-αββ-trimethylglutaric acid* (I), m. p. 189—190° (decomp.), which is decarboxylated at 200° to αββ-trimethylglutaric acid. The tricarboxylic acid obtained by Noyes and Skinner (A., 1918, i, 65) from *iso*aminocamphonanic acid has a mol. wt. of 192—194 and not 218 as previously stated. It cannot be identical with I, since it appears to be decarboxylated to ααβ-trimethylglutaric acid (A., 1928, 394). H. E. F. NOTTON.

α-*iso*Propylglutaconic acid. K. V. HARIHARAN, K. N. MENON, and J. L. SIMONSEN (J. Indian Inst. Sci., 1928, **11**, **A**, 207—214).—See A., 1928, 395.

Determination of configuration in the terpene series. II. Optically active forms of β-*iso*propyladipic acid and their relationship to the optically active limonenes. J. VON BRAUN and G. WERNER (Ber., 1929, **62**, [*B*], 1050—1058).—*p-iso*Propylphenol is readily hydrogenated in the presence of nickel at about 150° to a mixture of the *cis*- and *trans*-forms of *p-iso*propyl*cyclo*hexanol, which is oxidised by alkaline permanganate at a temperature not exceeding 10° to *dl*-β-*iso*propyladipic acid, m. p. 75° (yield 50%) (*ethyl* ester, b. p. 145—150°/12 mm., d_4^{20} 0·9776). The acid is resolved by strychnine in aqueous solution, thus giving d-β-iso*propyladipic acid*, m. p. about 66°, $[\alpha]_D$ +5·4° (as sodium salt). d-β-iso*Propyladipyl chloride*, b. p. 145—146°/15 mm., d_4^{20} 1·1023, $[\alpha]_D^{20}$ +1·134°, d-β-iso*propyladipamide*, m. p. 169·5°, $[\alpha]_D^{20}$ +9·5° in water, and *ethyl* d-β-iso*propyladipate*, b. p. 145—150°/13 mm., d_4^{20} 0·9776, $[\alpha]_D^{20}$ −1·534°, are described.

The initial step in establishing the connexion between α-limonene and β-*iso*propyladipic acid consists in the saturation of the Δ^a-linking of the hydrocarbon. Treatment with hydrogen chloride is unsatisfactory, since it induces marked racemisation at the C^4 atom and the activity of the limonene hydrochloride depends greatly on the duration of the action. The hydrocarbon is, however, readily hydrogenated in the presence of platinum-black to dihydrolimonene, $[\alpha]_{578}$ +118°, whereas when palladium is used as catalyst a mixture of dihydrolimonene, *p*-menthane, and limonene is produced. Ozonisation of dihydrolimonene in glacial acetic acid followed by reduction of the ozonide with zinc dust and water gives ε-keto-β-*iso*propylheptaldehyde, b. p. 130—132°/12 mm., d_4^{20} 0·9393, $[\alpha]_D^{20}$ −6·97° (semicarbazone, m. p. 182—183°), oxidised to *ε-keto*-β-iso*propylheptoic acid*, b. p. 188°/12 mm., d_4^{20} 1·020, $[\alpha]_D^{20}$ +2·5°, converted by alkaline hypobromite into +β-*iso*propyladipic acid.

H. WREN.

Potassium permanganate oxidation of carotinoids. P. KARRER (Helv. Chim. Acta, 1929, **12**, 558).—A question of priority (cf. Kuhn, Winterstein, and Karlovitz, this vol., 425). H. BURTON.

Effect of heat on malic acid. F. W. MORSE (J. Amer. Chem. Soc., 1929, **51**, 1276—1279).—In order to ascertain the cause of the decrease in free acid content observed in cranberries dried at 85°, samples of the two principal acid constituents (cf. Nelson, A., 1927, 798), citric and *dl*-malic acids, have been heated at 65—95°. The former remains unchanged, but the latter is slowly dehydrated at temperatures above 75°, giving finally an anhydride (?) $C_6H_6O_4(CO_2H)_2$ (cf. Walden, A., 1900, i, 10). This is almost completely hydrolysed when its neutralised solution is boiled for several hours, and the same effect is observed with extracts of the dried cranberries.

H. E. F. NOTTON.

Aconitic acids. I. R. MALACHOVSKI and M. MASLOVSKI (Rocz. Chem., 1929, **9**, 49—55).—See this vol., 172.

Osones for the synthesis of ketouronic acids. T. KITASATO and C. NEUBERG (Biochem. Z., 1929, **207**, 230—231).—Sufficient alkali-free lead carbonate to remove all hydrochloric acid is added with stirring to the solution obtained from the hydrolysis of an osazone with concentrated hydrochloric acid, free phenylhydrazine hydrochloride having first been removed by cooling with ice and filtration. As much lead chloride as possible is separated by preserving the cold liquid, part of the colouring matter which is also present being thus carried down. The filtered solution is then decolorised by shaking with animal charcoal at the ordinary temperature and can be used directly for the preparation of ketouronic acids (cf. following abstract). W. McCartney.

Further syntheses of α-keto-acids of the carbohydrate series. α-Keto-*d*-galactonic acid and α-ketomaltobionic acid. T. Kitasato (Biochem. Z., 1929, **207**, 217—229).—Osones of disaccharides can be oxidised by bromine to α-keto-acids in the same way as are those of monosaccharides (cf. A., 1927, 544). *d*-Galactosone gives *α-keto*-d-*galactonic acid*, $[\alpha]_D^{21}$ −7·8° [*barium* salt $+H_2O$; *calcium* salt; *brucine* salt, m. p. 175° (decomp.), $[\alpha]_D^{21}$ −24·55° in water]. The acid readily reduces alkaline copper solutions and ammoniacal silver nitrate solutions. Similarly, maltosone gives *α-keto*-d-*maltobionic acid*, $[\alpha]_D^{20}$ +54·9° [*brucine* salt, $+2H_2O$, and anhyd., m. p. 150—160° (decomp.), $[\alpha]_D^{20}$ +11·4° in water; *barium* salt, $[\alpha]_D^{20}$ +54·8° in water]. The acid reduces Fehling's solution and is hydrolysed by sulphuric acid and by maltase. W. McCartney.

Dithioformic acid. II. T. G. Levi (Atti R. Accad. Lincei, 1929, [vi], **9**, 170—175; cf. A., 1923, i, 996).—Dithioformic acid, $(CH_2S_2)_3$, m. p. 55—60° (decomp.), forms the following derivatives: *potassium*, m. p. 193° (decomp.); *ammonium*; *methyl*, m. p. 105·5; *ethyl*, liquid; *propyl*, m. p. 38—39°, two *benzyl*, probably *cis–trans*-isomerides, m. p. 154° and 77°, respectively; *monosulphide*, $C_2H_2S_3$, m. p. 195° (decomp.). When heated, the acid decomposes, giving hydrogen sulphide, carbon disulphide, carbon, and sulphur. The trimeric constitution of the acid and its esters indicates a cyclic structure with alternating carbon and sulphur atoms. T. H. Pope.

Constitution of high molecular substances. H. Staudinger (Naturwiss., 1929, **17**, 141). K. H. Meyer (*ibid.*, 255).—Polemical. R. A. Morton.

Formation of acetaldehyde from alanine in presence of pyrocatechol. F. Schaaf (Biochem. Z., 1929, **205**, 449—450).—Equivalent amounts of pyrocatechol and alanine shaken with oxygen yield small amounts of acetaldehyde, detected by its compound with dimethyldihydroresorcinol. This confirms the author's theory of the mechanism of the formation of melanin by oxidation of 3 : 4-dihydroxyphenylalanine. J. H. Birkinshaw.

Trimethyl- and dimethylethyl-acetaldehydes. J. B. Conant, C. N. Webb, and W. C. Mendum (J. Amer. Chem. Soc., 1929, **51**, 1246—1255).—Magnesium *tert.*-butyl chloride and excess of formaldehyde give, in addition to *tert.*-butylcarbinol, *methylene ditert.-butyl ether*, b. p. 182—185°. Magnesium *tert.*-amyl chloride gives similarly *tert.*-amylcarbinol and *methylene ditert.-amyl ether*, b. p. 220—224°. The carbinols are dehydrogenated by the method of Bouveault (A., 1908, i, 117) to trimethyl- and dimethylethyl-acetaldehydes, which autoxidise in air or oxygen to the corresponding acids (cf. Samec, A., 1907, i, 286). The change is retarded by quinol, but not to the same extent as with benzaldehyde. The photochemical decomposition of trimethylacetaldehyde into carbon monoxide and *iso*butane (cf. Hinterberger, Diss., Vienna, 1923) is effected mainly by light of wavelength 2950—3200 Å. Dimethylethylacetaldehyde behaves similarly. The proportions of (*a*) primary, (*b*) secondary alcohol formed from (A) trimethyl- and (B) dimethylethyl-acetaldehydes and excess of the following Grignard reagents are: magnesium *n*-propyl bromide: A (*a*) a trace, (*b*) 50% of the theoretical; B (*a*) 15%, (*b*) 45%; magnesium *iso*propyl bromide: A (*a*) 10%, (*b*) 33%; B (*a*) 33%, (*b*) 27%; and magnesium *tert.*-butyl chloride: A (*a*) 66%; B (*a*) 60%. These reactions illustrate the effect of branched chains on the course of the reaction (cf. this vol., 675). Trimethylacetaldehyde undergoes the Cannizzaro reaction to the extent of 60% in presence of alcoholic (but not aqueous) potassium hydroxide. H. E. F. Notton.

Derivatives of glycollaldehyde and methylglyoxal. H. O. L. Fischer and L. Feldmann (Ber., 1929, **62**, [*B*], 854—865; cf. A., 1927, 857).—Full details are given of the preparation of glycollaldehyde, m. p. 76°, by ozonisation of allyl or cinnamyl alcohol in glacial acetic acid and reduction of the ozonides by zinc dust. The yields are 20—25% and 6%, respectively; the poor yield in the latter case is due in part to the volatility of glycollaldehyde with steam. *Methyl allyl carbonate*, b. p. 38°/18 mm., $n_D^{20·3}$ 1·4118, prepared from allyl alcohol and methyl chloroformate in pyridine, is converted by successive treatment with ozone and zinc dust into O-*carbomethoxyglycollaldehyde*, $CO_2Me·O·CH_2·CHO$, b. p. 78—79°/17 mm., $n_D^{20·4}$ 1·4171 (yield 39%), transformed by ethyl orthoformate in presence of ethyl alcohol and ammonium chloride into the corresponding *diethylacetal*, b. p. 72—75°/0·3—0·4 mm., $n_D^{20·3}$ 1·4105. Ozonisation and subsequent reduction of allylglucoside tetra-acetate affords *glycollaldehydeglucoside tetra-acetate*, $C_2H_3O·O·C_6H_7O_5Ac_4$, which could not be caused to crystallise; it is hydrolysed by sulphuric acid to dextrose and glycollaldehyde; the amorphous substance is converted by methyl-alcoholic hydrogen chloride and subsequent re-acetylation by acetic anhydride and pyridine into its *dimethylacetal*, m. p. 84° after softening, $[\alpha]_D^{18}$ −20·48° in methyl alcohol, also obtained from acetobromoglucose, glycollaldehyde dimethylacetal, and silver carbonate in chloroform.

[With G. Dangschat.]—Vinyl acetate, dissolved in glacial acetic acid, is converted into its dibromide, which is transformed by potassium acetate into *glycollaldehyde triacetate*, m. p. 52°, also obtained by protracted ebullition of crystalline glycollaldehyde with acetic anhydride. *Diacetoxyacetone*, from dihydroxyacetone and boiling acetic anhydride, has m. p. 46—47·5°. Treatment of anhydrous, monomeric methylglyoxal with acetic anhydride affords the *diacetate*, $COMe·CH(OAc)_2$, b. p. 115—116°/13 mm., converted by concentrated hydrogen peroxide into a *substance*, $C_7H_{10}O_6$, m. p. 78—79° after softening, the nature of which has not been fully elucidated. Two mols. of the compound liberate 2 atoms of iodine from hydriodic acid and Freudenberg's method indicates the presence of three acetyl groups, obviously due to oxidation of the methylglyoxal residue during the determination. With an excess of phenylhydrazine acetate it yields methylglyoxalphenylosazone.

Full details are given of the preparation of methylglyoxal from dihydroxyacetone and phosphoric oxide, the apparatus being designed so that collection and re-distillation of the sensitive product are effected without exposing it to air. The oxidation of tartaric acid to dihydroxymaleic acid is described at length.

H. Wren.

Methylations with diazomethane in the presence of catalysts. II. H. Meerwein, T. Bersin, and W. Burneleit [with P. Pöhls] (Ber., 1929, **62**, [*B*], 999—1009; cf. A., 1928, 1217; Arndt and others, this vol., 328).—Acetone, undiluted or dissolved in ether, toluene, heptane, acetonitrile, chloroform, or acetic anhydride, does not react appreciably with diazomethane at 0° as shown by the rate of evolution of nitrogen and the diminution of the diazomethane content as indicated by titration with ethereal benzoic acid. Formation of an additive product of acetone and diazomethane does not appear to occur. Experiments with chloral and diazomethane show that such additive compounds are not decomposed by ethereal benzoic acid, which thus indicates only free diazomethane. The reaction of the last-named compound with ketones is greatly influenced by catalysts, both electrolytes and compounds of marked dipolar character such as water and alcohols. Acetone reacts fairly energetically with diazomethane in the presence of 70% of formamide, giving mainly *as*-dimethylethylene oxide; methyl ethyl ketone is produced to some extent, whereas the formamide is scarcely methylated.

Chloral hydrate is transformed by ethereal diazomethane mainly into γγγ-trichloropropylene αβ-oxide, b. p. 41—42°/10 mm., with small amounts of chloral dimethylacetal, methyl alcohol, methyl ether, and a nitrogenous compound, b. p. 98—103°/3 mm. Chloral hydrate must therefore have the constitution $CCl_3\cdot CH(OH)_2$ and its methylation is ascribed to its acidic character. The interaction of diazomethane with solutions of chloral alcoholates in the corresponding alcohols proceeds similarly, yielding γγγ-trichloropropylene αβ-oxide and the unsymmetrical chloral methylalkylacetals. Simultaneously a more or less considerable proportion of the alcohol (except *tert.*-butyl alcohol) passes, under the influence of the acidic alcoholate, into its methyl ether. The alcoholates are therefore normal valency compounds which are partly dissociated into their components in alcoholic solution at 0°. The percentage yield of γγγ-trichloropropylene αβ-oxide in presence of the various alcohols is ethyl (10·9), *n*-propyl (9·6), *iso*-propyl (23·4), *n*-butyl (16·6), *tert.*-butyl (88·8).

In the presence of 25% of βββ-trichloroethyl alcohol, acetone reacts vigorously with diazomethane, with formation of *as*-dimethylethylene oxide and methyl ethyl ketone, whilst a portion only of the alcohol is transformed into its methyl ether. Since reaction between acetone and diazomethane is not, in general, induced by organic acids, the process appears influenced by the nature of the anion as well as by the strength of the acid.

H. Wren.

Methyl ethers of diacetyldioxime. E. Thilo (Ber., 1929, **62**, [*B*], 866—871).—The monomethyl ether (Charrier, A., 1907, i, 829) and dimethyl ether (Avogadro and Tavola, A., 1925, i, 1040) of diacetyldioxime are shown to be *O*-compounds. Treatment of the dimethyl ether with fuming hydrochloric acid at about 60° results in the production of diacetyl and *O*-methylhydroxylamine (isolated as the hydrochloride) with unchanged di-ether. Similarly, the mono-ether affords diacetyl, diacetyldioxime, hydroxylamine, and *O*-methylhydroxylamine. With 1% hydrochloric acid at about 60° the mono-ether is partly unchanged, partly converted into diacetylmonoxime methyl ether and diacetyldioxime. One part of the mono-ether loses the oximino-group, whilst another portion loses the methylated oximino-group; if the mixture is cooled the products interact, giving mono-ether and diacetyldioxime and its di-ether in equivalent amounts. The disproportionation of the mono-ether into diacetyldioxime and its dimethyl ether shows that the alkyl group in the former is analogously linked to those in the latter, and this conclusion is confirmed by the formation of the di- from the mono-ether and methyl sulphate in feebly alkaline solution. Diacetylmonoxime is transformed by a slight excess of *O*-methylhydroxylamine into the monomethyl ether (yield 80%). Similarly, diacetylmonoxime methyl ether and *O*-methylhydroxylamine give the di-ether in almost theoretical yield.

H. Wren.

Compounds of sugars with sulphuric acid. II. Reaction for the differentiation of ring-isomeric, acylated halogeno-sugars. H. Ohle, W. Marecek, and W. Bourjau (Ber., 1929, **62**, [*B*], 833—854; cf. A., 1925, i, 634).—All acylated 1-halogeno-sugars containing a 1 : 5-oxygen bridge give esters of the type $R\cdot O\cdot SO_2\cdot O\cdot N(C_5H_5)\cdot R$ [R= acylated sugar residue) when treated with pyridine in the presence of silver sulphate. Furoid compounds appear to give salts of the type $R\cdot N(C_5H_5)\cdot O\cdot SO_2\cdot O\cdot N(C_5H_5)\cdot R$, but the available material is not sufficiently diverse in character to enable a decision to be reached with regard to the specificity of ester formation.

Benzyl chloride, pyridine, and silver sulphate give *benzylpyridinium sulphate*, $C_{24}H_{24}N_2SO_4$, m. p. 117—118°. Chloroacetic acid similarly affords *carboxymethylpyridinium sulphate*, m. p. 177° (decomp.), whereas ω-bromoacetophenone yields *phenacylpyridinium sulphate*, m. p. (indef.) 210—225° (probably an equimolecular mixture of the normal and hydrogen salts). Chlorodiethyl ether and pyridine yield pyridine hydrochloride and acetaldehyde diethylacetal.

The acylated 1-halogeno-sugars are obtained by the established method or by Pacsu's process (A., 1928, 1118), using titanium tetrachloride or tetrabromide. The halogen compound and silver sulphate (mol. ratio, 2 : 1) are shaken with the fivefold to tenfold weight of pyridine over-night at the atmospheric temperature. Tetra-acetyl-*l*-arabinose, b. p. 178°/1·5 mm., $[\alpha]_D^{18}$ +41·78° in chloroform, could not be caused to crystallise when prepared by treatment of *l*-arabinose with acetic anhydride in pyridine. It is converted into acetochloroarabinose, m. p. 146°, $[\alpha]_D^{18}$ +242·61° in chloroform, and thence into *triacetyl*-α-l-*arabinose*-1-*pyridinium triacetyl*-α-l-*arabinose*-1-*sulphate*, $C_{27}H_{35}O_{18}NS$, m. p. 153°, $[\alpha]_D^{18}$ +27·97° in chloroform. Similarly, tetra-acetyl-α-*l*-xylose, m. p. 124·5°, $[\alpha]_D^{18}$ —24·8° in chloroform, is transformed into acetochloroxylose, m. p. 100—101°, $[\alpha]_D^{18}$ +167·85° in chloroform, and *triacetyl*-α-l-*xylose*-1-*pyridinium triacetyl*-α-l-*xylose*-1-*sulphate*, m. p. 143°, $[\alpha]_D^{18}$ —41·71° in chloroform and alcohol. Tetra-acetylrhamnose is transformed by Pacsu's method into crystalline acetochlororhamnose, m. p. 72·5°, $[\alpha]_D^{20}$ —127·03° in chloroform, and thence into *triacetyl*-α-l-*rhamnose*-1-*pyridinium triacetyl*-α-l-*rhamnose*-1-*sulphate*, m. p. 142°, $[\alpha]_D^{18}$ —51·38° in chloroform, and, probably, the β-ester. Acetodibromoglucose, silver sulphate, and pyridine afford 5-*bromo*-2 : 3 : 4-*triacetyl*-β-d-*glucose*-1-*pyridinium* 6-*bromo*-2 : 3 : 4-*triacetyl*-β-d-*glucose*-1-*sulphate* (+2EtOH), m. p. 62—69°. 3-p-*Toluenesulphonyl*-2 : 4 : 6-*triacetyl*-β-d-*glucose*-1-*pyridinium* 3-p-*toluenesulphonyl*-2 : 4 : 6-*triacetyl*-β-d-*glucose*-1-*sulphate*, m. p. 145—146°, $[\alpha]_D^{20}$ —4·47° in chloroform, is described. The furoid 3-*p*-toluenesulphonyl-2 : 5 : 6-triacetyl-1-bromo-*d*-glucose yields a non-crystalline syrup in which sulphur is present entirely in the form of sulphate. Benzobromoglucose gives *tetrabenzoyl*-β-d-*glucose*-1-*pyridinium tetrabenzoyl*-β-d-*glucose*-1-*sulphate*, m. p. 193—194°, $[\alpha]_D$ +15·47° in chloroform. Acetobromogalactose, readily prepared from penta-acetylgalactose and hydrogen bromide in glacial acetic acid, is transformed into *tetra-acetyl*-β-d-*galactose*-1-*pyridinium tetra-acetyl*-β-d-*galactose*-1-*sulphate*, m. p. 172—173°, $[\alpha]_D$ ±0° in chloroform, and *tetra-acetyl*-d-*galactose*-1-*pyridinium sulphate*, m. p. about 170° (decomp.). Acetochloromannose, when prepared from penta-acetylmannose, aluminium chloride, and phosphorus pentachloride in chloroform, does not react with pyridine and silver sulphate, whereas the compound (or the corresponding bromo-derivative) prepared by Pacsu's method is converted into a syrup consisting mainly of the ester salt; in this instance, as with rhamnose, the sugars and their products belong to the same series. β-Penta-acetylfructose is transformed by Pacsu's method directly into tetra-acetylchloro-β-*d*-fructose, m. p. 82°, $[\alpha]_D^{18}$ —160·47° in chloroform, which with pyridine and silver sulphate appears to give a mixture of the ester salts of the α- and β-series in which the α-form preponderates (m. p. 97—109°, $[\alpha]_D^{18}$ —8·48° in chloroform). Acetobromocellobiose affords *hepta-acetyl*-d-*cellobiose*-1-*pyridinium hepta-acetyl*-d-*cellobiose*-1-*sulphate* (+2·5H_2O and anhydrous), m. p. 194—195° (decomp.). *Hepta-acetyl*-β-d-*lactose*-1-*pyridinium hepta-acetyl*-β-d-*lactose*-1-*sulphate*, m. p. 185—186°, $[\alpha]_D^{20}$ —9·44° in chloroform, is described. Acetobromoglucose and dimethylaniline at the ordinary temperature give phenyltrimethylammonium bromide, m. p. 213—214°, whereas the sugar product could not be caused to crystallise. In the presence of silver sulphate, acetobromoglucose is transformed by dimethylaniline into phenyltrimethylammonium tetra-acetyl-β-*d*-glucose-1-sulphate, m. p. 163—164°. H. WREN.

Constitution of chinovose. E. VOTOČEK (Coll. Czech. Chem. Comm., 1929, 4, 234—238).—Oxidation of chinovose with bromine water gave an acid which readily passed into a lactone; reduction of the latter with sodium amalgam furnished chinovose. This is regarded as proof that chinovose is an aldose (cf. Fischer and Liebermann, A., 1894, i, 4).

A. I. VOGEL.

Identity of chinovose with *d*-glucomethylose (*iso*rhodeose). E. VOTOČEK and F. RÁC (Coll. Czech. Chem. Comm., 1929, 4, 239—244).—Reduction of chinovose with sodium amalgam (solution maintained acid with sulphuric acid) gave a syrupy sugar-alcohol which yielded with benzaldehyde a product, m. p. 193—194°, identical with that similarly prepared from *iso*rhodeose, thus indicating that chinovose is a *d*-glucomethylose (cf. Freudenberg and Raschig, this vol., 427). A. I. VOGEL.

Fission of β-glucosan with titanium tetrachloride. G. ZEMPLÉN and Z. CSÜRÖS (Ber., 1929, 62, [*B*], 993—996).—A method is described which permits the preparation of glucose derivatives with a free hydroxyl in the ζ-position Triacetyl-β-glucosan is converted by an excess of titanium tetrachloride in chloroform into α-1-*chloro*-2 : 3 : 4-*triacetylglucose*, m. p. 124—125°, $[\alpha]_D^{19}$ +191·5° in chloroform, smoothly transformed by acetic anhydride and pyridine into α-chloroacetoglucose, m. p. 73°, $[\alpha]_D^{20}$ +165·3° in chloroform. It is converted by methyl alcohol and silver carbonate into 2 : 3 : 4-*triacetyl*-β-*methylglucoside*, m. p. 131—132°, $[\alpha]_D^{19}$ —13·59° in chloroform. With silver carbonate in benzene it gives a tetra-acetyl derivative converted into 1 : 2 : 3 : 4-tetra-acetyl-6-*p*-toluenesulphonyl-β-*d*-glucose (cf. Helferich and Klein, A., 1926, 386). Tribenzoyl-β-glucosan is not affected by titanium tetrachloride under these conditions, whereas pentabenzoylglucose smoothly yields 1-chlorotetrabenzoyl-α-glucose. Trimethyl-β-glucosan yields amorphous products containing relatively little halogen. Penta-acetylgluconic acid and hexa-acetylmannitol are unaffected. 2 : 3 : 4 : 6-Tetramethylglucose is decomposed into ill-defined products.

H. WREN.

Oxidation of dextrose and glycine by means of alkaline copper solutions. H. LUNDIN (Biochem. Z., 1929, 207, 91—106, 107—119).—Glycine (and also other amino-acids) if present in sufficient quantity interfere (at least at p_H 9·1—9·8) with the oxidation of dextrose by alkaline copper solutions such as those of Folin and of Folin and Wu, the interference being the greater the lower is the p_H. Increased time of boiling (standard time 10 min.) reduces the extent of interference. If the oxidation is carried out at p_H 9·8 or more the total reduction of copper is approximately the same as the sum of the reductions due to the dextrose and the glycine separately unless the alkalinity is very high. The extent of oxidation of glycine by the copper solutions increases rapidly with increase of p_H and with increased time of boiling and decreases with low carbonate contents. The optimum alkalinity for the oxidation of dextrose by alkaline copper solutions is p_H 9·2—9·8. When quantities of buffering substances are present in the sugar solutions these must be brought to the p_H of the copper reagent by the addition of sodium hydroxide. Boric acid interferes (at least at p_H 9·1—10·5) in the same way as does glycine with the oxidation of dextrose by alkaline copper solutions, and if very large proportions (400—500 : 1) of it are present the dextrose is not oxidised at all (boiling time 6—7 min.). Alkaline copper solutions containing borate oxidise amino-acids to the same extent as do similar solutions free from borate. A copper solution having the same p_H as the reagent of Folin and Wu and containing 56 g./litre of boric acid (or 86 g./litre of borax) scarcely oxidises small amounts of dextrose, but oxidises amino-acids to the same extent as does the Folin–Wu reagent. The difference in the values obtained when solutions containing glycine (up to 8 g./litre) or creatinine (up to 0·5 g./litre) and dextrose (up to 0·2 g./litre) are oxidised with the Folin–Wu reagent and with this reagent containing borate represents the concentration of dextrose present. The p_H values given are only approximate and refer to the reaction mixtures before heating. The p_H of sugar solutions containing quantities of buffering substances must be brought to the same value as that of the copper solution by the addition of sodium hydroxide before determinations are made. W. McCartney.

Formation of carbon monoxide by the action of oxygen or air on dextrose in alkaline solution. Influence of temperature and alkalinity. M. Nicloux (Compt. rend. Soc. Biol., 1928, 98, 1548—1551; Chem. Zentr., 1928, ii, 1668).—For a 0·5% solution of dextrose, the optimal temperature for the formation of carbon monoxide is 84—85°, and the optimal alkalinity about 0·1*N*. A. A. Eldridge.

Compounds of dextrose and phosphoric acid. B. Helferich and H. Du Mont (Z. physiol. Chem., 1929, **181**, 300—308).—1 : 2 : 3 : 4-Tetra-acetyl-β-glucose reacts with phosphoryl chloride in pyridine giving *tri-*(β-*tetra-acetyl*-d-*glucose*)-6-*phosphate*, m. p. 236—237°, $[\alpha]_D^{27}$ +30·2°. Under different conditions the same substances give β-tetra-acetyl-*d*-glucose-6-chlorohydrin. Hydrolysis of the tri(acetylglucose)-phosphate yields an amorphous product in which phosphoric acid is organically combined, but reacetylation gives back only a small amount of the original ester and secondary changes must have largely taken place. Triacetyl-α-methylglucoside reacts similarly in pyridine to give *tri*(*triacetyl-α-methylglucoside*)*phosphate*, m. p. 185°, $[\alpha]_D^{18}$ +151·9°. This substance on hydrolysis gives tri-(α-methyl-*d*-glucoside)-6-phosphate, which readily reacetylates and also when heated with sodium iodide in a sealed tube gives the corresponding 6-iodohydrin. P. W. Clutterbuck.

Walden inversion in the hexose series. P. A. Levene, A. L. Raymond, and A. Walti (J. Biol. Chem., 1929, **82**, 191—195).—Lævulose-γ-phosphoric acid yielded an *osazone*, m. p. 165—168° after softening at 160°, $[\alpha]_D^{20}$ −138°, which was thus different from the osazone prepared by Fischer and Zach (A., 1912, i, 678) from $\gamma\xi$-anhydroglucose; the new osazone is regarded as $\gamma\xi$-anhydroallosazone, Walden inversion having occurred during hydrolysis of the phosphoric acid group. C. R. Harington.

Syntheses in the carbohydrate group with the aid of sublimed ferric chloride. I. Preparation of biosides of the α-series. G. Zemplén (Ber., 1929, **62**, [*B*], 985—990).—Octa-acetyl-α-cellobiose is converted by sublimed ferric chloride in chloroform containing ethyl alcohol into *hepta-acetyl-α-ethylcellobioside*, m. p. 169—170° after softening, $[\alpha]_D^{18}$ +49·7° in chloroform. The bioside is transformed by hydrogen bromide in glacial acetic acid into acetobromocellobiose, m. p. about 180° (decomp.), $[\alpha]_D^{19}$ +90·5° in chloroform. Its specific rotation is increased to +52·6° by treatment with titanium tetrachloride, thus showing that it is not completely homogeneous. In the absence of alcohol, octa-acetyl-α-cellobiose is not affected by ferric chloride in chloroform. Octa-acetyl-β-maltose yields the amorphous *hepta-acetyl-α-ethylmaltoside*, m. p. about 90—100° after softening at 80—85°, $[\alpha]_D^{17}$ +122·2° in chloroform (changed to +124·4° by treatment with titanium tetrachloride). The method is not available for the synthesis of α-phenylbiosides. Replacement of aliphatic alcohols by tetra-acetyl derivatives of hexoses or hepta-acetyl compounds of bioses leads to the production of higher sugars from completely acetylated sugars in presence of ferric chloride. H. Wren.

Action of metallic aluminium and mercury salts on acetohalogeno-sugars. I. Syntheses of α-biosides. G. Zemplén (Ber., 1929, **62**, [*B*], 990—996).—Acetobromocellobiose is rapidly converted by aluminium filings and dry mercuric acetate in benzene into hepta-acetylcellobiose; reduction in presence of ethyl alcohol affords hepta-acetyl-β-ethylcellobioside, m. p. 186°, $[\alpha]_D^{18}$ −19·44° in chloroform. If phenol is added to the benzene solution, *hepta-acetyl-α-phenylcellobioside*, m. p. 217°, $[\alpha]_D^{17}$ +81·10° in chloroform, results, the specific rotation of which is unchanged after treatment with titanium tetrachloride; the compound is converted by hydrogen bromide in glacial acetic acid into acetobromocellobiose, m. p. about 178° (decomp.), $[\alpha]_D^{18}$ +92·0° in chloroform, and decomposed by sodium hydroxide with production of phenol. *Hepta-acetyl*-α-cyclo*hexylcellobioside*, m. p. 203·5°, $[\alpha]_D^{20}$ +63·4° in chloroform, is prepared in a similar manner. H. Wren.

Synthesis of sucrose. G. Zemplén and A. Gereces (Ber., 1929, **62**, [*B*], 984; cf. Pictet and Vogel, A., 1928, 510, 741).—The condensation of tetra-acetyl-γ-fructose with tetra-acetylglucose in the presence of phosphoric oxide causes the production of 10—15% of a disaccharide from which octa-acetyl-sucrose could not be obtained crystalline. The acetylated sucrose does not crystallise when seeded from mixtures of 50% of it with 50% of tetra-acetyl-γ-fructose or 50% of tetra-acetylglucose. The conditions for the synthesis of sucrose appear particularly subtle. H. Wren.

Condensation of dextrose and lævulose; *iso*sucrose. J. C. Irvine, J. W. H. Oldham, and A. F. Skinner (J. Amer. Chem. Soc., 1929, **51**, 1279—1293).—Freshly prepared ethyl-γ-fructoside is converted by acetic anhydride and sodium acetate into *ethyl-γ-fructoside tetra-acetate*, $[\alpha]_D$ +39·0° to +47·9° in chloroform, n_D 1·4528—1·4542. When this is treated with hydrogen chloride in acetyl chloride and the resulting chloro-derivative hydrolysed with moist silver oxide in benzene γ-fructose tetra-acetate, $[\alpha]_D$

+31·5° in chloroform, +38·7° in benzene, n_D 1·4645, is obtained. It is formed similarly, together with a little crystalline *anhydrofructose triacetate*, $[\alpha]_D$ +37·8° in chloroform, n_D 1·4662, from inulin triacetate. The tetra-acetate, now obtained pure for the first time, differs in rotatory power and solubility from that described by Pictet (A., 1928, 510, 741). It is characterised by its quantitative hydrolysis by 2*N*-sodium hydroxide and by its conversion through methyl-γ-fructoside tetra-acetate and tetramethylmethyl-γ-fructoside into tetramethyl-γ-fructose, $[\alpha]_D$ 26·4°, changing to +30·1°, the behaviour of which in several reactions followed polarimetrically is identical with that of a sample, $[\alpha]_D$ +31·8°, changing to 34·1°, prepared from octamethylsucrose. Of the ten possible disaccharide octa-acetates obtainable from the tetra-acetate and syrupy (α- and β-)glucose tetra-acetates in benzene in presence of phosphoric anhydride, only iso*sucrose octa-acetate*, m. p. 131—132°, $[\alpha]_D$ +19·9° in chloroform, —2·0° in benzene, has been obtained crystalline, although *iso*trehalose octa-acetate is also present. The former is converted by dimethylamine in absolute ethyl alcohol into iso*sucrose*, decomp. 194°, sintering from 152°, $[\alpha]_D$ +50·0° in methyl alcohol, +34·2° in water, which may be identical with Pictet's sucrose-*D* (A., 1928, 1223). It reduces Fehling's solution to a slight extent on prolonged boiling and is more easily hydrolysed by acid and alkali than is sucrose. The same *iso*sucrose is obtained from the condensation product of *chloro-γ-fructose tetra-acetate* (87% pure) with glucose tetra-acetate in chloroform in presence of silver carbonate and sodium sulphate. The crude mixtures of disaccharides obtained from the products of the above condensations have, coincidently, the same rotatory power, both before and after inversion, as sucrose and must therefore contain a disaccharide more dextrorotatory than sucrose. This is regarded as α-glucosido-β(γ)-fructose and *iso*sucrose as β-glucosido-β(γ)-fructose (cf. Pictet, *loc. cit.*), so that sucrose is α- or β-glucosido-β(γ)-fructose, probably the latter. Chloro- or bromo-glucose tetra-acetate does not condense with γ-fructose tetra-acetate in presence of bases. H. E. F. NOTTON.

Cardiac glucoside from *Convallaria majalis*, L. W. KARRER (Helv. Chim. Acta, 1929, **12**, 506—511).—The flowers are extracted with much water, and after treatment with lead acetate, the active principle is adsorbed on charcoal. Extraction of the adsorbate with chloroform and subsequent purification of the residue from alcohol affords *convallatoxin*, m. p. 212—213°. This gives Molisch's test, reduces Fehling's solution after hydrolysis with dilute acid, and yields a red colour changing to green when subjected to Liebermann's cholesterol reaction. Convallatoxin is about 1·5 times as toxic as ouabain. H. BURTON.

Solanine. G. ODDO (Gazzetta, 1929, **59**, 155—160).—See this vol., 299.

[Lignin and cellulose.] K. HESS (Ber., 1929, **62**, [*B*], 924—927).—A reply to Freudenberg (this vol., 430). The "insoluble" methylcellulose of Freudenberg is dissolved by water at 0° after being shaken with water or dissolved in methyl alcohol and chloroform (1 : 1). The non-identity of an anhydride of βγζ-trimethylglucose with trimethylcellulose for which the depression in dilute solution corresponds with that of a trimethylglucosan is not an argument for or against the main valency chain structure of cellulose. The high acetyl content of Freudenberg's preparations of the author's hexa-acetylbiosan is solely due to the presence of known products of acetolysis. H. WREN.

Selective action of three hydroxyl groups of cellulose. T. NAKASHIMA and I. SAKURADA (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, **8**, 272—276).—When cellulose mono-*p*-toluenesulphonate is heated with anhydrous hydrazine at 100° for 15—16 hrs. fission occurs, affording *p*-toluenesulphonic acid, a soluble product (4·55% N), and an insoluble product (2·28% N) (monohydrazine derivative of cellulose requires 16·1% N); both products absorb bromine, but it is not clear whether this is due to unsaturation or to the hydrazine group. The above result indicates the partial formation of a hydrazine derivative of cellulose at the former point of esterification, which is considered to be the secondary hydroxyl group in position 2 or 3 in the $C_6H_{10}O_5$ unit.

The preparation of *tribenzylcellulose* by heating dibenzylcellulose with benzyl chloride and silver oxide is described. C. W. SHOPPEE.

Cellulose benzyl ethers. T. NAKASHIMA (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, **8**, 261—264).—By treatment of cotton paper, which has been steeped in 40—50% sodium hydroxide solution, with sufficient benzyl chloride in benzene or toluene, dibenzylcellulose is obtained in quantitative yield in a single operation. If 10—20% sodium hydroxide solution is employed, a mixture of *monobenzylcellulose* and unchanged cellulose is obtained, from which the latter may be removed by treatment with ammoniacal copper oxide solution. C. W. SHOPPEE.

Celluloseamine and celluloseaniline. I. SAKURADA (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, **8**, 265—271).—Cellulose mono-*p*-toluenesulphonate (A) (Kita, Nakashima, and Sakurada, B., 1926, 944), when heated with concentrated aqueous ammonia at 100° for 24 hrs., affords a product (1 mol. celluloseamine + 1 mol. cellulose + $\frac{1}{2}$ mol. A); the proportion of celluloseamine in the product is not raised by heating for a longer period. Treatment with ammonia in dry ethyl alcohol at 0° for 20 hrs. yields a preparation (1 mol. celluloseamine + 1 mol. cellulose + $\frac{1}{6}$ mol. A). Aniline heated with A in glycerol at 100° for 20 hrs. furnishes a product (2 mols. celluloseaniline + 1 mol. cellulose + 2 mols. A) and after 100 hrs. a product (2 mols. celluloseaniline + $\frac{1}{2}$ mol. cellulose + 1 mol. A); methylaniline behaves similarly. By hydrolysis of any unchanged I in the above products, followed by removal of all cellulose with ammoniacal copper oxide solution, *celluloseamine*, $C_{12}H_{19}O_9{\cdot}NH_2$, and *celluloseaniline*, $C_{12}H_{19}O_9{\cdot}NHPh$, are obtained. C. W. SHOPPEE.

Identification of amines. IV. Methanesulphonamides. C. S. MARVEL and J. P. BELSLEY (J. Amer. Chem. Soc., 1929, **51**, 1272—1274).—Methanesulphonyl chloride (Carius, Annalen, 1860, **114**, 142), prepared by an improved method, gives with amines (2 mols.) in benzene methanesulphonamides, which are readily hydrolysed by boiling for

6 hrs. with 60% sulphuric acid. The following derivatives of methanesulphonanilide, m. p. 100·5° (cf. Duguet, A., 1902, i, 428), are described : o-*methyl*-, m. p. 103° ; p-*methyl*-, m. p. 102·5° ; o-*methoxy*-, m. p. 115·5° ; p-*methoxy*-, m. p. 116° ; p-*ethoxy*-, m. p. 125° ; o-*chloro*-, m. p. 90·5° ; p-*chloro*-, m. p. 148° ; p-*bromo*-, m. p. 136° ; 2 : 5-*dichloro*-, m. p. 174° ; N-*methyl*-, m. p. 76·5° ; N-*ethyl*-, m. p. 59° ; N-n-*propyl*-, m. p. 76° ; N-n-*butyl*-, m. p. 73° ; N-*benzyl*-, m. p. 122° ; oily p-*methyl*-N-*ethyl*- ; oily o-*methyl*-N-*ethyl*-, and N-sec.-*butyl*- ; also *methanesulphon*-α-*naphthylamide*, m. p. 125·5° ; -β-*naphthylamide*, m. p. 153·5° ; -δ-*phenoxybutylamide*, m. p. 79·5°, and oily -l-*menthylamide*, -*diethylamide*, -*di*-n-*butylamide*, and -*di*-n-*propylamide*. The separation of known mixtures of primary, secondary, and tertiary amines is satisfactorily effected by means of methanesulphonyl chloride and alkali, but with mixtures of unknown composition it is difficult completely to remove primary and secondary amines without converting the former into alkali-insoluble diacyl derivatives.

H. E. F. NOTTON.

Additive compound containing oxygen obtained by the action of ozone on tetramethylammonium hydroxide. W. TRAUBE and F. KUHBIER (Ber., 1929, 62, [*B*], 809—820 ; cf. A., 1927, 342).—Tetramethylammonium hydroxide, when exposed in successive thin layers to the action of ozonised oxygen, absorbs 6—8% of its weight of oxygen, yielding an intensely red compound ; repeated successive trituration and ozonisation permits the oxygen content to be raised to 9—10%. Better results are obtained if the product is dried from time to time in a high vacuum, whereby ultimately the hydroxide may absorb 20% of its weight of oxygen. Optimal results are obtained by using tetramethylammonium hydroxide containing 25—28% of water at 20—25°. The best specimens obtained contain 37—41% of their oxygen in evolvable form and contain up to 46% (or 60% if the water content is disregarded) of *tetramethylammonium hydroxyoxide*, $[NMe_4OH]_2O_2$; the remainder is carbonate, partly present in the original material and partly produced by unavoidable oxidation, and small amounts of formate and non-identified oxidation products of the ammonium hydroxide. Nitrite or nitrate is not present. Tetramethylammonium hydroxyoxide is remarkably stable and can probably be preserved indefinitely at the ordinary temperature. At about 75° it decomposes without explosion into oxygen and colourless tetramethylammonium hydroxide. It is converted by water or alcohol into " indifferent " oxygen (which does not liberate bromine from acidified potassium bromide) and tetramethylammonium hydroxide, the proportion of gas being identical with that obtained by thermal decomposition. The solution contains a small amount of hydrogen peroxide which is not connected with the liberation of oxygen from the red compound, since its amount is not increased if the latter is brought directly into acidified potassium iodide solution ; it is due to the presence of an ozonide or peroxide formed by the oxidising action of ozone on tetramethylammonium hydroxide. This action is also observed under conditions such that the formation of the red compounds is excluded, for example, when ozone is passed through an aqueous solution of the ammonium hydroxide ; in this case, also, the products are formic and carbonic acids. Other ammonium hydroxides give intensely-coloured, oxygen adducts with ozone provided they do not offer too great opportunity to the oxidising action of the gas. Tetra-alkylarsonium hydroxides behave similarly, but the behaviour of phosphonium hydroxides is uncertain. H. WREN.

s-Methyl*iso*propylhydrazine and methyl*iso*propyldi-imide. H. C. RAMSPERGER (J. Amer. Chem. Soc., 1929, **51**, 918—921).—Attempts to hydrogenate acetonemethylhydrazone and acetaldazine in presence of colloidal platinum were unsuccessful. αβ-Dibenzoyl*iso*propylhydrazine (cf. Lochte, A., 1922, i, 329) is converted by methyl sulphate and sodium hydroxide in alcohol into *dibenzoylmethyl*iso*propylhydrazine*, m. p. 76·2—76·7°. This is hydrolysed by hydrochloric acid at 100° to α-*methyl*-β-iso*propylhydrazine*, b. p. 79·5—79·7°/371 mm., *d* 0·7959, heat of vaporisation 9150 g.-cal./mol. (*hydrochloride*), which is oxidised by hydrogen peroxide at 0° to faintly yellow *methyl*-β-*azopropane*, b. p. 45·5—46·5°/760 mm., heat of vaporisation 7350 g.-cal./mol. This is the first known simple unsymmetrical aliphatic azo-derivative ; its chemical and physical properties are intermediate between those of azomethane and azo*iso*propane (A., 1928, 254, 255). Its thermal decomposition at 300° is a homogeneous unimolecular reaction.

H. E. F. NOTTON.

Determination of amino-acids formed by hydrolysis of proteins. II. Esters of acetylated amino-acids. E. CHERBULIEZ and P. PLATTNER (Helv. Chim. Acta, 1929, **12**, 317—329).—As a preliminary investigation on the separation of amino-acids obtained by hydrolysis of proteins, acetylated esters have been prepared by esterifying amino-acids with alcoholic hydrogen chloride, and after removal of volatile products the residue is treated with acetic anhydride and sodium acetate. The acetylated ester can then, with one exception (cystine), be obtained by vacuum distillation. If hydroxyl groups are present these are acetylated also. Partial racemisation occurs during the distillation but the b. p. of the *r*-ester is the same as that of the active form. The acetamido-acids are obtained by hydrolysis of the esters with barium hydroxide solution. The following are described : ethyl acetamidoacetate, b. p. 145°/11 mm. ; ethyl *r*-α-acetamidopropionate, b. p. 96°/1 mm., m. p. 38—39° ; *ethyl* α-*acetamido*iso*hexoate*, b. p. 114°/2 mm. ; *ethyl* α-*acetamidosuccinate*, b. p. 180°/15 mm. ; *ethyl* α-*acetamidoglutarate*, b. p. 142°/2 mm. ; *ethyl* r-α-*acetamido*-β-*phenylpropionate*, b. p. 155—157°/2 mm., m. p. 68° ; *ethyl* l-α-*acetamido*-β-p-*acetoxyphenylpropionate*, b. p. 184°/2 mm., m. p. 90°, $[\alpha]_D^{20}$ −16·3° in alcohol (the r-*ester* has b. p. 184°/2 mm., m. p. 102—103°) ; *ethyl* N-*acetylpyrrolidine*-2-*carboxylate*, b. p. 155°/13 mm., $[\alpha]_D^{24}$ −80·43° in alcohol ; *ethyl* N-*acetyl*-4-*acetoxypyrrolidine*-2-*carboxylate*, b. p. 142°/2 mm. ; *ethyl di*-(α-*acetamido*-β-*thiopropionate*), m. p. 123°, $[\alpha]_D^{20}$ −102·3° in alcohol, and *ethyl* α-*acetamido*-β-*thiolpropionate*, b. p. 150—151°/3 mm. H. BURTON.

Curtius and Goebel's glycine anhydride silver. T. ASAHINA (Bull. Chem. Soc. Japan, 1929, 4, 75—77).—A greyish-white compound, $C_4H_4O_2N_2Ag_2$,

apparently identical or isomeric with the glycine anhydride silver compound of Curtius and Goebel (A., 1888, 576), is formed when freshly precipitated silver oxide is agitated with a concentrated aqueous solution of glycine anhydride in presence of ammonia.
B. W. Anderson.

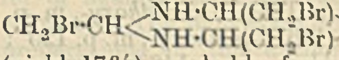
Preparation of lysine, histidine, and arginine from hydrolysed blood-corpuscles by electrical transport. G. J. Cox, H. King, and C. P. Berg (J. Biol. Chem., 1929, **81**, 755—764).—The solution obtained by hydrolysing red blood-corpuscles with sulphuric acid, removal of the latter, and concentration, is subjected, after removal of leucine and tyrosine by filtration, to electrolysis at 110 volts, 0·5 amp., in a three-compartment cell divided by parchmentised paper (compare Foster and Schmidt, A., 1926, 802). By separation of the solution in the cathode compartment at three appropriate stages, and by re-electrolysis of the middle fraction, two solutions are obtained, one containing arginine and lysine and the other histidine. The amino-acids are isolated by the usual methods, 4 kg. of blood-corpuscles yielding histidine monohydrochloride 51 g., arginine monohydrochloride 21 g., and lysine dihydrochloride 62 g.
C. R. Harington.

Carnitin. W. Linneweh (Z. physiol. Chem., 1929, **182**, 8—12; cf. Tomita and Sendju, A., 1927, 1058).—Krimberg's chloroaurate of γ-butyrobetaine, m. p. 201—203° (A., 1908, i, 41), is shown to be impure crotonobetaine chloroaurate, m. p. 214—216°. Crotonobetaine chloroaurate crystallises in different forms according to the source from which it is derived.
C. C. N. Vass.

Reactions of carbon monoxide with metallic compounds of cysteine. W. Cremer (Biochem. Z., 1929, **206**, 228—239).—Iron forms with cysteine and *iso*cysteine carbonyl *compounds* containing 1 g.-atom of iron to 2 mols. of carbon monoxide. These compounds are reversibly dissociated by light. Cobalt forms a *carbonylcobalt-cysteine* with 1 mol. of carbon monoxide, insensitive to light. Carbonylferrocysteine from *d*-cysteine has $[\alpha]_D$ +600°; the cobalt compound is inactive. The catalytic action of iron in the oxidation of cysteine is inhibited by carbon monoxide owing to formation of the complex.
J. H. Birkinshaw.

Physiological activity of -onium compounds. Phosphoric ester derivatives of choline. VIII. R. R. Renshaw and C. Y. Hopkins (J. Amer. Chem. Soc., 1929, **51**, 953—954).—*Phosphoryl* β-*chloroethoxydichloride*, b. p. 108—110°/15 mm., from phosphoryl chloride and ethylene chlorohydrin in carbon tetrachloride, gives with trimethylamine the *product* (?) $Cl_2PO\cdot O\cdot C_2H_4\cdot NMe_3Cl$, and with methyl alcohol *dimethyl* β-*chloroethyl phosphate*, b. p. 95—96°/4 mm. This yields with trimethylamine in toluene at the ordinary temperature the choline *ester*, $(MeO)_2PO\cdot O\cdot C_2H_4\cdot NMe_3Cl$, m. p. 136·5—137°, which is a powerful nicotine-like stimulant, but has little muscarine action.
H. E. F. Notton.

Action of ammonia on monobromoacetaldehyde and preparation of pyrazine from the latter substance. A. E. Tschitschibabin and M. N. Schtschukina (Ber., 1929, **62**, [*B*], 1075—1080).—The action of an excess of dry ammonia on monobromoacetaldehyde in benzene at 10—15° affords *tribromotrimethylhexahydrotriazine*,



$$CH_2Br\cdot CH{<}\begin{matrix}NH\cdot CH(CH_2Br)\\NH\cdot CH(CH_2Br)\end{matrix}{>}NH$$

, decomp. 100° (yield 17%), probably formed by polymerisation of monobromoacetaldimine. Under other conditions, bromoacetaldehyde and ammonia yield aminoacetaldehyde hydrobromide, which undergoes further change, yielding substances with completely ionisable bromine. Thus in anhydrous ether at −10° to −5°, a crystalline *product* is formed the composition of which is not always the same but generally agrees with the formula $(NH_2\cdot CH_2\cdot CH{:}NH)_3,3HBr,NH_3,H_2O$ (I), although in some cases it more closely approximates to $(NH_2\cdot CH_2\cdot CH{:}NH)_3,3HBr$. If the passage of ammonia is very protracted, a viscous oil is formed which, as the temperature rises, evolves ammonia and gives the compound I. The formation of glyoxalphenylosazone from the products confirms the conclusion that they are aminoacetaldehyde derivatives. Conversion of monobromoacetaldehyde into pyrazine is effected by treatment with ammonia in ether at −10° to −5°, followed by addition of sulphuric acid and then of water. The aqueous portion is treated with potassium hydroxide and a mercury salt and then distilled with steam. The yield is about 15·5%.
H. Wren.

Action of magnesium ethyl bromide on succintetraethyldiamide. M. Huan (Compt. rend., 1929, **188**, 1174—1176).—Magnesium ethyl bromide reacts in ether with succintetraethyldiamide (or ethyl succindiethylamate) to yield mainly (63%) γ-*keto*-n-*hexodiethylamide* (I), b. p. 142—143°/12 mm. (*semicarbazone*, m. p. 138°; *phenylhydrazone*, m. p. 107°; p-*nitrophenylhydrazone*, m. p. 165°) (hydrolysed with boiling 48% hydrobromic acid to the corresponding acid), together with 3% of $\gamma\zeta$-*diketo*-n-*octane* (II). The action of excess of magnesium ethyl bromide on I yields mainly γ-*hydroxy*-γ-*ethyl*-n-*hexodiethylamide* (III), b. p. 166—168°/13 mm., 5% of II, and 2 : 2 : 5-*trimethyldihydrofuran* (IV), b. p. 55—56°/11 mm., the last being obtained by elimination of 1 mol. of water from the unstable γ-ketol, which would be the normal product if both carbonyl groups of I reacted with the Grignard reagent. With alcoholic semicarbazide, however, IV yields the *semicarbazone*, m. p. 95°, of ethyl γ-hydroxy-γ-ethyl-*n*-amyl ketone. Acetic anhydride eliminates a molecule of diethylamine as acetdiethylamide from III, converting it into γ-ethyl-*n*-hexolactone (Hepworth, J.C.S., 1919, **115**, 1203) (additive *compound* with hydrazine hydrate, m. p. 78°).
J. W. Baker.

Determination of cyanide in small amounts. R. G. Smith (J. Amer. Chem. Soc., 1929, **51**, 1171—1174).—Quantities of about 0·1 mg. of cyanide ion may be determined with an accuracy of 1% by observing the colour developed in 5 min. at 100° with excess of sodium picrate and carbonate solution. Sodium hydroxide and some reducing agents must be absent, but the method is applicable to tissue distillates obtained by Bischoff's method (A., 1883, 1020). Qualitatively 1 part of cyanide ion in 50,000,000 parts may be detected.
H. E. F. Notton.

Constitution of Grignard's magnesium compounds. W. Schlenk and W. Schlenk, jun. (Ber., 1929, 62, [*B*], 920—924).—Dioxan precipitates magnesium halides and organohalides quantitatively from all Grignard solutions. The precipitates are not decomposition products which alter the nature of the organomagnesium compounds, since they bring about the same changes as the original solutions. The filtrates contain only magnesium dialkyls or diaryls, which must therefore be present, in addition to other magnesium organic compounds, in all Grignard solutions. Solutions of organomagnesium compounds which are not too dilute deposit the " Grignard compound " as etherates which melt at the atmospheric temperature in a coarsely crystalline form when cooled with carbon dioxide and acetone. By repeatedly freezing, decanting, and dissolving it is possible to obtain solutions in which Mg : halogen = 1 : 1. If such pure solutions are precipitated with dioxan, the filtrates contain magnesium dialkyl or diaryl, which under these conditions are formed spontaneously from the crystalline, homogeneous organomagnesium halide. The precipitates contain magnesium and halogen in the atomic ratio Mg : Hal<1. The occurrence of an equilibrium (I) $2R{\cdot}MgHal \rightleftharpoons MgR_2+MgHal_2$ or (II) $R_2Mg,MgHal_2 \rightleftharpoons MgR_2+MgHal_2$ is thus indicated, and is confirmed by the determination of the ratio Mg : Br in the precipitates obtained by the fractional addition of dioxan to an ethereal solution of pure magnesium α-naphthyl bromide. The decision in favour of I is based on the observation that the precipitates obtained from ethereal magnesium ethyl iodide and dioxan are independent in composition of the concentration of the ethereal solution. The part played by the ether in the formation of Grignard solutions is due to its solvent power, not only for the organo-metallic compounds, but also for the magnesium halides. The position of the equilibrium depends on the nature of the halide; in the case of ethyl iodide, 43% of the total magnesium is present as magnesium ethyl iodide, whereas in that of bromobenzene about 80% of the metal exists as magnesium phenyl bromide. As indicated by the behaviour of bromobenzene and magnesium towards benzophenone and fluorenone, respectively, both organomagnesium compounds and organomagnesium halides are agents of the Grignard synthesis. The establishment of equilibrium between organomagnesium halide and magnesium dialkyl or diaryl is not an instantaneous process. H. Wren.

Mercury dialkyls from organomagnesium halides. H. Gilman and R. E. Brown (J. Amer. Chem. Soc., 1929, 51, 928—930).—Improvements in the method of preparation of mercury diethyl (88% of the theoretical yield) and di-*n*-butyl (66%) (cf. Marvel and Gould, A., 1922, i, 329), involving (*a*) continuous introduction of the mercuric chloride by means of a Soxhlet extractor and (*b*) increases in the amount of solvent and time of heating, are described. H. E. F. Notton.

Benzene model on a basis of the electron theory and the substitution laws. M. Ulmann (Z. angew. Chem., 1928, 41, 674—680).—A benzene model is proposed in which alternate carbon atoms hold complete electron octets, these CH groups thus having each a resultant charge of −3, at the expense of the remaining CH groups, which therefore have each a resultant charge of +3. The reasons for this arrangement and its relation to the substitution laws are discussed. A. Davidson.

Action of acetylene on benzene in presence of aluminium chloride. J. Böeseken and A. A. Adler (Rec. trav. chim., 1929, 48, 474—485).—Acetylene condenses with benzene in presence of freshly-prepared aluminium chloride (prepared by heating aluminium in a current of chlorine) at 20°, in approximately molecular proportions, forming an insoluble powder which, when heated at 310°/cathode vac., gives a small amount of styrene (cf. Cook and Chambers, A., 1921, i, 332). Since styrene is polymerised by treatment with aluminium chloride in benzene solution, it is concluded that the small amount obtained is not an intermediate, but arises from an activated form (termed protostyrene). Normally the protostyrene polymerises, but the small amount protected by the micelle of the polymeride is stabilised, giving styrene. Using aluminium chloride (prepared other than by direct synthesis) or an aluminium–mercury couple in the above condensation gives polymerised styrene. With chlorobenzene the condensation product is polymerised *p*-chlorostyrene. This does not yield *p*-chlorostyrene when heated in a cathode vacuum, and it resembles the product obtained by treating the styrene derivative with aluminium chloride in chlorobenzene solution. The difference in the above condensations is ascribed to the smaller reactivity of chlorobenzene. The results are also explicable by the author's dislocation theory (A., 1926, 806; 1927, 1150). H. Burton.

Chlorine additive products of toluene. W. Qvist [with U. Sahlberg and O. Jansson] (Finska Kemistsamf. Medd., 1928, 37, 45—52; Chem. Zentr., 1928, ii, 1876).—In addition to mono-, di-, and trichlorotoluene, tetra-, hexa-, and possibly also pentachloro-additive products are obtained on chlorination of toluene. A. A. Eldridge.

Action of nitrogen trichloride on toluene and *cyclo*hexene. N. Stoll (Bull. Soc. chim. Belg., 1929, 38, 71—96).—When a 6·35% solution of nitrogen trichloride in toluene is allowed to decompose in the dark at 17—19° in presence of iodine as a catalyst, a mixture of *p*-chlorotoluene, benzyl chloride, a product corresponding with a trichlorotoluene, nitrogen, ammonium chloride, and hydrochloric acid is obtained in addition to unchanged toluene. The ratio Cl : N for the total reaction products is 8·22 as compared with the value 7·61 for nitrogen trichloride. The decomposition is complete after about 2 hrs., but in absence of catalyst it proceeds for several days. After 5 days the composition of the resulting products is very similar to the above; the amount of benzyl chloride formed increases somewhat at the expense of the *p*-chlorotoluene. Decomposition in sunlight causes a much larger increase in the amount of benzyl chloride, and indications of the formation of chloroamines were obtained (cf. Coleman and Noyes, A., 1922, i, 133). The following reactions are presumed to occur: $2NCl_3+3C_7H_8=N_2+3HCl+3C_7H_7Cl$

and $NCl_3+3C_7H_8=NH_3+3C_7H_7Cl$, the former predominating.

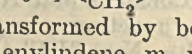
Treatment of *cyclo*hexene with nitrogen trichloride in benzene solution at 7—12° gives essentially 1 : 2-dichloro*cyclo*hexane, b. p. 186—188°/762 mm., d_4^{20} 1·1738, n_D^{20} 1·49006, formed thus: $2NCl_3+3C_6H_{10}=N_2+3C_6H_{10}Cl_2$. Small amounts of monochlorinated (substitution) derivatives are also formed.

H. Burton.

Tetra-*p*-tolylethylene. H. Gilman and F. B. Flick (Rec. trav. chim., 1929, 48, 461—463).—Tetra-*p*-tolylethylene, m. p. 151° (Staudinger and Goldstein, A., 1916, i, 850), is obtained by (*a*) heating di-*p*-tolylmethyl chloride or bromide, either alone or with pyridine, (*b*) the action of copper on the thioketone from di-*p*-tolyl ketone (I) and phosphoric sulphide, (*c*) treating the compound from di-*p*-tolylketen and quinoline with I, (*d*) reducing a mixture of *p*-tolylpinacol and I by Steinkopf and Wolfram's method (A., 1923, i, 216). Oxidation of the ethylene with chromic and acetic acids gives a 67% yield of I.

H. Burton.

***s*-Diphenyltetra*tert.*-butylethinylethane.** S. S. Rossander and C. S. Marvel (J. Amer. Chem. Soc., 1929, 51, 932—936).—The Grignard reagent from *tert.*-butylacetylene and magnesium ethyl bromide yields with ethyl benzoate *phenyldi*tert.*-butylethinylcarbinol*, $CPh(C\vdots C\cdot CMe_3)_2\cdot OH$, m. p. 46—47°, which is converted by sulphuric acid into an isomeric *ketone*, m. p. 108—110°, and by phosphorus tribromide in ether into *phenyldi*tert.*-butylethinylmethyl bromide* (I), m. p. 58—59° (*by-product*, m. p. 169—174°). With "molecular" silver in ether this affords s-*diphenyltetra*tert.*-butylethinylethane*, m. p. 98—99°. In presence of oxygen the debromination is accompanied by oxidation and no crystalline products are obtained (cf. A., 1928, 1365). Solutions of the ethane are stable towards oxygen; when heated at 100—140° they acquire a yellow, or in presence of air a red colour, which persists on cooling. The ethane linking is broken by sodium–potassium alloy or 40% (but not 1%) sodium amalgam and the resulting *sodio*-derivative gives with carbon dioxide *phenyldi*tert.*-butylethinylacetic acid*, m. p. 154—156°, which is also formed from the bromide, I, magnesium or sodium, and carbon dioxide in ether. H. E. F. Notton.

Benzopolymethylene compounds. XIV. Isomerisation of 1- to 2-arylindenes by heat. J. von Braun and G. Manz (Ber., 1929, 62, [*B*], 1059—1065).—In accordance with the procedure of Mayer, Sieglitz, and Ludwig (A., 1921, i, 554), 1-phenylindene is passed in an atmosphere of carbon dioxide over red-hot pumice, whereby a hydrocarbon is produced, identified as 2-phenylindene. Contrary to these authors, it is readily transformed by hydrogen in the presence of palladised charcoal and alcohol into 2-*phenyldihydroindene*, b. p. 162—163°/10 mm., d_4^{16} 1·0821, n_D^{15} 1·5955; it readily gives the *dibromide*, $C_{15}H_{12}Br_2$, m. p. 130—131°. 2-Hydrindone is converted by magnesium phenyl bromide into the *carbinol*,  $C_6H_4{<}{\substack{CH_2\\CH_2}}{>}CPh\cdot OH$, b. p. 160—165°/0·5 mm., transformed by boiling 20% sulphuric acid into 2-phenylindene, m. p. 167°. 2-Phenylindanone is converted into its oxime, m. p. 157°, which is reduced by sodium amalgam and dilute acetic acid to 1-*amino-2-phenyldihydroindene*, b. p. 180—184°/10 mm. (*picrate*, decomp. 121—123°). The base is converted into the corresponding, very hygroscopic, quaternary *iodide*, which, when boiled with 50% potassium hydroxide, gives trimethylamine and 2-phenylindene. 1-Hydrindone is converted by treatment with magnesium *p*-tolyl bromide and subsequent distillation of the product under diminished pressure into 1-p-*tolylindene*, b. p. 184—188°/11 mm., isomerised by heat to 2-p-*tolylindene*, m. p. 183—184°. The last-named hydrocarbon is also obtained from 2-hydrindone through 2-*hydroxy*-2-p-*tolylhydrindene*, b. p. 155—160°/0·2 mm. 2-m-*Tolylindene*, m. p. 99—100°, is obtained analogously through 2-*hydroxy*-2-m-*tolylhydrindene*, b. p. 165—170°/0·5 mm.

H. Wren.

1 : 2- and 2 : 3-Diphenylindenes. A. García Banús and F. Calvet (Anal. Fis. Quím., 1929, 27, 49—59).—Benzylhydrobenzoin (αβγ-triphenylpropane-αβ-diol) (Orékhoff, A., 1919, i, 205) is converted by boiling with excess of commercial acetyl chloride, or acetyl chloride to which sulphuryl chloride has been added, into 1 : 2-diphenylindene, m. p. 173—175° (Orékhoff and Tiffeneau, A., 1922, i, 458). 1-Oximino-2 : 3-diphenylindene, obtained by the action of amyl nitrite and alcoholic sodium ethoxide on 1 : 2-diphenylindene (cf. Thiele and Ruggli, A., 1912, i, 866; Orékhoff, A., 1920, i, 225), is reduced to 1-*amino*-2 : 3-*diphenylindene* (*hydrochloride*; *chloroplatinate*) by zinc and acetic acid. 2 : 3-Diphenylindene, m. p. 110°, is obtained by the isomerisation of 1 : 2-diphenylindene by boiling with alcoholic potassium ethoxide. It yielded on ozonolysis, not the expected "diphenyl*iso*chroman hydrate" (this vol., 324), but *benzoyl*(o-*benzoylphenyl*)*carbinol*, m. p. 121—123° (*monophenylhydrazone*, m. p. 143—145°; *dioxime*, m. p. 178—180°), which yielded *o*-benzoylbenzil when oxidised by permanganate in acetone solution. This reaction confirms the constitution of 2 : 3-diphenylindene. Homophthalaldehyde, an alternative starting-point for the synthesis of "diphenyl*iso*chroman hydrate," could not be obtained by ozonolysis of indene.

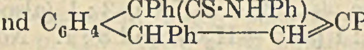
R. K. Callow.

Stereochemistry of aromatic ring systems. II. W. Schlenk and E. Bergmann (Ber., 1929, 62, [*B*], 745—750).—Further examples are cited of the isolation of isomerides, the existence of which cannot be explained by the classical theory of stereochemistry and for which the hypothesis is adopted that the single rings of condensed systems are inclined to one another in space. 9-*Benzoylfluorene*, m. p. 180°, is obtained by the action of benzoyl chloride on the lithium derivative of fluorene; *phenyldi*-9-*fluorenylcarbinol*, m. p. 290°, is simultaneously produced. 9-*Phenyl*-9-*benzoylfluorene*, m. p. 125—126°, is prepared with the isomeride, m. p. 139° (cf. Gomberg and Cone, A., 1906, i, 822), from sodium 9-phenylfluorene and benzyl chloride; it is converted into the form of m. p. 139° by treatment with chromic acid in cold, glacial acetic acid. *Benzylidenefluorene*, m. p. 153°, and p-*anisylidenefluorene*, m. p. 145°, are present in addition to the forms described previously (cf. Thiele and Henle, A., 1906, i, 571) in the condensation products of fluorene with benzaldehyde and *p*-anisaldehyde. 4 : 4′-*Tetramethyldiaminodiphenylmethylenefluorene*, red prisms, m. p. 238—240°, is obtained in addition to the isomeride, yellow needles, m. p. 239—240° (cf. Rodd and Linch, A., 1927, 1067), by the action of sodium on a mixture of Michler's ketone and fluorene. The two varieties show marked depression of m. p. when mixed. They are not interconvertible by seeding in solution or when molten. The orange is transformed into the yellow variety by addition of sodium and treatment of the product with mercury.

H. WREN.

Explanation of Schlenk's isomerism. E. BERGMANN and H. MARK (Ber., 1929, 62, [*B*], 750—757).—In order to depart as little as possible from the classical assumption of stereochemistry, the existence of Schlenk's isomerides (preceding abstract) has been explained by the hypothesis of the inclination of the rings in complex ring systems. An attempt is now made to establish a theory on a less hypothetical, physical basis founded on the "puckered" ring of W. H. and W. L. Bragg. Detailed consideration is given to benzene, naphthalene, anthracene, phenanthrene, and fluorene.

H. WREN.

Two supposed instances of isomerism in the aromatic series. O. BLUM (Ber., 1929, 62, [*B*], 881—893).—ββ-Diphenylvinyl bromide slowly forms a red solution when treated with sodium powder in ether and, on addition of alcohol, 1 : 2 : 4-*triphenyl*-1 : 4-*dihydronaphthalene*, m. p. 142·5—144°, is obtained in 10% yield; two *compounds*, $C_{28}H_{20}$, b. p. 283—285°/13 mm., and $C_{14}H_{13}$, m. p. 82—84°, are isolated as by-products. Treatment of the organo-metallic derivative with carbon dioxide affords 1 : 2 : 4-*triphenyl*-1 : 4-*dihydronaphthalene*-1-*carboxylic acid*, m. p. 238—239° (decomp.), whilst with phenylthiocarbimide the compound  $C_6H_4{<}\begin{array}{l}CPh(CS{\cdot}NHPh)\\ CHPh\text{———}CH\end{array}{\geqslant}CPh$, m. p. 243—244°, is produced. The last-named compound is also derived by the action of phenylthiocarbimide on the product of the action of sodium on 1 : 2 : 4-triphenyl-1 : 4-dihydronaphthalene, thus proving that the hydrocarbon undergoes substitution instead of addition. Catalytic hydrogenation of 1 : 2 : 4-triphenyl-1 : 4-dihydronaphthalene in presence of palladium affords 1 : 2 : 4-*triphenyl*-1 : 2 : 3 : 4-*tetrahydronaphthalene*, m. p. 126—129°. The constitution of the dihydro-compound is established by its oxidation to *o*-dibenzoylbenzene, m. p. 146—148°, whereby under milder conditions 1 : 2 : 4-*triphenylnaphthalene*, m. p. 158—159°, and the *keto-acid*, $CO_2H{\cdot}CHPh{\cdot}C_6H_4{\cdot}CHPhBz$, m. p. 232—233° (decomp.), are produced. 1 : 2 : 4-Triphenylnaphthalene is unaffected by hydrogen in the presence of palladised barium sulphate, but is reduced by sodium and boiling amyl alcohol to 1 : 2 : 4-triphenyl-1 : 2 : 3 : 4-tetrahydronaphthalene, m. p. 125—129°, and an *isomeride*, m. p. 186—187°. 1 : 2 : 4-Triphenylnaphthalene, m. p. 158°, is identical with the second form of ααδδ-tetraphenyl-$\Delta^{\alpha\beta\gamma}$-butatriene described by Purdie and Arup (J.C.S., 1910, 97, 1537) and by Buttenberg. The supposed isomerism with Brand's authentic compound (A., 1921, i, 783) does not therefore exist.

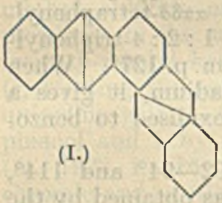
The action of lithium on ββ-diphenylvinyl bromide is rather more complicated than that of sodium, yielding 1 : 2 : 4-triphenyl-1 : 4-dihydronaphthalene, m. p. 143—144°, in very small amount, particularly if the action is very protracted. The normal reaction consists of stabilisation of the primary diphenylvinyl residues by production of the compound $CPh_2Li{\cdot}CH{:}CH{\cdot}CLiPh_2$, hydrolysed by alcohol to ααδδ-tetraphenyl-Δ^{β}-butene, m. p. 139—140°, and converted by iodine or phenylthiocarbimide into tetraphenylbutadiene, m. p. 200—201°. If the reaction is curtailed, the tetraphenylbutene is accompanied by an isomeric *hydrocarbon*, $C_{28}H_{24}$, m. p. 126·5—127·5°, not identical with ααδδ-tetraphenyl-Δ^{β}-butene, m. p. 126—127°, or 1 : 2 : 4-triphenyl-1 : 2 : 3 : 4-tetrahydronaphthalene, m. p. 127°. When hydrogenated in presence of palladium, it gives a *dihydro*-derivative, $C_{28}H_{26}$; it is oxidised to benzophenone and benzoic acid.

Two 9-methylacridines, m. p. 92—94° and 114°, respectively, have been described as obtained by the action of diphenylamine on glacial acetic acid in the presence of zinc chloride. It is shown that the compound of higher m. p. (now 117—118°) is the true 9-methylacridine, whereas that of lower m. p. (now 99—100°) is an additive *compound* of 1 mol. of 9-methylacridine and 1 mol. of diphenylamine. The compound of m. p. 117—118° adds 2 atoms of sodium and the product is hydrolysed to 9-methyl-9 : 10-dihydroacridine, m. p. 124—125·5° (cf. Sastry, J.C.S., 1916, 109, 270). The substance of m. p. 99—100° gives a transitory red solution with sodium and ether, from which, after addition of alcohol, 9-methyl-9 : 10-dihydroacridine and diphenylamine are obtained. The two substances last named combine in light petroleum, giving the compound of m. p. 99—100° in quantitative yield.

H. WREN.

Polynuclear, aromatic hydrocarbons and their derivatives. II. 2′ : 3′-Naphtho-1 : 2-anthracene, its homologues and oxidation products. E. CLAR, F. JOHN, and B. HAWRAN. **III. Anthracenoanthracenes and their quinones.** E. CLAR, H. WALLENSTEIN, and R. AVENARIUS (Ber., 1929, 62, [*B*], 940—950, 950—955; cf. this vol., 435).—II. The action of magnesium *o*-tolyl bromide on terephthalyl chloride in benzene and ether yields a mixture of 1 : 4-*di*-o-*toluylbenzene*, m. p. 82°, and 4-o′-*toluylbenzoic acid*, m. p. 177° (corresponding *chloride*) oxidised by alkaline permanganate to benzophenone-2 : 4′-dicarboxylic acid, m. p. 234°. *s*-Phthalyl chloride gives similarly the non-crystalline 1 : 2-*di*-o-*toluylbenzene*. 1 : 3-*Di*-2′ : 4′-*dimethylbenzoylbenzene*, b. p. 243°/12 mm., is obtained from *iso*phthalyl chloride and *m*-xylene in the presence of aluminium chloride; 1 : 4-*di*-2′ : 4′-*dimethylbenzoylbenzene*, m. p. 128°, is analogously prepared. Contrary to the literature, 2-2′ : 5′-dimethylbenzoylbenzoic acid, m. p. 147·5°, is readily prepared from phthalic anhydride, excess of *p*-xylene, and aluminium chloride. It is converted by zinc and 80% acetic acid into 3-p-*xylylphthalide*, leaflets, m. p. 112°, or needles, m. p. 115°, transformed by magnesium *p*-xylyl bromide into the non-crystalline 1 : 3-*di*-p-*xylylisobenzofuran*, oxidised by chromic acid to 1 : 2-*di*-2′ : 5′-*dimethylbenzoyl*-

benzene, m. p. 138·5° (corresponding *azine*, m. p. 136·5°). Condensation of the crude but ash-free diketones to hydrocarbons is effected by distillation with a free flame. Water and a little oil at first volatilise, followed by anthracene or 2-methylanthracene. The distillation is then rapidly completed and the distillates are purified by crystallisation from xylene, sublimation, or crystallisation from benzene in presence of picric acid, if much anthracene or β-methylanthracene is present. The yields from *o*-diketones are small owing to rupture of the molecules, but attain 20—25% with *m*- and *p*-compounds. The following substances are described: 2′ : 3′-*naphtho*-1 : 2-*anthracene* (I), m. p. 265°; 6′ : 7-*dimethyl*-2′ : 3′-*naphtho*-1 : 2-*anthracene* (II), m. p. 265—266°; 7 : 7′-*dimethyl*-2′ : 3′-*naphtho*-1 : 2-*anthracene* (III). Compound II is oxidised by chromic acid to 1′(?4′)-*keto*-6′ : 7-*dimethyl*-1′ : 4′-*dihydro*-2′ : 3′-*naphtho*-1 : 2-*anthraquinone*, m. p. 323°, whereas III affords 1′(?4′)-*keto*-7 : 7′-*dimethyl*-1′ : 4′-*dihydro*-2′ : 3′-*naphtho*-1 : 2-*anthraquinone*, m. p. 332°. 2′ : 3′-Naphtho-1 : 2-anthracene is oxidised by chromic acid to 1 : 2-phthalylanthraquinone, m. p. 322—323°, whereas dimethylphthalylanthrone affords 1′ : 4′-*diketo*-6′ : 7-*dimethyl*-1′ : 4′-*dihydro*-2′ : 3′-*naphtho*-1 : 2-*anthraquinone*, m. p. 338°, converted by hydrazine hydrate in boiling pyridine into the *azine* of *dimethyl*-1 : 2 : 3 : 4-*diphthalylbenzene*, which does not melt below 380°. Dimethylphthalylanthrone is oxidised by dilute nitric acid at 190—200° to 1 : 2 : 3 : 4-*diphthalylbenzene*-4′ : 4″-*dicarboxylic acid*, not molten below 380°.

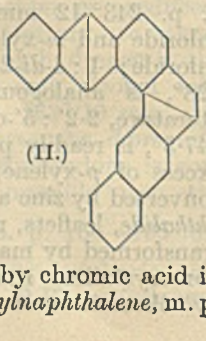


(I.)

III. In the production of anthracenoanthracenes by the action of heat on suitable diketones, the yields are severely restricted by the decomposition of the ketones into smaller fragments, notably benzaldehyde and benzoic acid. The method appears to reach its limit of applicability with the production of hydrocarbons with seven condensed benzene nuclei.

1 : 5-*Dibenzoyl*-2 : 6-*dimethylnaphthalene* is produced in good yield by the action of aluminium chloride on benzoyl chloride and 2 : 6-dimethylnaphthalene in cold carbon disulphide. Under similar conditions, acetic anhydride affords 1-*acetyl*-2 : 6-*dimethylnaphthalene*, m. p. 70—71° (*picrate*, m. p. 139—140°). 2 : 7-Dimethylnaphthalene appears to be converted by an excess of benzoyl chloride into a mixture of 1 : 5- and 1 : 8-dibenzoyl-2 : 7-dimethylnaphthalenes. 9 : 10-*Dihydroxy*-9 : 10-*di*-o-*tolylacenaphthene*, m. p. 164°, prepared from magnesium *o*-tolyl bromide and acenaphthenequinone, is oxidised by chromic acid in glacial acetic acid to 1 : 8-*di*-o-*toluoylnaphthalene*, m. p. 238°. The diketones are converted by heat respectively into 2′ : 1′-anthraceno-1 : 2-anthracene (I), m. p. about 400°, and 1′ : 2′-anthraceno-1 : 2-anthracene (II), m. p. 308°. Oxidation of the hydrocarbons affords 2′ : 1′-*anthraquinono*-1 : 2-*anthraquinone* [1 : 2 : 5 : 6-*diphthalylnaphthalene*], m. p. about 395°, and 1′ : 2′-*anthraquinono*-1 : 2-*anthraquinone* [1 : 2 : 7 : 8-*diphthalylnaphthalene*], not molten below 360°, respectively. H. WREN.

(I.)



(II.)

Absorption spectra of rubrenes. A. WILLEMART (Compt. rend., 1929, 188, 988—990).—Rubrene, dimethylrubrene, and dibenzorubrene have similar absorption spectra with three bands having maxima 4650 Å., 4950 Å., and 5300 Å., the spectra differing only in the intensity of the absorption. Accordingly the two naphthalene residues present in dibenzorubrene are not an integral part of the chromophoric group, but are present as univalent substituents. The mechanism of formation of rubrenes previously suggested (A., 1928, 996) thus finds support in their absorption spectra. R. BRIGHTMAN.

Rubicene. A. ECKERT (J. pr. Chem., 1929, [ii], **121**, 278—280).—Exposure of an acetic acid solution of di(diphenylene)ethylene to sunlight gives di(diphenylene)ethane and fluorenone. When fluorene is subjected to prolonged thermal decomposition using Meyer's method (A., 1917, i, 641), small amounts of rubicene (cf. Schlenk and Karplas, A., 1928, 1235) and a substance, m. p. 218°, are obtained. H. BURTON.

Double salts of aniline hydrohalides with metallic halides. G. D. BYRKIT and W. M. DEHN (J. Amer. Chem. Soc., 1929, **51**, 1167—1171).—The known compounds of the general formula $(PhNH_3Hal)_x(MHal_n)_y$ have been classified into 17 types, $x : y$ being: 1 : 2; 1 : 1 (also $+H_2O$), 4 : 3, 3 : 2, 2 : 1 (also +1, 2, or $3H_2O$), 3 : 1 (also +1 or $2H_2O$), 4 : 1, 6 : 1 (also $+H_2O$), and 8 : 1. No theory accounts for the composition and properties of all the compounds. The simpler compounds are formed at higher temperatures. All the salts readily dissociate into simple ions in aqueous solution. The following new double *salts* are described ($A=NH_3Ph\cdot$): $8ACl,HgCl_2$, m. p. 231·5°; $3ACl,2HgCl_2$, m. p. 167°, softening from 160°; $ABr,2HgBr_2$, m. p. 156°; AI,HgI_2, m. p. 61°; $2ACl,CoCl_2$, m. p. 135°; $2ACl,AuCl_3$, m. p. 95°, softening from 85°; $ACl,BiCl_3$, decomp. 210°; $ACl,MnCl_2$; $2ACl,MnCl_2,2H_2O$, m. p. above 230°; $3ACl,AlCl_3$; $3ACl,SnCl_4$; $3ABr,AsBr_3$; also $PhNH_2,HgBr_2$, m. p. 127°, and $PhNH_2,PbCl_2$. H. E. F. NOTTON.

Action of aromatic amines on alkyl nitrates. H. RYAN and M. T. CASEY (Sci. Proc. Roy. Dubl. Soc., 1928, **19**, 101—111).—Primary aromatic amines react with alkyl nitrates to yield the nitrate of the base and the appropriate alkylamine; no trace of the alcohol corresponding with the alkyl nitrate is formed. Aniline heated with ethyl nitrate (I) for several days at 70°, butyl nitrate (II) for 24 hrs. at 100°, or amyl nitrate (III) for 8 hrs. at 100° gives *aniline nitrate*, m. p. 198° (decomp.), butylaniline being isolated in the second case; with mannitol hexanitrate (IV) at 80—90° a violent reaction with charring occurs. *p*-Toluidine with I for 4—5 hrs. at

100°, II for 8 hrs. at 100°, or III for 4 hrs. at 100° affords p-*toluidine nitrate*, m. p. 202° (decomp.). Similarly, *o*-toluidine with I, II, or III at 100° yields o-*toluidine nitrate*, m. p. 189° (decomp.), and *m*-xylidine with I, II, or III at 100° gives m-*xylidine nitrate*, m. p. 208—209° (decomp.). The chief reaction between a secondary amine and an alkyl nitrate appears to be one of oxidation, accompanied by slight nitration; methylaniline heated with I at 100° or with IV in alcoholic solution at 78° yields red, viscous products, whilst diphenylamine with I or II at 100° affords a green, amorphous solid together with some diphenylnitrosoamine. Tertiary amines are also oxidised by alkyl nitrates with production of a reddish-violet coloration which appears to be independent of the nature of the alkyl group. If the relative decomposition velocities of alkyl nitrates be measured by the colorations produced with dimethylaniline by heating for 40 hrs. at 60—70° the velocities for ethyl, butyl, amyl, and cellulose nitrates and mannitol hexanitrate are in the ratio 1, 2·85, 0·17, 9·4, and 22·9, respectively.

C. W. SHOPPEE.

Nitration of phenylbenzylamine derivatives. J. REILLY, P. J. DRUMM, and T. V. CREEDON (J.C.S., 1929, 641—644).—Nitrosobenzylaniline gives, on nitration with nitric acid (*d* 1·42, at 0—5°), nitroso-4-nitrophenylbenzylamine accompanied by smaller quantities of the nitroso-2-nitro-compound. Nitration in acetic acid solution gives slightly greater yields.

The conclusion of Schultz, Rohde, and Bosch (A., 1904, i, 992) that benzylethylaniline is nitrated in sulphuric acid solution in the benzyl ring (cf. Gnehm and Scheutz, A., 1901, i, 519) is supported by the isolation of mainly *phenyl*-3-*nitrobenzyl*-n-*butylamine*, m. p. 44—45°, from the mixed-acid nitration of phenylbenzyl-*n*-butylamine dissolved in sulphuric acid. Nitration of dibenzylaniline (m. p. 69—70°; lit. 67°, 71°) in sulphuric acid solution gives no *op*-nitro-compounds, only *phenyldi*-m-*nitrodibenzylamine*, m. p. 128—129°, being obtained. Treatment of aniline with *m*-nitrobenzyl chloride affords the same substance. The experimental evidence suggests that direct nitration of phenylbenzylamines leads to the formation of nitro-derivatives substituted in the aniline ring, whereas nitration through the salt promotes substitution in the benzyl nucleus.

R. J. W. LE FÈVRE.

Complex compounds of aromatic diamines. Compounds of *o*-phenylenediamine with metallic salts. W. HIEBER, C. SCHLIESZMANN, and K. RIES (Z. anorg. Chem., 1929, **180**, 89—104).—By interaction of *o*-phenylenediamine and the following salts in aqueous or alcoholic solution, complex *compounds* containing the salt molecule combined with 1, 2, 3, 4, or 6 mols. of base have been obtained: with 1 mol., zinc, cupric, and cobalt chlorides, and cadmium chloride, bromide, and iodide; with 2 mols., chlorides, bromides, and iodides of cadmium and nickel, cupric, cobalt, nickel, zinc, and cadmium sulphates, and cupric nitrate; with 3 mols., nickel iodide, zinc bromide and iodide, and cadmium sulphate; with 4 mols., chlorides, bromides, and iodides of cobalt and nickel, nickel sulphate, and zinc iodide and perchlorate; with 6 mols., cobalt, nickel, and zinc chlorides. In general, these compounds are comparatively unstable in aqueous solution, being readily oxidised in air. By utilising their property of adding ammonia with simultaneous loss of diamine, it has been shown that in those compounds containing 4 and 6 mols. of base the secondary valency of the diamine is 1 and the same is also true for most of the other compounds.

R. CUTHILL.

Constitution of compounds of metallic salts with *p*-phenylenediamine and benzidine. W. HIEBER and K. RIES (Z. anorg. Chem., 1929, **180**, 105—109).—Cobalt chloride and the chlorides, bromides, iodides, and sulphates of zinc and cadmium react with *p*-phenylenediamine in aqueous or alcoholic solution to form *compounds*, the molecules of which contain an equal number of molecules, apparently two, of salt and base, and zinc chloride forms a similar *compound* with benzidine, and also a *compound* containing twice this amount of benzidine. The secondary valency of the base is two, *i.e.*, both amino-groups are linked with the metal, in all these compounds except the last, in which it is one. Cobalt chloride also appears to form a *compound*, $2CoCl_2,3C_6H_4(NH_2)_2$.

R. CUTHILL.

Catalytic reduction of phenol and naphthol ethers with hydrogen and platinum. E. WASER, H. SOMMER, C. LANDWEER, and C. GAZA (Helv. Chim. Acta, 1929, **12**, 418—443).—Reduction of the following phenol ethers (Ph·OR), anisole, b. p. 152·2—152·4°/728 mm. (all b. p. are corr.), phenetole, b. p. 168·1—168·6°/731 mm., d_4^{20} 0·9689, n_D^{20} 1·50845, phenyl *n*-propyl ether, b. p. 190—191°/725 mm., phenyl *iso*propyl ether, b. p. 170—172°/720 mm., phenyl *n*-butyl ether, b. p. 198—200°/721 mm., phenyl *iso*butyl ether, phenyl *iso*amyl ether, b. p. 215—217°/718 mm., and phenyl *n*-hexyl ether, b. p. 240—241°/721 mm., with hydrogen in presence of platinum-black and acetic acid shows that about one third of the ether is converted into the *cyclo*hexyl derivative C_6H_{11}·OR. Two other courses of reduction also occur: (*a*) elimination of R with the production of the hydrocarbon R·H, and *cyclo*hexanol, (*b*) elimination of OR and formation of the alcohol R·OH and *cyclo*hexane. In the change (*a*) *cyclo*hexanone is produced as an intermediate, since reduction in presence of semicarbazide hydrochloride affords *cyclo*hexylsemicarbazide. The amount of hydrogen absorbed varies from 3·57 to 3·8 mols. (limits). Reduction of α-naphthyl ethyl ether gives about 50% of *α-decahydronaphthyl ethyl ether*, b. p. 236—238°/728 mm., d_4^{20} 0·9446, n_D^{20} 1·47824, together with ethyl alcohol, a small amount of ethane, decahydronaphthalene, and α-decahydronaphthol. β-Naphthyl ethyl ether yields about 50% of β-*decahydronaphthyl ethyl ether*, b. p. 239—240°/713 mm., d_4^{20} 0·9542, n_D^{20} 1·47718, *cis*-β-decahydronaphthol, and *cis*-β-decahydronaphthalene. Methane, methyl alcohol, *cyclo*hexane, *cyclo*hexanol, and *hexahydroguaiacol*, b. p. 175—180°/730 mm., d_4^{20} 0·9775, n_D^{20} 1·45687, are obtained from guaiacol. The following ethers appear to be new: cyclo*hexyl* n-*propyl ether*, b. p. 170·5—171·5°/728 mm., d_4^{20} 0·8665, n_D^{20} 1·43936; cyclo*hexyl* iso*propyl ether*, b. p. 168—169°/716 mm., d_4^{20} 0·9285, n_D^{20} 1·48332; cyclo*hexyl* n-*butyl ether*, b. p. 193·5—194·5°/734 mm., d_4^{20} 0·8664, n_D^{20} 1·43853; cyclo*hexyl* iso*butyl ether*, b. p. 175—177°/719 mm., d_4^{20} 0·8618, n_D^{20}

1·44137; cyclo*hexyl* iso*amyl ether*, b. p. 206—207°/718 mm., d_4^{20} 0·8523, n_D^{20} 1·44136, and cyclo*hexyl* n-*hexyl ether*, b. p. 222·5—224·5°/728 mm., d_4^{20} 0·8515, n_D^{20} 1·44275. H. Burton.

***m*-Hydroxytolylsulphones and *m*-cresolsulphonic acids.** J. Zehenter, H. Bohunck, and E. Nowotny (J. pr. Chem., 1929, [ii], **121**, 223—236).—α-*m*-Hydroxytolylsulphone [5 : 5′-dihydroxy-di-*o*-tolylsulphone] (I) (A., 1920, i, 544), when treated with boiling sodium carbonate solution yields a *monosodium* derivative (+4H_2O); the *disodium* derivative (+EtOH) is obtained by the action of sodium on an alcoholic solution of I. Concentrated sulphuric acid converts I at the ordinary temperature into a *disulphonic acid* (II), m. p. 65—66° [*dipotassium* (+4H_2O) salt; the *barium* (+9·5H_2O) and *lead* (+8H_2O) salts contain 1·5 atoms of metal in 1 mol.], whilst at 100—120°, *m*-cresol-6-sulphonic acid (potassium +2H_2O, barium +5H_2O, and *lead* +4H_2O, salts) and II are obtained. At 180° cresol-mono- and -di-sulphonic acids are produced. When a mixture of *m*-cresol, *m*-cresol-6-sulphonic acid, and phosphoric oxide is heated at 170°, I is obtained, thus indicating its constitution. β-*m*-Hydroxytolylsulphone [3 : 3′-dihydroxydi-*p*-tolylsulphone (?)] (III) (*loc. cit.*), also gives a *monosodium* derivative when treated with sodium carbonate solution. Treatment with concentrated sulphuric acid at the ordinary temperature yields a *disulphonic acid* (+4·5H_2O), m. p. 139—140° (*tetrapotassium* salt +4·5H_2O); at 100—120° cresol-mono- and -di-sulphonic acids result. Bromination of III in ethereal solution gives a *tetrabromo*-derivative, m. p. 220° (decomp.). Treatment of *m*-cresol-6-sulphonic acid with an excess of bromine water affords 2 : 4 : 6-tribromo-*m*-cresol (IV) together with a small amount of another substance which contains bromine and no sulphur. Bromination of the acid in acetic acid solution and in ethereal suspension, or of the potassium salt in water, gives IV as the sole product. *m*-Cresol-4-sulphonic acid, m. p. 109—110° (copper salt +3H_2O), is converted by an excess of bromine water into a mixture of IV and 2(or 6) : 4 : 5-*tribromo*-m-*cresol*, m. p. 131° (decomp.), whilst the potassium salt yields IV and the *potassium* salt of a dibromo-*m*-cresol-4-sulphonic acid. H. Burton.

Condensation of *o*-aminophenol and oxalic acid. I. A. A. Levine and L. Wehmhoff (J. Amer. Chem. Soc., 1929, **51**, 1243—1246; cf. Kehrmann and Bener, A., 1925, i, 443).—*o*-Aminophenol (2 mols.) and anhydrous oxalic acid (1 mol.) at 180—200° give a red *substance*, $(C_{14}H_{12}O_4N_2)_n$, m. p. 271—272°, which is recovered unchanged from its sulphuric acid solution. At 130—140° a little *o*-hydroxyoxanilide is also formed. The red product loses 1 mol. of carbon dioxide at 280°, and gives yellow *disodium* and *potassium* salts. With methyl sulphate and alkali it yields a *trimethyl* (?) ester, m. p. 246—247°; with acetic anhydride an impure red *acetyl* derivative, m. p. 189°, which decomposes in boiling benzyl alcohol into *oo*′-diacetoxyoxanilide; and with aniline a *monoanilide*, m. p. 250°. H. E. F. Notton.

Methylurethanes of isomeric α-hydroxyphenylethyldimethylamines and their miotic activity. Edgar Stedman and Ellen Stedman (J.C.S., 1929, 609—617).—α - o - *Hydroxyphenylethyldimethylamine methylurethane*, m. p. 90° [*methiodide*, m. p. 148° (efferv.)], α-m-*hydroxyphenylethyldimethylamine methylurethane*, m. p. 86° [*hydrochloride*, m. p. 169° (efferv.); *methiodide*, m. p. about 130° (efferv. and after previous sintering)], and α-p-*hydroxyphenylethyldimethylamine methylurethane*, an oil [*hydrochloride*, m. p. 203° (after previous sintering); *methiodide*, m. p. 173° (efferv.)] are prepared from the appropriate methoxybenzaldehydes through the methoxyphenylmethylcarbinols, the carbinyl bromides, and the α-methoxyphenylethyldimethylamines. The last-named are demethylated by hydrobromic acid and the resulting phenols converted into the methylurethanes by interaction with methylcarbimide; in the case of the *m*-compound condensation was directly effected in an inert solvent, but with the *o*- and *p*-isomerides addition of metallic sodium to the reactants in benzene or ether solution was necessary.

The miotic actions of the urethane hydrochlorides and methiodides (tested by instillation of 1·5% solutions of substances in physiological saline into cat's eyes) were estimated as: *m*-HCl>*o*-MeI>*p*-HCl, *o*-HCl, *m*-MeI>*p*-MeI. This order of relative strengths does not agree with those found for similar salts of the hydroxybenzyldimethylamines, where the order is *o*->*p*->*m*-. In both series conversion of the tertiary bases into quaternary ammonium salts increases the miotic activity of the *o*- and diminishes that of the *m*- and *p*-isomerides, the methiodides of the *p*-compounds being inactive at the concentrations employed.

The following compounds are described incidentally: α-m-*methoxyphenylethyldimethylamine methiodide*, m. p. 142°, α - m - *hydroxyphenylethyldimethylamine hydrochloride*, m. p. 197—198°, and *methiodide*, m. p. 160° (with sintering at 145°), α-o-*methoxyphenylethyldimethylamine methiodide*, m. p. 136—137°, α - o - *hydroxyphenylethyldimethylamine hydrochloride*, m. p. 136—137°, α-p-*methoxyphenylethyldimethylamine hydrochloride*, m. p. 213°, and *methiodide*, m. p. 128—130°, *di*-(α-p-*methoxyphenylethyl*)*dimethylammonium bromide monohydrate*, m. p. 109°, and α-p-*hydroxyphenylethyldimethylamine hydrochloride*, m. p. 183°.

It is concluded that the physiological properties of the urethanes investigated are due to the common phenylcarbamate structure coupled with a necessary basic group. R. J. W. Le Fèvre.

Dehydrogenation of *ar*-1 : 3-dibromo-β-tetralol with bromine. M. Jakeš (Coll. Czech. Chem. Comm., 1929, 1, 245—256).—Treatment of *ar*-1 : 3-dibromo-β-tetralol with 2 mols. of bromine and subsequent heating at 180—185° gave a mixture of two dibromo-β-naphthols, b. p. 195—229°/10 mm., m. p. 112—142°, separated by fractional crystallisation from carbon tetrachloride into two compounds, m. p. 181—183° (I) and m. p. 124—125° (II), respectively. The constitution of I was established as 3 : 7-*dibromo*-β-*naphthol* by reduction with sodium amalgam to 7-bromo-β-naphthol, m. p. 132—133° (mixed m. p. with 6-bromo-β-naphthol, 100—105°), identical with 7-bromo-β-naphthol, m. p. 132—133°, produced from 7-hydrazino-β-naphthol and cupric bromide, whilst that of II as 3 : 6-*dibromo*-β-*naphthol* follows from its reduction with sodium amalgam to 6-bromo-β-naphthol, m. p. 126—127°, identical with that obtained by the reduction of 1 : 6-dibromo-β-naphthol with tin and hydrochloric acid, by the production of 1 : 3 : 6-tribromo-β-naphthol, m. p. 133°, with bromine and acetic acid, and by its formation from 3 : 6-dibromo-β-naphthylamine through the diazonium compound and decomposition of the latter with aqueous cupric sulphate. The compound described by Franzen and Stäuble (A., 1922, i, 450) as 3 : 6-dibromo-β-naphthol is probably 4 : 6-dibromo-β-naphthol. Dehydrogenation of 1 : 3-dibromo-2-acetoxynaphthalene by heating with 2 mols. of bromine at 185° followed by hydrolysis of the product with alcoholic potassium hydroxide gave a mixture of I and II; 1 : 3 : 6-tribromo-β-naphthol, m. p. 133° (reduced by tin and hydrochloric acid in the presence of alcohol to 3 : 6-dibromo-β-naphthol), is formed when excess of bromine is employed in the dehydrogenation.

A. I. Vogel.

Manufacture of *o*-nitro- and *o*-amino-diaryl ethers. I. G. Farbenind. A.-G.—See B., 1929, 349.

Manufacture of hydrogenated aromatic amino-compounds. I. G. Farbenind. A.-G.—See B., 1929, 350.

Action of diazo-hydrates on azoxyphenols. D. Bigiavi and S. Stefanic (Atti R. Accad. Lincei, 1929, [vi], 9, 326—331).—Various reactions showing the differences in behaviour between the two isomeric *p*-hydroxyazoxybenzenes and the analogy of the β-isomeride with *p*-nitrophenol are cited. The statement that *p*-bromobenzeneazo-*p*-nitrophenol (cf. Dimroth and Hartmann, A., 1909, i, 66) does not yield salts with aqueous alkali hydroxide is inaccurate, as a red *sodium* salt, easily reconvertible into the original compound, is readily obtainable. When treated with *p*-bromodiazobenzene hydrate: (1) α-benzeneazoxyphenol yields the corresponding *oxyazo*-compound, $\mathrm{O{:}NPh{:}N\cdot C_6H_3(OH)\cdot N_2\cdot C_6H_4Br}$, m. p. 178—180°, which gives aniline, *p*-bromoaniline, and 2 : 4-diaminophenol when reduced with tin and hydrochloric acid and forms the derivatives: *copper*, deflagrating at 285°, *nickel*, altering at about 290°, *ethyl ether*, m. p. 163·5°, *acetyl*, m. p. 154—156°, *benzoyl*, m. p. 175°. (2) β-Benzeneazoxyphenol yields the *diazo-ether*, $\mathrm{NPh{:}NO\cdot C_6H_4\cdot O\cdot N_2\cdot C_6H_4Br}$, m. p. about 110° (decomp.), which may be coupled with sodium β-naphthol-3 : 6-disulphonate or β-naphthol, and at 80—90° is converted into the *azo*-derivative, $\mathrm{NPh{:}NO\cdot C_6H_3(OH)\cdot N_2\cdot C_6H_4Br}$, m. p. 157°, this forming the following derivatives: *sodium* salt, *copper* salt, m. p. 266—270° (decomp.), *ethyl*, m. p. 118°, *acetyl*, m. p. 149—150°.

T. H. Pope.

Neutral reduction of nitro-compounds. W. M. Cumming and G. S. Ferrier (J. Roy. Tech. Coll. Glasgow, 1929, 2, [1], 40—43).—Reduction of nitrobenzene with zinc dust and ammonium chloride in alcoholic solution yields chiefly phenylhydroxylamine with small quantities of aniline and occasionally a little azoxybenzene, but no hydrazobenzene. Nitrosobenzene under the same conditions gives a 60% yield of hydrazobenzene, phenylhydroxylamine affords aniline, and azoxybenzene a 77% yield of hydrazobenzene together with traces of azobenzene.

A. R. Powell.

Neutral reduction and double basic zinc salts. W. M. Cumming and G. Howie (J. Roy. Tech. Coll. Glasgow, 1929, 2, [1], 43—49).—When a nitro-compound or one of its reduction products is reduced with zinc and ammonium chloride in boiling alcohol an organo-zinc compound is formed as an intermediate product, but in most cases this decomposes rapidly, with the formation of a basic zinc salt; the salt formed in the reduction to the azoxy-stage is always the white, crystalline *compound*, $\mathrm{2NH_4Cl,5Zn(OH)_2}$, and conversely reduction to the azoxy- and hydrazo-stage takes place only in the presence of this compound. Reduction of 1 : 1′-azoxynaphthalene to the hydrazo-stage by means of zinc and ammonium chloride affords the *compound* $\mathrm{9Zn(OH)_2,4NH_4Cl,6H_2O}$; under similar conditions *p*-nitrophenol affords *p*-aminophenol and the compound $\mathrm{ZnCl_2,Zn(NH_3)_2,NH_4Cl}$. In the case of *m*-nitrobenzaldehyde, the azoxy-compound formed by reduction is obtained in combination with a zinc complex as the *compound* $\mathrm{ZnCl_2,3NH_4Cl,2C_{14}H_{10}O_3N_2,9Zn(OH)_2}$, from which the azoxy-compound can be isolated only by treatment with acids or alkalis. From *p*-nitrotoluene a complex zinc *compound* of *p*-toluidine, $\mathrm{4C_6H_4Me\cdot NH_2,NH_4Cl,ZnCl_2}$, m. p. 250°, was obtained in the reduction to hydrazotoluene. By the reduction of nitronaphthalene with zinc and calcium chloride in alcoholic solution a 98% yield of naphthylamine is obtained but no azoxynaphthalene.

A. R. Powell.

Action of the Grignard reagent on azoxybenzene. W. M. Cumming and G. S. Ferrier (J. Roy. Tech. Coll. Glasgow, 1929, 2, [1], 49—51).—An attempt has been made to determine the best conditions for the interaction between magnesium methyl iodide and azoxybenzene. The reaction products were azobenzene and a brown oil which had the odour of ethylaniline but could not be identified as such.

A. R. Powell.

Esters of aminoazobenzenesulphonic acids, $\mathrm{NR_2\cdot C_6H_4\cdot N{:}N\cdot SO_2\cdot OC_nH_{2n+1}}$. A. Hantzsch (Ber., 1929, 62, [*B*], 966—968).—Diethylhelianthin is converted by diazomethane in ether into *methyl diethylaminoazobenzenesulphonate*, m. p. 125°, which is slowly attacked by cold sodium hydroxide, readily by hydrochloric acid. *Methyl dimethylaminoazobenzenesulphonate*, decomp. about 280°, is obtained similarly in very poor yield. *Methyl methylaminoazobenzenesulphonate*, decomp. 113°, and *methyl dimethylamino-o-tolueneazobenzenesulphonate*, m. p. 77—78°, are described. Aminoazobenzenesulphonic acid is converted mainly into violet helianthin, the methyl ester being formed only in traces. Yellow and red helianthins do not exhibit any fundamental difference in their behaviour towards diazomethane. The methyl esters of dimethyl- and diethyl-helianthin are also prepared from the sodium salts and methyl sulphate in boiling toluene.

H. Wren.

Aminoazobenzenes and their salts. A. Hantzsch and W. Voigt (Ber., 1929, 62, [*B*], 968—975; cf. preceding abstract).—To the yellow and red salts of aminoazobenzenes, the azoid and quinonoid structures, $\mathrm{PhN{:}N\cdot C_6H_4\cdot NR_2,HX}$ and $\mathrm{PhNH\cdot N{:}C_6H_4{:}NR_2X}$, have been ascribed by

Hantzsch and Hilscher (A., 1908, i, 484). The assumption of the existence of more strongly absorbing and therefore quinonoid yellow salts is rendered unnecessary by the observation of the dissociation (etherolysis) of the oxalate, trichloroacetate, and monochloroacetate of dimethyl-yellow in ether into base and acid or their etherates (cf. Thiel, Fortschr. Chem., Phys., u. physikal. Chem., 1924, 18, 112). Similarly, alcoholysis also occurs to a marked extent; solutions of amino- and dimethylamino-azobenzene hydrochlorides have a close optical resemblance to those of the free base and become optically constant only after addition of widely varying amounts of hydrochloric acid. It is remarkable that amino- and diethylamino-azobenzene yield primarily yellow salts, whereas dimethyl- and dipropyl-aminoazobenzene afford red compounds (*dipropylaminoazobenzene hydrochloride* has m. p. 86°). As expected, water causes hydrolysis, whereas "solvolysis" is observed even in indifferent media. To the yellow and red helianthins, the structures $\underline{HNR_2\cdot C_6H_4\cdot N{:}N\cdot C_6H_4\cdot SO_3}$ and $\underline{NR_2{:}C_6H_4{:}N\cdot NH\cdot C_6H_4\cdot SO_3}$ are now ascribed. The absorption spectrum of methyl diethylaminazobenzenesulphonate is closely similar to that of the corresponding yellow azoid sodium salt. Helianthin closely resembles aminoazobenzene in alcohol and therefore exists in solution mainly in the open form, $NH_2\cdot C_6H_4\cdot N{:}N\cdot C_6H_4\cdot SO_3[H_2\cdot OEt]$. Dimethylamino-*o*-tolueneazobenzenesulphonic acid exists in alcohol as the internal azoid salt $\underline{HNMe_2\cdot C_6H_3Me\cdot N{:}N\cdot C_6H_4\cdot SO_3}$; even in acid solution it remains yellow and undergoes only partial conversion into the open benzenoid salt. Its stability is imputed to the *o*-methyl group. The yellow helianthins evolve nitrogen from diazoacetic ester, whereas the red compounds do not react or cause the change very much more slowly.

H. WREN.

Absorption spectra and composition of azo-dyes. I. Effect of position isomerism on absorption of methyl derivatives of benzeneazophenol. W. R. BRODE (J. Amer. Chem. Soc., 1929, 51, 1204—1213).—The absorption spectra of 4-hydroxyazobenzene and its mono- and di-methyl derivatives, which have only one methyl group on each ring, have been measured in approximately 0·00015*M*-solutions in 3% sodium hydroxide. All show an intense band at frequency 670—750 and a weaker one at 1125—1200, the former being composed of two overlapping bands, A and B. Observed and calculated values for A, B, and A+B are tabulated. In the parent compound A and B are of nearly equal intensity. The effect of the introduction of methyl groups in various positions on (*a*) A/B, (*b*) A+B (calc.) are: 3′-, (*a*) and (*b*) no change; 4′-, (*a*) no change, (*b*) increased; 2′-, (*a*) and (*b*) considerably decreased; 3-, (*a*) increased; 2-, (*a*) decreased. The disubstituted derivatives show the combined effects of the two substituents. The results are regarded as indicating the presence of two tautomerides in proportions [given by A/(A+B)] varying from 68% of A in the 3-methyl to 41% in the 2 : 3′-dimethyl derivative.

H. E. F. NOTTON.

Constitutional influences on the conversion of azonaphthols into their azo-sulphites and their bearing on the structure of α- and β-naphthol. A. T. KING (J.C.S., 1929, 601—609).—The conversion of azonaphthols into their azo-sulphites occurs more readily with β-naphthol derivatives than with α-naphthol derivatives and is materially affected by the orientation of substituent sulphonic groups. Thus *p*-sulphobenzeneazo-α-naphthol reacts with concentrated aqueous sodium hydrogen sulphite less readily than *p*-sulphobenzeneazo-β-naphthol and 4-sulpho-α-naphthaleneazo-α-naphthol less readily than the corresponding β-naphthol compound. Sulphonation of the naphthol component enhances the reactivity of the β-naphthol derivatives (probably by increasing their solubility) in contradistinction to the α-naphthol series, the reactivities of which are diminished. The following derivatives of the former class are described: *sodium* salts of *benzene*- and 4-*sulpho-α-naphthaleneazo*-6-*sulpho*-β-*naphthyl sulphite*, *sodium benzene*-, m-*xylene*-, o-*carboxybenzene*-, *α-naphthalene*-, and 4-*sulpho-α-naphthalene-azo*-3 : 6-*disulpho*-β-*naphthyl sulphite*, *sodium* 4-*sulpho-α-naphthaleneazo*-6 : 8-*disulpho*-β-*naphthyl sulphite*, and *sodium* 4-*sulpho*-α-*naphthaleneazo*-3 : 6 : 8-*trisulpho*-β-*naphthyl sulphite*. The non-reactivity conferred by a sulphonated α-naphthol component prevents formation of sulphites from α-naphthaleneazo-α-naphthol-4 : 8- and -3 : 6-disulphonic acids, 4-sulpho-α-naphthaleneazo-α-naphthol-4- and -5-sulphonic acids, and 6-sulpho-β-naphthaleneazo-α-naphthol-4-sulphonic acid, although α-naphthaleneazo-α-naphthol-5-sulphonic acid gives *sodium α-naphthalenazo*-5-*sulpho*-α-*naphthyl sulphite*.

The mechanism of azo-sulphite formation is discussed. The explanations of Spiegel (A., 1885, 987) and Voroschcov (A., 1911, i, 819) (namely, that rate of addition is controlled by steric hindrance or ketonisation of the naphthol residue, respectively) are not in accord with present facts. It is suggested that in the α-naphthol type there is a disability to assume the ketonised form, whereas the β-naphthol type readily ketonises. This contrast is explained on the ordinary unsymmetrical naphthalene formula by assuming that in the β-naphthol type the ring tends to stabilise with a double linking across the 1 : 2-positions, but in the α-naphthol type with only a single linking. Such an explanation agrees with the opposing directions in which reduction of α- and β-naphthol to their tetrahydro-derivatives occurs.

The azo-sulphites are regarded as additive products with hydrazone structures (since the nitrogen linking is stable to hydrogen sulphite) which analyses show not to have reverted to azo-compounds by loss of water.

R. J. W. LE FÈVRE.

Purification of picric acid. S. R. BENEDICT.—See this vol., 730.

Occurrence of ergosterol in phytosterols. I. M. HEILBRON and W. A. SEXTON (Nature, 1929, 123, 567).—It is suggested that, concurrently with its reduction to sitostanol, oxidation of sitosterol (possibly γ-) to ergosterol may occur. The fact that neither of the two known tetrahydroergosterols is identical with the isomeric γ-sitosterol is not remarkable.

A. A. ELDRIDGE.

Preparation of ethers of aromatic alcohols by catalytic action of alkali hydrogen sulphates. J. B. Senderens (Compt. rend., 1928, 188, 1073—1076).—Benzyl alcohol and β-phenylethyl alcohol are converted into the corresponding ethers when heated at 120—180° in contact with potassium hydrogen sulphate or, better, sodium hydrogen sulphate, which act as dehydrating catalysts. Mixtures of benzyl alcohol and aliphatic alcohols similarly treated yield the respective mixed ethers as well as dibenzyl ether, but never the aliphatic ether.

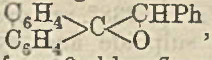
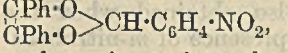
B. W. Anderson.

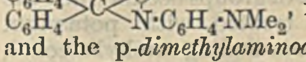
Action of sulphur dioxide on the halogenomagnesyl derivatives of carbinols. W. Schmidt-Nickels (Ber., 1929, 62, [*B*], 917—919).—The product obtained by the action of magnesium phenyl bromide on benzophenone in ether readily absorbs sulphur dioxide with production of *magnesium triphenylmethyl sulphite*, m. p. 186°; at 200° the compound loses the whole of its sulphur dioxide, leaving a magnesium compound converted by dilute sulphuric acid into triphenylcarbinol. *Magnesium phenyldiphenylenemethyl sulphite*, from sulphur dioxide and the product from magnesium, bromobenzene, and fluorenone in ether, is more thermostable, but loses sulphur dioxide at about 320°. The product derived from magnesium methyl iodide and benzophenone is converted by the successive action of sulphur dioxide and hot water into ααγγ-tetraphenyl-Δ^{α}-butene, m. p. 113—114°.

9-Chloro-9-phenylfluorene is transformed by magnesium phenyl bromide into diphenyldibiphenylene-ethane, identified as the peroxide, m. p. 192°.

H. Wren.

Occurrence of free, substituted methylenes in chemical reactions. E. Bergmann and J. Hervey (Ber., 1929, 62, [*B*], 893—916).—The isolation of the disodium compound of tetraphenylallene by Schlenk and Bergmann (A., 1928, 1031) establishes the possibility of the existence of free, substituted methylenes under certain conditions and indicates their, probably, extraordinary reactivity. For the proof of their production, for example, during the conversion of *p*-nitrobenzyl chloride into a mixture of *cis*- and *trans*-*pp*′-dinitrostilbene under the influence of alcoholic alkali, it is necessary to work in the presence of a compound which unites readily with the free methylene. For this purpose, aromatic aldehydes, *o*-diketones, fluorenone, thioketones, and nitroso-compounds are suitable, whereas substances containing the C:C and C:N linkings are unsuitable. Free substituted methylenes have been obtained from *p*- and *o*-nitrobenzyl chlorides, 9-chlorofluorene, benzyl chloride, and 9-bromoanthrone, but not from diphenylmethyl bromide, di-*p*-anisylmethyl chloride, or 10-chloro-9 : 9-diphenyl-9 : 10-dihydroanthracene. Two groups of aromatically substituted methyl halides appear to exist, one of which yields primarily the corresponding methylene when treated with alcoholic alkali, whereas the other undergoes double decomposition with production of the corresponding alkyl ether.

9-Chlorofluorene and *p*-nitrobenzaldehyde in boiling methyl alcohol in the presence of solid potassium carbonate afford p-*nitrobenzylidenefluorene oxide*, m. p. 153° (in an isolated instance, a *substance*, decomp. 217° after softening, was obtained). In one experiment the oxide,  $\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\!>\!C\!<\!\begin{matrix}CHPh\\O\end{matrix}$, m. p. 131—132°, was obtained from 9-chlorofluorene and benzaldehyde under the influence of potassium hydroxide; particularly when potassium carbonate is employed, the chief product is 9-α-*hydroxybenzylfluorenyl methyl ether*, m. p. 187—188°, obtained also by addition of benzaldehyde to the product of the action of sodium on fluorenone dimethylacetal. *p*-Nitrobenzyl chloride and *p*-nitrobenzaldehyde in presence of potassium carbonate afford the two isomeric pp′-*dinitrostilbene oxides*, m. p. 200—201° and 153—154°, respectively; both are converted by potassium iodide and boiling glacial acetic acid into *pp*′-dinitrostilbene. Similarly, *p*-nitrobenzyl chloride with *o*-nitrobenzaldehyde gives the two op′-*dinitrostilbene oxides*, m. p. 158—160° and 112°, respectively, and with *m*-nitrobenzaldehyde the mp′-*dinitrostilbene oxides*, m. p. 148° and 116°, respectively. p-*Nitrostilbene oxide*, m. p. 125—126°, is converted by potassium iodide in boiling glacial acetic acid into *p*-nitrostilbene, m. p. 157°. With anisaldehyde, *p*-nitrobenzyl chloride affords p-*nitro*-p′-*methoxystilbene oxide*, m. p. 138°, and with diphenylacetaldehyde the isomeric α-p-*nitrophenyl*-β-*benzhydrylethylene oxides*, m. p. 147° and 188°, respectively. *o*-Nitrobenzyl chloride and *p*-nitrobenzaldehyde give the isomeric *op*′-dinitrostilbene oxides, m. p. 160—161° and 111° (see above). The reaction between benzyl chloride and *o*-nitrobenzaldehyde occurs less smoothly than the changes described above, chiefly owing to the preponderating formation of *methyl* p-*nitrobenzyl ether*, b. p. 145—147°/17 mm.; p-*nitrostilbene oxide*, m. p. 187—189°, is produced only in minimal amount. 9-Bromoanthrone and benzaldehyde yield a very difficultly separable mixture of anthraquinone and benzylideneanthrone oxide; with anisaldehyde, the only isolable compound is anthraquinone. *p*-Nitrobenzyl chloride is converted by benzil in presence of potassium carbonate and methyl alcohol into the p-*nitrobenzylidene ether* of stilbenediol,  $\begin{matrix}CPh\cdot O\\CPh\cdot O\end{matrix}\!>\!CH\cdot C_6H_4\cdot NO_2$, m. p. 138°, and by phenanthraquinone into the p-*nitrobenzylidene* derivative of phenanthraquinol, m. p. 153°. 9-Chlorofluorene and fluorenone afford dibiphenylene-ethylene and *dibiphenylene-ethylene oxide*, m. p. 234° (decomp.), whilst *p*-nitrobenzyl chloride and the ketone give *p*-nitrobenzylidenefluorene oxide, m. p. 149°. 2 : 7-*Dibromofluorenone*, m. p. 202°, prepared by oxidising 2 : 7-dibromofluorene, and *p*-nitrobenzyl chloride yield p-*nitrobenzylidene*-2 : 7-*dibromofluorene oxide*, m. p. 230°. o-*Nitrobenzylidenefluorene oxide*, m. p. (indef.) 111°, and *biphenylenemethyleneanthrone oxide*, m. p. 252—254°, are described.

9-Chlorofluorene and *p*-nitrobenzyl chloride with *p*-nitrosodimethylaniline yield respectively p-*dimethylaminophenyldiphenylenemethylenenitrone*,  $\begin{matrix}C_6H_4\\C_6H_4\end{matrix}\!>\!C\!<\!\begin{matrix}O\\N\cdot C_6H_4\cdot NMe_2\end{matrix}$, m. p. 223—224° (decomp.), and the p-*dimethylaminoanil* of p-*nitrobenzaldehyde*, m. p. 206°; an isomeride of the latter compound, m. p. 221°, is obtained from *p*-aminodimethylaniline and *p*-nitrobenzaldehyde. p-*Nitrobenzylidene*-p′-*amino*-

diethylaniline, m. p. 136°, *o*-nitrobenzylidene-*p′*-aminodimethylaniline, m. p. 94—95°, and anthraquinonemono-*p*-dimethylaminoanil, m. p. 238°, are described.

The action of hydrogen sulphide and hydrogen chloride on a solution of fluorenone in alcohol yields *dimeric thiofluorenone*, m. p. 232°, instead of the desired monomeride. *p*-Nitrobenzyl chloride and Michler's thioketone in presence of potassium carbonate and boiling propyl alcohol yield *α-*p*-nitrophenyl-ββ-di-*p*-dimethylaminophenylethylene*, m. p. 175—176° (from primarily formed ethylene sulphide). Under similar conditions, 9-chlorofluorene affords di-*p*-dimethylaminophenylmethylenefluorene, m. p. 238—240°, *tetra-*p*-dimethylaminodibenzhydryl disulphide*, $[\cdot S\cdot CH(C_6H_4\cdot NMe_2)_2]_2$, and *di-9-fluorenyl disulphide*, m. p. 169—170°. The last-named compound has been obtained by Smedley (J.C.S., 1905, **87**, 1249, 1253) from 9 : 9-dichlorofluorene and potassium hydrosulphide and regarded as dimeric thiofluorenone. Its constitution follows from its solubility in alcoholic alkali and from its synthesis from 9-chlorofluorene and sodium disulphide. The trustworthiness of the method is established by the production of dibenzyl disulphide, m. p. 74°, from benzyl chloride under analogous conditions. Chlorofluorene and sodium hydrosulphide in alcohol yield exclusively *di-9-fluorenyl sulphide*, m. p. 250° after becoming discoloured at 238°.

p-Nitrobenzyl chloride could not be caused to condense with benzophenone, di-*p*-anisyl ketone, xanthone, 9 - methoxy - 9 - phenylanthrone, 9 : 9-diphenylanthrone, benzoin ethyl ether, benzylideneacetophenone or its oxide, benzophenonephenylhydrazone, benzylideneaniline, *as*-diphenylethylene, or benzylidenefluorene. 9-Chlorofluorene does not react with benzophenone.

Diphenylmethyl bromide is transformed by boiling methyl-alcoholic potassium hydroxide into *benzhydryl methyl ether*, b. p. 147—148°/17 mm., the constitution of which is established by conversion into diphenylthioacetanilide, m. p. 187°, by successive treatment with sodium in ether and phenylthiocarbimide. The ether is also obtained when the reaction is performed in the presence of *m*-nitrobenzaldehyde. Anisyl chloride, b. p. 140—141°/14 mm., from the acid and thionyl chloride, is converted by anisole and aluminium chloride in carbon disulphide into di-*p*-anisyl ketone (yield 88%), reduced by zinc dust in alcoholic, alkaline solution to *pp′*-dimethoxybenzhydrol, m. p. 70—72°, which is transformed by thionyl chloride in presence of toluene into *di-*p*-anisylmethyl chloride*, m. p. 83—84°; the last-named compound exchanges chlorine for methoxyl when treated with methyl-alcoholic potassium hydroxide. 9 : 9-Diphenylanthrone, in boiling 95% alcohol, is reduced by aluminium amalgam to 10-hydroxy-9 : 9-diphenyl-9 : 10-dihydroanthracene, m. p. 142°, converted by hydrogen chloride in glacial acetic acid into *10-chloro-9 : 9-diphenyl-9 : 10-dihydroanthracene*, m. p. 226°; simple exchange of groups occurs when the last-named compound is treated with potassium carbonate and benzaldehyde in boiling methyl alcohol, *10 - methoxy-9 : 9 - diphenyl - 9 : 10 - dihydroanthracene*, m. p. 147°, being produced; the corresponding *ethyl ether*, m. p. 163°, is formed analogously. H. WREN.

Resin acids. G. ROUIN (Bull. Inst. Pin, 1928, 167—172, 173—175; Chem. Zentr., 1928, ii, 2015).—The dihydrobromide (m. p. 146—151°) of abietic acid from Aleppo colophony appears to be identical with that (m. p. 170—175°) from American colophony.

A. A. ELDRIDGE.

Does anthranilyl chloride exist ? L. ANSCHÜTZ and H. BOEDEKER (Ber., 1929, **62**, [*B*], 826—830).—*Sodium anthranilate* ($+H_2O$) is converted by thionyl chloride into *o*-aminobenzoylanthranilic anhydride, m. p. 160° (cf. Schroeter, A., 1909, i, 576), and, apparently, an *isomeride*, m. p. 136—139°. Barium anthranilate combines with 1 mol. of water, which is very firmly retained. The anhydrous silver or lead anthranilate is converted by thionyl chloride in presence of anhydrous ether into o-*thionylaminobenzoyl chloride*, $COCl\cdot C_6H_4\cdot N{:}S{:}O$, b. p. 98°/0·07 mm., m. p. 34—35°. In contact with atmospheric moisture it is converted into sulphur dioxide and amorphous products. With *p*-toluidine it affords *p*-toluidine hydrochloride and anthranil-*p*-toluidide. Lead *p*-aminobenzoate and thionyl chloride yield p-*thionylaminobenzoyl chloride*, but the corresponding *m*-compound cannot be prepared analogously.

H. WREN.

Hydrogenation of anthroic acid and the question of the existence of two isomeric 9 : 10-dihydroanthracene - 9 - carboxylic acids. H. MEERWEIN and A. MIGGE (Ber., 1929, **62**, [*B*], 1046—1050).—The action of hydrogen on a boiling solution of anthroic acid in *iso*propyl alcohol in the presence of palladised barium sulphate leads to the evolution of carbon dioxide. 1 : 2 : 3 : 4-Tetrahydroanthracene, m. p. 104—105°, and octahydroanthracene, m. p. 72—74°, are isolated from the portion of the product insoluble in sodium carbonate. The soluble portion yields small amounts of dihydroanthroic acid, m. p. 203·5—204·5° (methyl ester, m. p. 97—98°), identical with the so-called " α " acid obtained by Schlenk and Blum (A., 1928, 1036) by the action of carbon dioxide on the monosodium additive compound of anthracene. The main product is *1 : 2 : 3 : 4-tetrahydroanthracene-9-carboxylic acid*, m. p. 204·5—205·5° (*methyl* ester, m. p. 67—68°), oxidised to 1 : 2 : 3 : 4-tetrahydroanthraquinone, m. p. 157—158°. Dihydroanthroic acid is also formed. Schlenk and Blum's " β-9 : 10-dihydroanthroic acid " is therefore regarded as a mixture of products and an instance of " superfluous " isomerism is disproved. H. WREN.

Action of carbon dioxide on sodium β-naphthoxide. The Kolbe–Schmitt synthesis. E. SCHWENK [with M. KNOB and H. STEIN] (Chem.-Ztg., 1929, **53**, 297—299, 333—336).—The mechanism of the Kolbe synthesis of phenolcarboxylic acids is investigated by a study of the action of carbon dioxide on sodium β-naphthoxide under varying conditions. When carbon dioxide is passed under slight pressure over carefully dried sodium β-naphthoxide at 18—20° the additive compound, $C_{10}H_7\cdot O\cdot CO_2Na$, is formed which is decomposed by water in accordance with the equation

$$2C_{10}H_7\cdot O\cdot CO_2Na+H_2O=C_{10}H_7\cdot ONa+C_{10}H_8O+CO_2+NaHCO_3,$$ and by heating in a sealed tube at 120—130° yields, after acidification of the product,

β-naphthol-1-carboxylic acid. The sodium salt of this acid (obtained by the action of alcoholic sodium ethoxide), after very careful drying over phosphoric oxide and finally by heating at 105—110°/8 mm., does not absorb dry ammonia (cf. Tijmstra and Eggink, A., 1906, i, 179) and when heated in a sealed tube at 250—260° is converted into β-naphthol and β-naphthol-3-carboxylic acid, the carboxyl group migrating from the 1 to the 3 position. The mechanism of this reaction involves the initial decomposition of the sodium salt into sodium β-naphthoxide and carbon dioxide, these products then interacting according to temperature conditions to yield either β-naphthol-1- or -3-carboxylic acid. The liberation of carbon dioxide during the reaction is proved by the partial conversion of sodium phenoxide, placed in an open second tube inside the sealed tube, into sodium salicylate. When in the latter experiment the tube is heated only at 150—160°, the conversion of the sodium phenoxide into sodium salicylate is more complete, and the sole reaction products are β-naphthol and a little β-naphthol-1-carboxylic acid. Potassium β-naphthol-1-carboxylate is stable up to 200° (the sodium salt begins to decompose at 130°) and by heating in a sealed tube at 230° is converted into β-naphthol and β-naphthol-3-carboxylate, but no -6-carboxylate is obtained. Similarly, substitution of potassium β-naphthoxide for sodium phenoxide in the earlier sealed tube experiments (above) yields only a small quantity of the -3-carboxylic acid, but again no 6-acid. Thus the β-naphthol-6-carboxylic acid said to be obtained in G.P. 436524 cannot be formed from the potassium β-naphthol-1-carboxylate, but is produced in some other way. J. W. Baker.

p-Methoxycinnamylideneacetic acid. D. Vorländer and K. Gieseler (J. pr. Chem., 1929, [ii], **121**, 247—254).—Condensation of p-methoxycinnamaldehyde and malonic acid in presence of acetic acid at 50—60°, or aqueous-alcoholic ammonia at 100°, gives p-*methoxycinnamylidenemalonic acid* (anhydrous and $+H_2O$), m. p. 182° (decomp.). Elimination of carbon dioxide from this by heating with pyridine and a small amount of piperidine first at 100° and then over a free flame affords mainly the crystalline-liquid form (*trans–trans*) of p-*methoxycinnamylideneacetic acid* (I), m. p. 179° and 222—223° (corr.) [*tetrabromide*, m. p. 180° with elimination of hydrogen bromide; *methyl* ester, m. p. 126°; *ethyl* ester, m. p. 66—68°; n-*propyl* ester, m. p. 47—49°; *acid chloride*, m. p. about 110°; p-*ethoxyphenyl* ester, m. p. 150° and 211° (corr.); *anilide*, m. p. 189° (corr.); p-*toluidide*, m. p. 214° (corr.); p-*anisidide*, m. p. 193° and 218° (corr.); p-*phenetidide*, m. p. 182° and 220° (corr.); *piperidide*]. Exposure of a solution of the sodium salt of I to ultra-violet light causes the formation of salts of two *acids* (or mixtures of acids), m. p. 90—96° and 106—110°, respectively, both of which regenerate I in benzene solution containing iodine exposed to sunlight. When the thermal decomposition is effected in presence of acetic anhydride at 130° or quinoline at 160° some allo(trans–cis)-p-*methoxycinnamylideneacetic acid*, m. p. 128—131° (corr.) [*tetrabromide*, m. p. about 165° (decomp.)], is also obtained. This is also converted into I by exposing a benzene solution containing iodine to sunlight. Reduction of I and II with sodium amalgam and water yields the same δ-p-*methoxyphenyl*-Δ^{β}-*pentenoic acid*, m. p. 57°, oxidised by alkaline potassium permanganate to oxalic and anisic acids, and converted by boiling with 10% sodium hydroxide solution into β-p-*methoxyphenylpropylideneacetic acid*, m. p. 136—138°.

p-*Methoxycinnam*-p-*anisidide* and -p-*phenetidide* have m. p. 184—185° (corr.) and 180°, respectively.
H. Burton.

γ-Resorcylic acid [2 : 6-dimethoxybenzoic acid]. F. Mauthner (J. pr. Chem., 1929, [ii], **121**, 259—265).—When 6 - nitro - 2 - methoxybenzonitrile (Lobry de Bruyn, Rec. trav. chim., 1883, **2**, 205) is treated with methyl-alcoholic potassium hydroxide solution, 2 : 6-dimethoxylbenzonitrile, m. p. 118°, results. Hydrolysis of this with concentrated sulphuric acid at 60—65° gives 2 : 6-*dimethoxybenzamide*, m. p. 207—208°, whilst prolonged treatment with boiling concentrated potassium hydroxide solution yields a small amount of the amide together with 2 : 6-dimethoxybenzoic acid (methyl ester, m. p. 88°, obtained either with diazomethane or by esterification with methyl alcohol and hydrogen chloride). Treatment of the acid with aluminium chloride in boiling chlorobenzene solution affords resorcinol.
H. Burton.

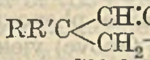
Reaction of thiocarbimides and hydrogen chloride with polyhydric phenols. P. Karrer and E. Weiss (Helv. Chim. Acta, 1929, **12**, 554—557).—Substituted thiobenzamides are obtained by treating a mixture of a phenol and a thiocarbimide in dry ether with hydrogen chloride in presence of zinc chloride. Reaction occurs through the intermediate thiocarbamyl chloride. The following are described: 2 : 4-*dihydroxythiobenzethylamide*, m. p. 96°; 2 : 4 : 6-*trihydroxythiobenzethylamide*, m. p. 152°; 2 : 3 : 4-*trihydroxythiobenzallylamide*, m. p. 206° (decomp.); 2 : 4-*dihydroxythiobenzanilide*, m. p. 176°; 4-*hydroxythionaphthanilide* (?), m. p. 206° after sintering at 198°, and 2:4-*dihydroxythiobenz*-β-*naphthylamide*, m. p. 177—179° after sintering at 167°. H. Burton.

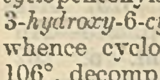
Halogen derivatives of thyronine (deiodothyroxine). K. Schuegraf (Helv. Chim. Acta, 1929, **12**, 405—414).—Bromination of 3 : 5-di-iodothyronine (cf. Harington, this vol., 313) gives 3′ : 5′-*dibromo*-3 : 5-*di-iodothyronine*, m. p. 245—246° (decomp.) [3′ : 5′-*dichloro*-derivative, m. p. 262° (decomp.)]. 3 : 5-Dibromo-4-iodonitrobenzene reacts with quinol monomethyl ether in presence of methyl ethyl ketone and anhydrous potassium carbonate yielding 3 : 5-*dibromo*-4-p-*methoxyphenoxynitrobenzene*, m. p. 151—152°. Reduction of this with stannous chloride and hydrogen chloride in acetic acid gives the corresponding *amine*, m. p. 117°, converted by the usual method into the corresponding *nitrile*, m. p. 107°. This is converted by Stephen's method into 3 : 5-*dibromo*-4-p-*methoxyphenoxybenzaldehyde*, m. p. 98°, which condenses with hippuric acid in presence of acetic anhydride and sodium acetate, yielding the corresponding *azlactone*, m. p. 195°. Treatment of this with red phosphorus and hydriodic acid (d 1·7) in acetic anhydride solution affords 3 : 5-*dibromothyronine*, m. p. 257° (decomp.), brominated further to 3 : 3′ : 5 : 5′-*tetrabromothyronine*, m. p. 241—242°

(decomp.). 3′ : 5′-*Dichloro*-3 : 5-*dibromo*-, m. p. 234° (decomp.), and 3 : 5-*dibromo-3′ : 5′-di-iodo-thyronine*, m. p. 229° (decomp.), are described. 3 : 5-*Dichloro-4-*p*-methoxyphenoxynitrobenzene*, m. p. 147°, is converted as above through the corresponding *amine*, m. p. 144°, and *nitrile*, m. p. 97°, into 3 : 5-*dichloro-4-*p*-methoxyphenoxybenzaldehyde*. The *azlactone*, m. p. 191°, from this affords 3 : 5-*dichlorothyronine*, m. p. 266° (decomp.) [3′ : 5′-*dibromo*-derivative, m. p. 240° (decomp.); 3′ : 5′-*di-iodo*-derivative, m. p. 229° (decomp.)]. 3 : 3′ : 5 : 5′-*Tetrachlorothyronine* has m. p. 231° (decomp.). H. BURTON.

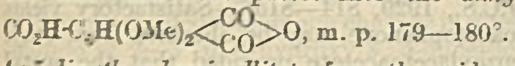
Modified Curtius synthesis of primary amines. R. H. F. MANSKE (J. Amer. Chem. Soc., 1929, 51, 1202—1204).—When direct hydrolysis of alkylcarbamides and -urethanes to primary amines is difficult, they may be converted by phthalic anhydride into alkylphthalimides, which are then hydrolysed by means of hydrazine (cf. A., 1926, 1132). Thus, αθ-dimethylurethano-octane and phthalic anhydride at 230° give *αθ-diphthalimido-octane*, m. p. 138° (corr.), which with hydrazine gives αθ-diamino-octane. γ-Phenoxybutyrylhydrazide is converted through the azide into *s-di-γ-phenoxypropylcarbamide*, m. p. 150°, which with phthalic anhydride gives γ-phenoxypropylphthalimide. Similarly, *s*-di-β-indolylethylcarbamide yields β-3-*indolylethylphthalimide*, m. p. 164—165°, quantitatively hydrolysed by hydrazine to tryptamine. H. E. F. NOTTON.

Keto–lactol tautomerism. II. Influence of the *cyclo*hexane ring on the tautomeric character of *cyclo*hexane-1-acetone-1-malonic acid, a comparison with *cyclo*pentane-1-acetone-1-malonic acid, and synthesis of the corresponding δ-keto-monobasic acids. M. QUDRAT-I-KHUDA (J.C.S., 1929, 713—721).—Condensation of *cyclo*hexenylacetone with cyanoacetamide in alcoholic sodium ethoxide solution gives cyclo*hexanes*piro*cyclo-3-hydroxy-6-cyano-3-methyl-5-piperidone*, m. p. 258°, hydrolysed by aqueous potassium hydroxide to cyclo*hexane-1-acetone-1-malonic acid*, m. p. 116°, decomp. 118° [*semicarbazone*, m. p. 183° (decomp.); *ethyl* ester, b. p. 192°/14 mm., $d_4^{18\cdot5}$ 1·0681, $n_D^{18\cdot5}$ 1·46984; *ethyl ester semicarbazone*, m. p. 104°). Analogous treatment of *cyclo*pentenylacetone affords cyclo*pentanes*piro*cyclo-3-hydroxy-6-cyano-3-methyl-5-piperidone*, m. p. 282°, whence cyclo*pentane-1-acetone-1-malonic acid*, m. p. 106°, decomp. about 130° (*semicarbazone*, m. p. 177°; *ethyl* ester, b. p. 179°/13 mm., d_4^{18} 1·0767, n_D^{18} 1·4632; *ethyl ester semicarbazone*, m. p. 109°), is prepared.

The behaviour of *cyclo*hexane- and *cyclo*pentane-1-acetone-1-malonic acids supports the views previously advanced by the Thorpe–Ingold school; in particular, the second acid resembles α-carboxy-γ-acetyl-ββ-dimethylbutyric acid (this vol., 295). In the liquid state the two acids exist as an equilibrium mixture of the keto- and lactol forms. When heated they decompose similarly: *cyclo*hexane-1-acetone-1-malonic acid gives at 130—140° the *dilactone*, m. p. 141°, and cyclo*hexane-1-acetone-1-acetic acid*, m. p. 73° (*semicarbazone*, m. p. 185°) (I, RR′=[CH$_2$]$_5$), whilst *cyclo*pentane-1-acetone-1-malonic acid gives at 140—150° the *dilactone*, m. p. 139°, and cyclo*pentane-1-acetone-1-acetic acid*, m. p. 53° (*semicarbazone*, m. p. 191°) (I, RR′=[CH$_2$]$_4$). These acetic acids were synthesised as follows for confirmation of their constitution. *cyclo*Hexane-1 : 1-diacetic anhydride gives by boiling with methyl alcohol the *silver* salt of *methyl hydrogen* cyclo*hexane*-1 : 1-*diacetate*; the *acid ester* is converted by thionyl chloride into the *chloride*, which with zinc methyl iodide in cold benzene solution gives *methyl* cyclo*hexane-1-acetone-1-acetate*, b. p. 152°/18 mm., $d_4^{20\cdot4}$ 1·0363, $n_D^{20\cdot4}$ 1·46748 (*semicarbazone*, m. p. 137°). When heated with alcoholic sodium ethoxide the keto-ester gives *cyclo*hexane*spirocyclo*hexane-3 : 5-dione, and with methyl-alcoholic aqueous potassium hydroxide, *cyclo*hexane-1-acetone-1-acetic acid and small amounts of *cyclo*hexane-1 : 1-diacetic acid. *cyclo*Pentane-1 : 1-diacetic acid is transformed into methyl hydrogen *cyclo*pentane-1 : 1-diacetate (*silver* salt), and this, through the acid chloride by interaction with zinc methyl iodide, gives *methyl* cyclo*pentane-1-acetone-1-acetate*, b. p. 130°/12 mm., $d_4^{17\cdot7}$ 1·0386, $n_D^{17\cdot7}$ 1·46021 (*semicarbazone*, m. p. 119°), from which either *cyclo*pentane*spirocyclo*hexane-3 : 5-dione or *cyclo*pentane-1-acetone-1-acetic acid can be prepared. Acetyl chloride reacts with *cyclo*hexane-1-acetone-1-acetic acid at the ordinary temperature and with *cyclo*pentane-1-acetone-1-acetic acid at 100° to give the *lactones*,  $RR'C{<}{\substack{CH{:}CMe\\ CH_2{-}CO}}{>}O$ (RR′=[CH$_2$]$_5$), b. p. 144°/17 mm., $d_4^{19\cdot9}$ 1·0533, $n_D^{19\cdot9}$ 1·4952, and (RR′=[CH$_2$]$_4$), b. p. 124°/14 mm., $d_4^{18\cdot9}$ 1·0573, $n_D^{18\cdot9}$ 1·49043, respectively. R. J. W. LE FÈVRE.


(I.)

Constitution of *iso*chondodendrine. III. F. FALTIS and K. ZWERINA [with A. B. G. ATTIA] (Ber., 1929, 62, [*B*], 1034—1041; cf. A., 1922, i, 569; 1928, 433).—The synthesis is described of certain acids required in connexion with the constitution of the tricarboxylic acid, $C_{17}H_{14}O_9$, derived from *iso*chondodendrine. Opianic acid is transformed by an excess of bromine in water into bromo-opianic acid, m. p. 204°, converted by cautious treatment with hydroxylamine hydrochloride into the corresponding oxime anhydride, m. p. 220° (m. p. of bromohemipinimide), which with boiling water affords 6-*bromohemipinic anhydride*, m. p. 193°. The anhydride is not smoothly esterified by methyl alcohol and sulphuric acid, but is transformed by potassium hydroxide and methyl sulphate under defined conditions into *methyl 6-bromohemipinate*, m. p. 56—57°. Condensation of the bromo-ester with the potassium compound of methyl *p*-hydroxybenzoate in presence of copper powder and copper acetate at 150—170° yields *methyl* 3-p-*carbomethoxyphenoxy*-5 : 6-*dimethoxybenzene*-1 : 2-*dicarboxylate*, m. p. 108—109° [corresponding *tricarboxylic acid*, m. p. 242° (decomp.)], not identical with the product of the degradation of *iso*chondodendrine. Similarly, the potassium derivative of methyl *m*-hydroxybenzoate and methyl bromohemipinate afford *methyl* 3-m-*carbomethoxyphenoxy*-5 : 6-*dimethoxybenzene*-1 : 2-*dicarboxylate*, m. p. 111—112° [corresponding *acid*, m. p. 185° (decomp.) when rapidly heated]. During the methoxyl determinations with the *p*- and *m*-esters, carbon dioxide is also lost and *acids*, $C_{14}H_{10}O_7$, m. p. 250° (decomp.) and 248° (decomp.), are produced. Treatment of the *p*-acid with molten potassium hydroxide yields *p*-hydroxybenzoic acid, the expected hydroxyquinolcarboxylic acid undergoing total decomposition. *m*-Hydroxybenzoic acid is derived similarly from the *m*-acid. H. WREN.

4 : 5-Dimethoxyhemimellitic acid. F. FALTIS and F. KLOIBER (Ber., 1929, 62, [*B*], 1041—1045).—Diazohemipinic acid is very cautiously neutralised with 0·2*N*-potassium hydroxide and the solution is added to potassium cuprocyanide at 60—70°; the crude nitrile thus obtained is converted by hydrochloric acid into 4 : 5-dimethoxyhemimellitic acid, m. p. 160—162° (decomp.) after softening at 156° when very rapidly heated (the m. p. depends greatly on the rate of heating owing to the conversion of the acid into the anhydro-acid); the calcium salt has $3H_2O$. At 120—130° the acid passes into the *anhydro-acid*,  $CO_2H\cdot C_6H(OMe)_2<\begin{matrix}CO\\CO\end{matrix}>O$, m. p. 179—180°. *Methyl 4 : 5-dimethoxyhemimellitate*, from the acid and diazomethane, has m. p. 86—87°. The acid is converted by heating at 300—320° and subsequent treatment with ethylamine into *m*-hemipinethylimide. H. WREN.

Different behaviour of some bile acids in the classical colour reactions. L. CUNY (Compt. rend. Soc. Biol., 1928, 99, 613—615; Chem. Zentr., 1928, ii, 1700).—Pettenkofer's reaction with sucrose and sulphuric acid depends on the presence of glycocholic, taurocholic, or cholalic acid; deoxycholic and other complex bile acids react differently. A. A. ELDRIDGE.

Derivatives of methyl 2 : 2-dimethyl*cyclo*pentan-3-one-1-carboxylate. C. S. GIBSON, K. V. HARIHARAN, and J. L. SIMONSEN (J. Indian Inst. Sci., 1928, 11, A, 215—220).—See A., 1928, 173.

Thiophthalic acids. I. G. C. CHAKRAVARTI (J. Indian Inst. Sci., 1928, 11, A, 221—225).—See A., 1928, 1241.

Pyrolysis of benzaldehyde and of benzyl benzoate. C. D. HURD and C. W. BENNETT (J. Amer. Chem. Soc., 1929, 51, 1197—1201).—After being heated for 2 hrs. in a sealed tube at (*a*) 300—310°, (*b*) 350—370°, benzaldehyde is changed to the extent of (*a*) 5—12%, (*b*) 30%, mainly into benzyl benzoate and a trace of benzoic acid (cf. Lachman, A., 1924, i, 649). Benzene is also formed in (*b*), but no toluene or benzyl ether. These changes are analogous to the pyrolysis of hydrobenzamide and of dibenzylidene-*o*-phenylenediamine (cf. Hinsberg, A., 1896, i, 536; Bahrmann, A., 1883, 799). Benzyl benzoate at 350° gives mainly benzoic anhydride, toluene, and benzaldehyde, the last two probably arising from the decomposition of benzyl ether. Benzaldehyde, passed slowly through a pyrex tube at 680—690°, undergoes 66% decomposition, giving mainly benzene and carbon monoxide with small quantities of diphenyl, 1 : 4-diphenylbenzene, regarded by Peytral (A., 1921, i, 166) as anthracene, hydrogen, and carbon dioxide. H. E. F. NOTTON.

Conjugated unsaturated compounds. VIII. R. KUHN and A. WINTERSTEIN (Helv. Chim. Acta, 1929, 12, 493—498).—Condensation of benzaldehyde with crotonaldehyde in presence of aqueous-alcoholic sodium hydroxide gives 10% of cinnamylideneacetaldehyde, b. p. 160—162°/12 mm.: subsequent condensation of this with succinic and dihydromuconic acids affords pure conjugated unsaturated hydrocarbons (A., 1928, 281). Treatment of αζ-diphenylhexatriene with sodium–potassium alloy in dry ether yields a 1 : 4-additive product, since decomposition with moist nitrogen affords αδ-dibenzylbutadiene; with carbon dioxide an acid, decomp. 170° with elimination of carbon dioxide, is produced. Decomposition of the reaction product from lithium and αζ-diphenylhexatriene gives an oily acid. αθ-Diphenyloctatetraene reacts only slowly with lithium.

Nyctanthin (Perkin, J.C.S., 1912, 101, 1538; Hill, *ibid.*, 1907, 91, 1501) is identical with α-crocetin (A., 1928, 869). H. BURTON.

***p*-Methoxycinnamaldehyde and *p*-methoxycinnamylideneacetaldehyde.** D. VORLÄNDER and K. GIESELER (J. pr. Chem., 1929, [ii], 121, 237—246).—Condensation of anisaldehyde with acetaldehyde in presence of aqueous methyl-alcoholic sodium hydroxide (cf. Scholtz and Wiedemann, A., 1903, i, 436) gives *p*-methoxycinnamaldehyde (I), m. p. 58° [*phenylhydrazone*, m. p. 138° (corr.); *hydrazone*, m. p. 210—212° and 231° (corr.); here and wherever two m. p. are recorded it is indicated that the substance exhibits enantiotropic crystalline-liquid properties (cf. Vorländer and Gahren, A., 1907, ii, 441; Walter, A., 1926, 17)]. Condensation *products* of I with the following amines are described: aniline, m. p. 125° (corr.); *p*-toluidine, m. p. 126° and 138° (corr.) from alcohol, 122° and 129° (corr.) from benzene; *p*-chloroaniline, m. p. 133° and 147° (corr.); *p*-aminophenol, m. p. 196°; *p*-anisidine, m. p. 167° and 180° (corr.); *p*-phenetidine, m. p. 146° and 181° (corr.); *p*-aminoazobenzene, m. p. 168° (corr.) and about 240° with darkening; *p*-aminobenzoic acid, m. p. 200—202°; ethyl *p*-aminobenzoate, m. p. 97° and 129° (corr.); ethyl *p*-aminocinnamate, m. p. 134° and 188° (corr.), and β-naphthylamine, m. p. 171°. Condensation of I with acetone gives *p*-methoxycinnamylidene-, m. p. 108°, and di-*p*-methoxycinnamylidene-acetone, m. p. 168° and 183° (corr.) [*octabromide*, m. p. 163° (decomp.)]. *Di*-p-*methoxycinnamylidene*-cyclo*pentanone*, m. p. 237° (corr.), and -cyclo*hexanone*, m. p. 201° and 212°, are obtained by effecting condensation of I and the ketones in presence of methyl-alcoholic sodium hydroxide solution, whilst p-*methoxycinnamylidene*-p-*hydroxyacetophenone*, m. p. 169°, -p-*methoxyacetophenone*, m. p. 112°, and -p-*acetoxyacetophenone*, m. p. 134°, are prepared using hydrogen chloride as the condensing agent. Condensation of I with acetaldehyde in presence of aqueous-alcoholic sodium hydroxide below 10° gives a small amount of impure *p*-methoxycinnamylideneacetaldehyde (II) [phenylhydrazone, m. p. 173° and 184° (decomp.; corr.)], oxidised by ammoniacal silver oxide to *p*-methoxycinnamylideneacetic acid, m. p. 176° and 216—218° (corr.). Condensation *products* from II and the following amines are described: aniline, m. p. 125° and 135° (corr.); *p*-toluidine, m. p. 133° and 180° (corr.); *p*-anisidine, m. p. 192° and 218—220° (corr.); *p*-phenetidine, m. p. 167° and 217° (corr.); *p*-aminoazobenzene, m. p. 174° (corr.), and β-naphthylamine, m. p. 162° and 200° (corr.). As by-products in the preparation of II there are obtained partly hydrogenated aldehydes and some β-p-*methoxyphenylpropylideneacetic acid*, m. p. 136—138°, oxidised by potassium permanganate to oxalic and β-*p*-methoxyphenylpropionic acids. These substances appear to be formed during the vacuum distillation of the reaction mixture of I and acetaldehyde. H. BURTON.

Electrolytic reduction of aldehydes. V. Cinnamaldehyde. VI. Complete reduction of the carbonyl group. G. SHIMA.—See this vol., 521.

Aldehydophenolphthalein dyes. R. N. SEN and K. C. KAR.—See B., 1929, 350.

Synthesis of cyclic compounds. V. Catalytic and thermal decomposition of some normal dibasic acids. Ease of formation of simple carbon rings. A. I. VOGEL (J.C.S., 1929, 721—733).—From comparative experiments on the preparation of suberone in which suberic acid was heated with different mixtures of iron filings and baryta it is concluded that, in this reaction, an intermediate iron salt is formed at lower temperatures and undergoes decomposition into the corresponding ketone at higher temperatures. If less iron than that required for formation of the ferrous salt be present, then variable quantities of *n*-heptoic acid are also formed. The use of baryta facilitates formation of the intermediate iron salt, lowers the decomposition temperature, and thus gives a purer product.

Application of the optimum conditions employed for suberic acid to glutaric, adipic, pimelic, and azelaic acids gave <1%, 51%, 56%, and 10% of cyclic ketone respectively. Sebacic acid gave only methyl octyl ketone. The results differ quantitatively more from those obtained using thorium salts than from those with calcium salts.

A discussion of methods for comparing ease of formation of simple carbon rings shows that there must be (1) a main reaction involving the formation of the cyclic compound, and (2) an alternative side reaction giving an open-chain product. Accordingly in the present work slow thermal distillation of the normal dibasic acids has been utilised. Glutaric acid yields only *n*-butyric acid; adipic and pimelic acids give 80% and 52%, respectively, of *cyclo*pentanone and *cyclo*hexanone. Suberic, azelaic, and sebacic acids give mainly *n*-heptoic, *n*-octoic, and *n*-nonoic acids, respectively, and but little ketone in each case. It follows that, in particular, the *cyclo*pentane ring is formed more readily than the *cyclo*hexane ring. The results obtained are compared with the theoretical probabilities of formation of an *n*-membered ring (cf. Wojnicz-Sianozencki, A., 1922, i, 330) and with the conclusions reached from calculations based on other physical measurements and considerations.

R. J. W. LE FÈVRE.

Di-*p*-tolylketen. H. GILMAN and C. E. ADAMS (Rec. trav. chim., 1929, 48, 464—465).—Oxidation of 4 : 4'-dimethylbenzilmonohydrazone with mercuric oxide (cf. Curtius and Kastner, A., 1911, i, 324) affords the corresponding azo-derivative, which when heated at 80—90° in a vacuum yields di-p-*tolylketen*. This is decomposed by water and alcohol to di-*p*-tolylacetic acid and its ethyl ester, respectively. It furnishes a *quinoline* compound, which when treated with di-*p*-tolyl ketone affords tetra-*p*-tolylethylene (cf. Gilman and Flick, this vol. 688). H. BURTON.

Radical nature of dark-coloured, dimeric diarylketens. W. LANGENBECK (Ber., 1929, 62, [*B*], 962—963; cf. Langenbeck and Langenbeck, A., 1928, 762; Wittig and von Lupin, *ibid.*, 1233).—Anisilic acid is converted when heated into a dark, bluish-green, molten mass which becomes colourless when cold. The solution in toluene is yellow at the ordinary temperature, becomes green at 50—80° and greenish-blue at the b. p. At 80°, the solution shows marked deviation from Beer's law, so that the presence of a radical is established. H. WREN.

***o*-Nitroacetophenone.** W. O. KERMACK and J. F. SMITH (J.C.S., 1929, 814—815).—Satisfactory yields of *o*-nitroacetophenone may be obtained from ethyl *o*-nitrobenzoylacetoacetate provided that the acetyl group is removed before hydrolysis of the ester group takes place. Thus, by boiling an alcoholic solution of ethyl *o*-nitrobenzoylacetoacetate to which 10% by weight of sulphuric acid has been added the acetyl group is removed as ethyl acetate; the acetate and the bulk of the alcohol are distilled off and the residue is refluxed for an hour. The yield of redistilled *o*-nitroacetophenone exceeds 75%.

R. J. W. LE FÈVRE.

9-Benzhydrylanthrone and *iso*dianthranyl. E. DE B. BARNETT and N. F. GOODWAY (J.C.S., 1929, 813—814).—Treatment of anthrone with benzhydryl chloride in potassium hydroxide solution gave *benzhydrylanthrone*, m. p. 188—189° (acetate, m. p. 234—235°, lit. 228—229°), reduction of which by zinc dust and boiling acetic and hydrochloric acids gave a yellow *iso*dianthranyl (accompanied by some diphenylmethane), m. p. 312° (decomp. 305°), probably identical with that of Schlenk (A., 1928, 1031) and different from that of Barnett and Matthews (J.C.S., 1923, 123, 380). R. J. W. LE FÈVRE.

Preparation of semicarbazones in pyridine solution. I. V. HOPPER (J. Roy. Tech. Coll. Glasgow, 1929, 2, [1], 52—56).—A generally applicable method of preparing semicarbazones is to allow semicarbazide hydrochloride to react with an aldehyde or a ketone in aqueous pyridine solution, the pyridine acting both as a solvent and as a base to combine with the liberated hydrochloric acid. Under these conditions benzil gives the monosemicarbazone at the ordinary temperature and diphenyloxytriazine at 100° but no disemicarbazone. *Acetophenone-5-benzylsemicarbazone*, CPhMe:N·NH·CO·NH·CH_2Ph, m. p. 128°, has been prepared by this method. A. R. POWELL.

Stereochemistry of the phenyl styryl ketones; ethylenic isomerism and polymorphism of the phenyl α-bromo-β-alkoxystyryl ketones. C. DUFRAISSE and A. GILLET (Ann. Chim., 1929, [x], 11, 5—21).—When the methylacetal of bromodibenzoylmethane, Bz·CHBr·CPh(OMe_2), is heated above 150° a mixture, m. p. about 58°, is obtained of two isomeric *phenyl α-bromo-β-methoxystyryl ketones*, which are distinguished by their different crystalline forms. Seeding under aseptic conditions gave an isomeride *A*,

m. p. 101—102°; the other isomeride is dimorphous, the two forms B_α, m. p. 64—65°, and B_β, m. p. 71—72°, differing in their crystalline form and solubility in light petroleum, b. p. 80—85°, and in ethyl alcohol. *A* is partly converted into *B* by heat. Under the influence of light in neutral or slightly acid solution *A* is completely converted into *B*, but in an alkaline medium *B* passes completely into *A*. Bromodibenzoylmethane is formed from *A* in the presence of strong acids, particularly under the influence of light. *Phenyl α-bromo-β-ethoxystyryl ketone*, similarly prepared, was separated into three forms, m. p. 65°, 73°, and 76°, respectively. Phenyl α-bromo-β-propoxystyryl ketone was isolated in one form, m. p. 50—51° (lit. 49°). A. I. Vogel.

Synthesis of acetosyringone. F. Mauthner (J. pr. Chem., 1929, [ii], **121**, 255—258).—2 : 6-Dimethoxyphenyl acetate is isomerised by treatment with finely-divided aluminium chloride in nitrobenzene solution at 2—3° to 4-hydroxy-3 : 5-dimethoxyacetophenone, m. p. 122—123° (cf. Bradley and Robinson, A., 1928, 894) (p-*nitrophenylhydrazone*, m. p. 189—190°). Methylation of this with methyl iodide and methyl-alcoholic potassium hydroxide solution gives 3 : 4 : 5-trimethoxyacetophenone (trimethylgallacetophenone). H. Burton.

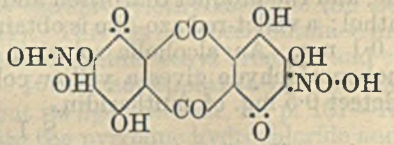
Chalkones [related to hyssopin]. R. L. Shriner and E. C. Kleiderer (J. Amer. Chem. Soc., 1929, **51**, 1267—1270).—2 : 4 : 6 - *Trihydroxyacetophenone*, m. p. 213—214°, from phloroglucinol and acetyl chloride in nitrobenzene in presence of aluminium chloride, gives with piperonal and alcoholic potassium hydroxide yellow 2 : 4 : 6-*trihydroxyphenyl* 3 : 4-*methylenedioxystyryl ketone* (I), decomp. 300—310° (*triacetate*, m. p. 218—220°). 2 : 4 : 6-Trihydroxybenzaldehyde and acetopiperone (Mauthner, A., 1927, 972) give similarly 3 : 4-*methylenedioxyphenyl* 2 : 4 : 6-*trihydroxystyryl ketone* (II), decomp. 265—270° (*triacetate*, m. p. 205—206°). The chalkone, decomp. 262—263° (triacetate, m. p. 196—197°), from hyssopin is probably identical with II, and not with I as stated by Oesterle (A., 1922, i, 849). H. E. F. Notton.

Syntheses of polyhydroxy-chalkones, -hydrochalkones, and -flavanones. IV. Synthesis of 5 : 7-dihydroxy-3′ : 4′-dimethoxyflavanone and constitution of eriodictyol and homoeriodictyol. V. Synthesis of eriodictyol and homoeriodictyol. J. Shinoda and S. Sato (J. Pharm. Soc. Japan, 1929, **49**, No. 563, 5—6, 7—9).—IV. Phloroglucinol condensed with 3 : 4-dimethoxycinnamoyl chloride in presence of aluminium chloride and nitrobenzene yields 5 : 7-*dihydroxy*-3′ : 4′-*dimethoxyflavanone*, m. p. 200° (*oxime*, m. p. 252°), converted by diazomethane into 5-*hydroxy*-7 : 3′ : 4′-*trimethoxyflavanone* (I), m. p. 136° (*acetyl* derivative, m. p. 155°). Hesperetin (this vol., 189), eriodictyol (II) (*tetra-acetyl* derivative, m. p. 137°), and homoeriodictyol (III) (*triacetyl* derivative, m. p. 115—116°; *oxime*, m. p. 224°), are all converted by diazomethane into I. Prolonged acetylation of I, II, and III gives acetyl derivatives, m. p. 160°, 196—197°, and 163—164°, respectively (cf. Power and Tutin, J.C.S., 1907, **91**, 887; Mossler, A., 1907, ii, 291), which are probably substituted phenyl styryl ketones.

V. Phloroglucinol and 3 : 4-dicarbethoxyoxycinnamoyl chloride (Fischer and Oetker, A., 1914, i, 143) condense in presence of aluminium chloride, yielding eriodictyol (5 : 7 : 3′ : 4′-tetrahydroxyflavanone), m. p. 267°, and a *substance* $[(OH)_2\cdot C_6H_3\cdot CH{:}CH\cdot CO]_2C_6H(OH)_3$, m. p. 267°. Carbethoxyvanillin reacts with malonic acid in presence of pyridine and a small amount of piperidine, forming 3-*methoxy-4-carbethoxyoxycinnamic acid*, m. p. 180°, the acid chloride of which condenses with phloroglucinol, yielding homoeriodictyol (5 : 7 : 4′-trihydroxy-3′-methoxyflavanone), m. p. 224—225°, together with a substance, m. p. 233°. H. Burton.

Polyiodoanthraquinones. A. Eckert and M. Klinger (J. pr. Chem., 1929, [ii], **121**, 281—288).—When tetraiodobenzoylbenzoic acid (I) (Hofmann, A., 1916, i, 143) is heated rapidly to 190—200° with 10 parts of concentrated sulphuric acid some iodine is eliminated, but 1 : 2 : 3 : 4-*tetraiodoanthraquinone*, decomp. about 476°, was isolated from the reaction mixture. With fuming sulphuric acid at 100°, reaction occurs but no anthraquinone derivative is formed. Treatment of I with aluminium chloride at 150—175° affords a small amount of a *di-iodoanthraquinone*, m. p. 290—292°. Treatment of anthraquinone with iodine in presence of fuming sulphuric acid (70% SO_3) at 140—180° gives a mixture of *tri-iodo-*, m. p. 277°, *pentaiodo-*, decomp. 368°, and *tetraiodo-anthraquinones*, not melted at 500° (main product). This last compound, probably the 1 : 4 : 5 : 8-derivative, is relatively stable. It resists nitration, does not react with aniline, yields a halogen-free, uncrystallisable substance when boiled with potassium methoxide, and when heated with a mixture of potassium acetate and acetic acid gives anthraquinone. Anthraquinone is also obtained by treatment with zinc dust and ammonia. H. Burton.

Oxidising nitration and quinonenitronic acids. G. Heller, E. Mertz, and A. Siller (Ber., 1929, **62**, [*B*], 928—937).—1 : 2 : 5 : 6 - Tetrahydroxyanthraquinone is converted by 100% nitric acid in glacial acetic acid into 3 : 7-*dinitro*-1 : 2 : 5 : 6-*tetrahydroxyanthraquinone*, which gradually darkens above 225° but does not melt below 300° (*pyridine* salt). It is reduced by sodium sulphide in aqueous alkaline solution or by stannous chloride and hydrochloric acid in glacial acetic acid suspension to 3 : 7-*diamino*-1 : 2 : 5 : 6-*tetrahydroxyanthraquinone*, which does not show a characteristic m. p. (*sodium* salt; *acetyl* derivative, $C_{28}H_{22}O_{12}N_2$, not molten below 300°). Concentrated sulphuric and fuming nitric acids transform 1 : 2 : 5 : 6-tetrahydroxyanthraquinone into 1 : 2 : 5 : 6- *tetrahydroxyanthraquinone* -4 : 3 : 8 : 7-*diquinonenitronic acid* (I) (also +2AcOH), decomp. about 265° after softening (*sodium* salt, $C_{14}H_4O_{12}N_2Na_2$; *phenylhydrazine* salt, not molten below 290°; *hydroxylamine* salt). The quinonenitronic acid is also obtained by the action of nitrous fumes on

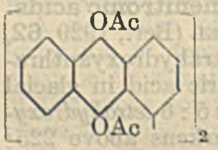


(I.)

1 : 2 : 5 : 6-tetrahydroxyanthraquinone or by nitration of 1 : 2 : 4 : 5 : 6 : 8-hexahydroxyanthraquinone in sulphuric acid. It is isomerised by dilute sulphuric acid to 3 : 7-*dinitro*-1 : 2 : 4 : 5 : 6 : 8-*hexahydroxyanthraquinone*, decomp. about 290° (accompanied by a *substance*, m. p. 225°), whereas the reverse transformation is effected in the presence of alkali or under the influence of pure nitric acid in presence of glacial acetic acid. A yellow *variety* of the nitronic acid is produced by the action of an excess of nitric acid on the form described above. Reduction of the nitronic acid is not effected by sulphurous acid or hydrogen sulphide, which induce isomerisation. Sodium sulphide converts the acid in alkaline solution into 1 : 2 : 5 : 6-*tetrahydroxyanthraquinone*-4 : 3, 8 : 7-*diquinoneoxime* (or 3 : 7-*dinitroso*-1 : 2 : 4 : 5 : 6 : 8-*hexahydroxyanthraquinone*), not molten below 300° (*pyridine* salt, m. p. 224°). 3 : 7-*Diamino*-1 : 2 : 4 : 5 : 6 : 8-*hexahydroxyanthraquinone* (*sodium* salt) is prepared by alkaline reduction of the corresponding dinitro-compound or of the nitronic acid; it is also obtained by catalytic reduction of the nitronic acid (after isomerisation) in presence of palladised barium sulphate.

1 : 2 : 7 : 8 - Tetrahydroxyanthraquinone, with glacial acetic and 100% nitric acid, affords 3 : 6-*dinitro*-1 : 2 : 7 : 8-*tetrahydroxyanthraquinone*, m. p. 295—296° (decomp.), whereas with sulphuric and nitric (*d* 1·52) acids it gives 1 : 2 : 7 : 8-*tetrahydroxyanthraquinone*-4 : 3, 5 : 6-*diquinonenitronic acid* (also +2AcOH), decomp. about 246°. The last-named compound is isomerised by dilute sulphuric acid to 3 : 6-dinitro-1 : 2 : 4 : 5 : 7 : 8-*hexahydroxyanthraquinone*, decomp. 285°. H. WREN.

Reduction products of 1 : 1′-dianthraquinonyl. A. ECKERT (J. pr. Chem., 1929, [ii], **121**, 273—277).—Reduction of 1 : 1′-dianthraquinonyl with zinc dust and boiling acetic anhydride gives a *tetra-acetyl-1 : 1′-dianthrahydroquinonyl* (annexed formula). The ready conversion of dianthrahydroquinonyl into *meso*benzdianthrone, by elimination of 2 mols. of water, indicates that this last compound reacts as a hydroxyanthrone. Reduction of dianthraquinonyl with sodium hyposulphite affords helianthrone. H. BURTON.



Manufacture of condensation products [from benzanthrones and naphthols]. I. G. FARBENIND. A.-G.—See B., 1929, 350.

Reactions of cantharidin. H. W. VAN URK (Pharm. Weekblad, 1929, 66, 313—317).—The material is evaporated on the water-bath with 50% nitric acid, the nitro-compound reduced with stannous chloride, and the product diazotised and coupled with β-naphthol; a violet-red azo-dye is obtained with as little as 0·1 mg. An alcoholic solution of *p*-dimethylaminobenzaldehyde gives a yellow coloration, which will detect 0·5 mg. of cantharidin.

S. I. LEVY.

Beet-saponin. K. REHORST (Z. Ver. deut. Zucker-Ind., 1929, 79, 155—175).—Purified beet-saponin was completely hydrolysed by treatment with successive quantities of 0·5—2% sulphuric acid at temperatures rising from 96° to 147°. The *d*-glycuronic acid was separated as the barium salt and further identified by preparation of the lactone and saccharic acid. The sapogenin, repeatedly crystallised from alcohol and dried at 105—110°, had m. p. 301—306°, $[\alpha]_D^{20}$ +78·82°. Analysis, neutralisation equivalent, and mol. wt. indicated the formula $C_{31}H_{48}O_3$; this was confirmed by similar determinations on the acetyl derivative and by the proportion in the original saponin. Preparations several years old, which had originally given elementary analyses agreeing with this formula, were now found to give results suggesting the addition of water or oxygen. Distillation of sapogenin with zinc dust yielded a mixture of sesquiterpenes. Dehydrogenation by selenium gave a product from which two sesquiterpenes, cadalene and eudalene, and a substance, $C_{30}H_{20}O$ or $C_{30}H_{18}O$, were isolated. It is concluded that beet-saponin has the formula $C_{37}H_{56}O_9$, and that the sapogenin portion of its molecule contains two reduced naphthalene groups. F. E. DAY.

Natural and synthetic rubber. I. Destructive distillation of natural rubber. T. MIDGLEY, jun., and A. L. HENLE (J. Amer. Chem. Soc., 1929, 51, 1215—1226; cf. Ipatiev, A., 1897, i, 233; Harries, A., 1903, i, 189, 642; Bouchardat, A., 1875, 1259; Staudinger, A., 1926, 841).—Distillation of pale crêpe rubber at atmospheric pressure (*a*) alone, and (*b*) in presence of magnesium (10%), which increases the proportion of aromatic products, gives an oil (A) from which, in addition to a substantial amount of polymerised material, the following fractions were obtained: γ-methyl-Δ^{α}-butene [% of A: (*a*) 0·04, (*b*) 0·2]; β-methyl-Δ^{α}-butene [(*a*) 0·04, (*b*) 0·2]; isoprene [(*a*) and (*b*) 10·0]; β-methyl-Δ^{β}-butene [(*a*) 0·04, (*b*) 0·2]; a β-methylpentene [(*a*) 0·06, (*b*) 0·3], b. p. 59—60°, *d* 0·730, *n* 1·4117 (d_{20}^{20} and n^{20} in all cases), hydrogenated to β-methylpentane; γ-methyl-Δ^{β}-pentene [(*a*) 0·03, (*b*) 0·15]; an impure diene [(*a*) 0·03, (*b*) 0·15], b. p. 76—79°, *d* 0·742, *n* 1·4346, hydrogenated to γ-methyl-Δ^{β}-pentene, possibly γ-methyl-$\Delta^{\alpha\gamma}$-pentadiene; benzene [(*a*) 0·005, (*b*) 0·1]; an impure (?) γ-methylhexene [(*a*) 0·03, (*b*) 0·15], b. p. 93—95°, *d* 0·744, *n* 1·422, hydrogenated to a (?) γ-methylhexane, b. p. 92—95°, *d* 0·723, *n* 1·4032, which contains methyl*cyclo*hexane; Δ^3- [(*a*) 0·01, (*b*) 0·1], Δ^2-, and Δ^1- [(*a*) 0·1, (*b*) 1·0], -tetrahydrotoluenes; an impure β-methylheptene [(*a*) 0·02, (*b*) 0·1], b. p. 109—110°, *d* 0·783, *n* 1·4413, hydrogenated to impure *iso*octane; toluene [(*a*) 0·05, (*b*) 1·0]; fractions, b. p. 121—122° and b. p. 124—125° [(*a*) 0·04, (*b*) 0·2], hydrogenated to impure *iso*octane, probably mainly mixtures of β-methylheptenes; a dihydro-*m*-xylene [(*a*) 0·1, (*b*) 1·01], b. p. 129—130°, *d* 0·795, *n* 1·4451, probably the $\Delta^{1:3}$-isomeride; *m*- [(*a*) 0·05, (*b*) 1·0], but no *o*- or *p*-xylenes; Δ^1- or Δ^3-*p*-ethyltetrahydrotoluene [(*a*) 0·08, (*b*) 0·8], b. p. 144—145°, *d* 0·813, *n* 1·4529; a dicyclic *terpene* [(*a*) 0·04, (*b*) 0·8], b. p. 158—159°, *d* 0·834, *n* 1·4665, possibly isomeric with thujene, and hydrogenated to a product, b. p. 158—161°, *d* 0·813, *n* 1·4498, apparently identical with thujane; *p*-ethyltoluene [(*a*) 0·04, (*b*) 0·8]; a monocyclic *substance*, $C_{10}H_{18}$, b. p. 162—163°, *d* 0·828, *n* 1·46, obtained only in presence of magnesium and hydrogenated to a *compound*, $C_{10}H_{20}$, b. p. 162—164°, *d* 0·794, *n* 1·4407; a product, b. p. 162—163°, *d* 0·8105, *n* 1·456, obtained in absence of magnesium, probably a mixture of dimethyloctadienes, and, finally, dipentene [(*a*) and (*b*) 20·0]. Myrcene, a terpene, b. p. 168—169°, and dimethylbutadiene were not detected. The carbon skeletons of all the above products except benzene are derivable from fragments of Staudinger's formula for rubber. The proportions in which they occur throw light on the relative ease of scission of the linkings in the rubber molecule and on the laws governing the transformation of the primary scission products into stable molecules.

H. E. F. NOTTON.

Action of alcoholic hydrochloric acid on diphenylmethyltetrahydropyrone. H. RYAN and J. J. LENNON (Sci. Proc. Roy. Dubl. Soc., 1928, **19**, 121—124; cf. A., 1925, i, 1282).—Treatment of 2:6-diphenyl-3-methylpyran (I) with dry alcoholic hydrogen chloride at 15° affords a product from which 3:4-diphenyl-2-methyl-Δ^3-*cyclo*pentenone (II) has been isolated (cf. Japp and Maitland, J.C.S., 1904, **85**, 1488). The conversion, with benzaldehyde and alcoholic hydrochloric acid, of (I) into 3:4-diphenyl-2-benzylidene-5-methyl-Δ^3-*cyclo*pentenone (III) recorded by Ryan and Devine (A., 1916, i, 654) therefore proceeds by way of II. An account of the direct conversion of γ-benzylidenemethyl ethyl ketone into III with benzaldehyde in concentrated alcoholic hydrochloric acid solution is given, and an improved preparation of I is described. C. W. SHOPPEE.

Synthesis of 5 : 7 : 2′ : 4′-tetrahydroxyflavone and of 7 : 2′ : 4′ : 6′-tetrahydroxyflavone. N. M. CULLINANE, J. ALGAR, and H. RYAN (Sci. Proc. Roy. Dubl. Soc., 1928, **19**, 77—83).—Phloroacetophenone 4:6-dimethyl ether condenses with methyl 2:4-dimethoxybenzoate in presence of sodium at 150—160° to give 2-*hydroxy*-4 : 6 : 2′ : 4′-*tetramethoxybenzoylacetophenone* (I), m. p. 151°, converted by brief treatment with hydriodic acid (*d* 1·7) into 5 : 7 : 2′ : 4′-*tetramethoxyflavone*, m. p. 186°. Demethylation by hydriodic acid (*d* 1·94) affords 5 : 7 : 2′ : 4′-*tetrahydroxyflavone*, darkens at 270°, chars at 300°. This substance closely resembles natural lotoflavin and is also obtained directly from I under similar conditions. Condensation of phloroacetophenone 2 : 4 : 6-trimethyl ether with methyl 2 : 4-dimethoxybenzoate gives 2 : 4 : 6 : 2′ : 4′-*pentamethoxybenzoylacetophenone* (II), m. p. 153° (*copper* derivative), converted by hydriodic acid (*d* 1·7) into 7 : 2′ : 4′ : 6′-*tetramethoxyflavone*, m. p. 171°, demethylated by hydriodic acid (*d* 1·94) to 7 : 2′ : 4′ : 6′-*tetrahydroxyflavone*, m. p. 240° (decomp.) (*acetyl* derivative, m. p. 230°), which is also obtained directly from II under similar conditions. C. W. SHOPPEE.

Naphthophenoxanthones. A. PIERONI (Atti R. Accad. Lincei, 1929, [vi], **9**, 420—424).—The general reactions of formation of xanthones serve for the preparation of ββ- and βα-naphthophenoxanthones but not for that of the αβ-isomeride, possibly owing to the readiness with which the α-carboxyl is eliminated. This *compound*, m. p. 173°, may, however, be obtained by heating 1-benzoyl-β-naphthol with aluminium chloride for 2 hrs. at 150°. T. H. POPE.

Difurylethylene. P. F. BRUINS (J. Amer. Chem. Soc., 1929, **51**, 1270—1271).—Polythiofurfuraldehyde (Lintner, Z. ges. Brauw., 1910, **15**, 189), precipitated by acid as a rubber-like mass from 3% aqueous furfuraldehyde saturated with hydrogen sulphide, is converted by distillation at 95—135°/10—15 mm., into 18% of the theoretical of s-*di*-2-*furylethylene*, m. p. 100°. H. E. F. NOTTON.

Constitution of carthamin. II. (MISS) C. KURODA (Proc. Imp. Acad. Tokyo, 1929, **5**, 82—85; see this vol., 430).—By heating carthamin with dilute phosphoric acid and extracting with ether, yellow, crystalline *carthamidin*, $C_{15}H_{12}O_6,H_2O$, m. p. 218°, was obtained, accompanied by iso*carthamidin*, m. p. 238°. From these were prepared α-, β-, and γ-*acetylcarthamidins*, m. p. 158°, 143°, and 179°, respectively, and *acetyl*iso*carthamidin*, m. p. 180°. From a comparison of the colour (and other) reactions of these compounds with those of naringenin and phloretin it was deduced that probably *iso*carthamin is 1 : 3 : 4 : 4′-tetrahydroxychalkone-4-glucoside, the quinonoid form of this being carthamin; carthamidin is 1 : 3 : 4 : 4′-tetrahydroxyflavanone and *iso*carthamidin 1 : 2 : 3 : 4′-tetrahydroxyflavanone.

B. W. ANDERSON.

Constitution of carthamidin. III. (MISS) C. KURODA (Proc. Imp. Acad. Tokyo, 1929, **5**, 86).—Methylation of β-acetylcarthamidin by Freudenberg's method gave a substance identical with 2 : 3 : 4 : 6 : 4′-*pentamethoxychalkone*, m. p. 112°, as proved by an independent synthesis of the latter, thus confirming the formulæ suggested (preceding abstract).

B. W. ANDERSON.

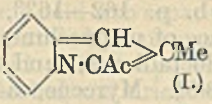
Pyrrolines from γ-chloropropyl- and *cyclo*propyl ketimines. J. B. CLOKE (J. Amer. Chem. Soc., 1929, **51**, 1174—1187).—Magnesium phenyl bromide and γ-chlorobutyronitrile in ether give the *bromomagnesium* derivative of phenyl-γ-chloropropylketimine, which is decomposed by ice and ammonium chloride to the impure *ketimine*. This gives an impure *hydrochloride*, m. p. 85—88°, which is rapidly hydrolysed by water at 0° to *phenyl γ-chloropropyl ketone*, b. p. 130—133°/4 mm. (decomp.) (*semicarbazone*, m. p. 136—137°), and when heated rearranges to 2-phenylpyrroline hydrochloride. This is also formed in small yield from phenyl γ-chloropropyl ketone and alcoholic ammonia at the ordinary temperature. Phenyl*cyclo*propylketimine (Bary, A., 1923, i, 226) (*hydrochloride*, m. p. 104—105°, with immediate isomerisation) changes rapidly at 200°, or, in presence of a trace of hydrochloride, at lower temperatures, giving mainly 2-phenylpyrroline. This appears to be a general reaction for *cyclo*propyl and *cyclo*butyl ketones. Similarly, magnesium ethyl bromide and γ-chlorobutyronitrile give 2-ethylpyrroline, previously described as *cyclo*propylethylketimine (de Booseré, A., 1923, i, 311). This has now been obtained in an impure state from magnesium ethyl bromide and cyano*cyclo*propane. It does not appear to yield 2-ethylpyrroline at 185°, but its *hydrochloride*, m. p. 101—103°, passes at 130° into the pyrroline hydrochloride and is readily hydrolysed by water to *cyclo*propyl ethyl ketone. Contrary to the statement of de Booseré, 2-ethylpyrroline does not yield with alkali *cyclo*propyl ethyl ketone. H. E. F. NOTTON.

Substituted aromatic aldehydes in Hantzsch's pyridine condensation. I. Methoxy-, chloro-, and hydroxy-benzaldehydes. L. E. Hinkel and W. R. Madel (J.C.S., 1929, 750—754).—In all cases the introduction of a substituent into benzaldehyde lowers the yield of dihydropyridine obtained compared with that obtained from benzaldehyde itself. Apart from the observed general depressant effect the results are not in agreement with the theory of alternate polarities, but appear to correspond with the depressant effects of substituents on the affinity of benzaldehyde for hydrogen cyanide (Lapworth and Manske, A., 1928, 1245). The abnormal behaviour of salicylaldehyde is attributed to co-ordination between the hydroxyl and the aldehyde group, whereby the typical properties of each radical are modified.

The following derivatives of ethyl 4-phenyl-2 : 6-dimethylpyridine-3 : 5-dicarboxylate are described (the substituent being in the phenyl group in each case): p-, o-, and m-*methoxy*-, m. p. 50°, 65°, and 82°, respectively; p-, o-, and m-*chloro*-, m. p. 68°, 62°, and 53°, respectively; also the 1 : 4-*dihydro*-derivatives of these, m. p. 159°, 151°, 120°, 149°, 132°, and 142°, respectively, and of the 4'-*p*- and 4-*m*-hydroxyphenyl compounds, m. p. 227° and 202°, respectively. With the exception of derivatives of the hydroxy-aldehydes, the oxidation of the dihydropyridines proceeded normally and in no case was any elimination of phenyl observed. R. J. W. Le Fèvre.

2 : 6-Dibromo- and 2 : 6-dichloro-pyridine-4-carboxylic acids and some derivatives. W. H. Levelt and J. P. Wibaut (Rec. trav. chim., 1929, 48, 466—473).—Crude 2 : 6-dihydroxypyridine-4-carboxylic acid (I) (Behrmann and Hofmann, A., 1885, 138) is converted by phosphoryl chloride at 200° into a mixture of 2 : 6-dichloropyridine-4-carboxylic acid (II), m. p. 208—209° after previous sintering [acid chloride (III), b. p. 243—246°/760 mm., m. p. 25—27°; amide, m. p. 207—208° (lit. 200°)], and 2 : 6-*dichloro-4-cyanopyridine*, m. p. 95·5—96·5° (derived from the admixed amide of I). Hydrolysis of this with 30% hydrochloric acid gives II. Treatment of I with phosphoryl bromide at 170° yields 2 : 6-*dibromopyridine-4-carboxylic acid* (IV), m. p. 184—185° [*acid chloride* (V), b. p. 160°/21 mm., m. p. 9—11°; *amide*, m. p. 202—204°], together with 2 : 6-*dibromo-4-cyanopyridine*, m. p. 139—140°. Thermal decomposition of the silver salt of IV affords 2 : 6-*dibromopyridine*, m. p. 118—119°, also formed in small amount, together with unchanged material, by the action of hydrogen on V in presence of xylene and a palladium–barium sulphate catalyst. Similar treatment of III with hydrogen furnishes a small amount of 2 : 6-dichloropyridine together with unchanged material. H. Burton.

Picolide of M. Scholtz and acetyl derivatives of indolizine and 2-methylindolizine. A. E. Tschitschibabin and F. N. Stepanov (Ber., 1929, 62, [*B*], 1068—1075).—2-Methylindolizine, prepared by the condensation of 2-methylpyridine with chloroacetone and distillation of the product with steam in the presence of sodium hydrogen carbonate, is converted by anhydrous sodium acetate and boiling acetic anhydride into 1-*acetyl-2-methylindolizine* (I), b. p. 159—160°/7 mm., m. p. 83°, in which the ketonic group cannot be detected by phenylhydrazine or hydroxylamine under the usual conditions. It does not react normally with Grignard reagents, yielding with magnesium ethyl bromide a compound, b. p. 95°/9 mm., m. p. 59—60°, with the composition of methylethylindolizine (also obtained by reduction of the acetyl compound with aluminium amalgam). The acetyl compound is converted by acetic anhydride at 230—240° into 1 : 3-*diacetyl-2-methylindolizine*, m. p. 123°, in which the presence of only one ketonic group is readily established [*monophenylhydrazone*, m. p. 210° (decomp.)]; it is converted by 25% sulphuric acid into 2-methylindolizine. 1-Acetylindolizine, b. p. 148—149°/9·5 mm., prepared according to Scholtz (A., 1912, i, 385, 648; 1913, i, 514), is converted by acetic anhydride at 220—230° into picolide, m. p. 176°. The complete analogy in the properties of the acetyl derivatives of methylindolizine, acetylindolizine, and picolide leads to the conclusion that the last-named compound is 1 : 3-diacetylindolizine. H. Wren.


(I.)

Indoline and 2-methyl-4 : 5 : 6 : 7-tetrahydroindole. G. Plancher (Ber., 1929, 62, [*B*], 1088—1089).—*o*-Dihydroindole (cf. Ferber, this vol., 308) has been isolated previously by the author (A., 1905, i, 611). 2-Methyl-4 : 5 : 6 : 7-tetrahydroindole (cf. von Braun, A., 1924, i, 545) has been obtained by Plancher and Zambonini from ethyl acetoacetate and 2-chloro*cyclo*hexanone and hydrolysis followed by distillation with lime of the product. H. Wren.

Additive reaction of indolenines. III. Ketonic fission of acetoacetic esters. H. Leuchs, A. Heller, and A. Hoffmann (Ber., 1929, 62, [*B*], 871—881; cf. A., 1925, i, 1281; 1928, 528).—Ethyl αα-dibenzylacetoacetate, m. p. 57°, undergoes acid fission when treated with alkali, whereas it is converted by a mixture of glacial acetic acid and hydriodic acid (*d* 1·7) at 115° into as-*dibenzylacetone*, b. p. 186°/10 mm., 190—192°/15 mm., in 80% yield; dibenzylacetic acid does not appear to be formed. The *semicarbazone*, m. p. 153—154°, *oxime*, m. p. 75—76°, and unstable *phenylhydrazone*, m. p. 86—87°, of the ketone are described. The crude phenylhydrazone is converted by zinc chloride in anhydrous alcohol at 100—120° into the non-crystalline 2-*methyl*-3 : 3-*dibenzylindolenine* [*picrate*, m. p. 180—181° (decomp.); *hydrochloride*, m. p. 180—182°]. The free base is transformed by acetic anhydride and sodium acetate at 100° into N-*acetyl*-3 : 3-*dibenzyl-2-methyleneindoline*, m. p. 96—97°, not affected by methyl alcohol at 100° or by aqueous ammonia or alkali. Similarly, with benzoic anhydride and sodium benzoate the base affords N-*benzoyl*-3 : 3-*dibenzyl-2-methyleneindoline*, m. p. 164°, which behaves similarly to the acetyl compound.

Phenyl *iso*propyl ketone, from benzene and *iso*butyryl chloride, is converted by successive treatment with phenylhydrazine and zinc chloride into non-crystalline 2-*phenyl*-3 : 3-*dimethylindolenine* (*picrate*, m. p. 158—160°), which does not add acetic anhydride. With benzoyl chloride and sodium carbonate the base affords 1-*benzoyl-2-phenyl*-3 : 3-*dimethylindolin*-2-*ol*, m. p. 138° after softening. The *methiodide* of the base, m. p. 203°, is converted by silver carbonate in the presence of alcohol into 2-phenyl-1 : 3 : 3-trimethylindolin-2-ol, m. p. 107—108°. 2-*Phenyl*-3 : 3-*dimethylindoline*, m. p. 93°, its *hydrochloride*, m. p. 193—194°, *nitrate*, m. p. 187° (decomp.), and *acetyl* derivative, m. p. 82—83°, are described. Methyl iodide in methyl alcohol at 100° converts 2-phenyl-3 : 3-dimethylindoline into a *substance*, $C_{17}H_{19}N$, m. p. 88°, and 2-phenyl-1 : 3 : 3-trimethylindoline methiodide.

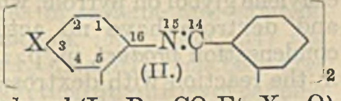
3 : 3-Dimethylindolenine, $(C_{10}H_{11}N)_3$, is transformed by acetic anhydride and sodium acetate at 100° into O^2 : 1-*diacetyl*-3 : 3-*dimethylindolin*-2-*ol*, m. p. 60—61°, converted by boiling methyl alcohol into 1-*acetyl*-2-*methoxy*-3 : 3-*dimethylindoline* and by boiling 90% acetic acid into 1-*acetyl*-3 : 3-*dimethylindolin*-2-*ol*, m. p. 117—118°. Methyl-alcoholic ammonia at 100° converts the diacetyl derivative into 2-*amino*-1-*acetyl*-3 : 3-*dimethylindoline*, m. p. 78° (*picrate*, m. p. 159—161°). O^2 : 1-*Dibenzoyl*-3 : 3-*dimethylindolin*-2-*ol*, m. p. 147—148°, 1-*benzoyl*-2-*methoxy*-3 : 3-*dimethylindoline*, m. p. 71—72°, 1-*benzoyl*-3 : 3-*dimethylindolin*-2-*ol*, m. p. 202—204°, and 2-*amino*-1-*benzoyl*-3 : 3-*dimethylindoline*, m. p. 115—117° (*picrate*, m. p. 191—194° after softening), are described. The indolenine, $(C_{10}H_{11}N)_3$, could not be caused to add phthalic anhydride or phenylhydrazine. H. WREN.

5 : 8-Dihydroxy-β-anthrapyridinequinone. H. RAUDNITZ [with G. LAUBE] (Ber., 1929, **62**, [*B*], 938—939).—Comparison of the absorption spectra of β- and α-anthrapyridinequinones shows that the maxima of the bands lie more towards the red end with the β- than with the α-compound. Treatment of cinchomeronic anhydride and quinol with a mixture of sodium and aluminium chlorides at 180—200° affords 5 : 8-*dihydroxy*-β-*anthrapyridinequinone*, m. p. 211° (*sodium* salt). 5 : 8-*Dihydroxy*-6 : 7-*benzo*-β-*anthrapyridinequinone*, m. p. 343° (*sodium* salt), is derived similarly from 1 : 4-dihydroxynaphthalene. H. WREN.

Diphenyl derivatives of the Kaufler type, and the formation of dibenzoctdiazines. R. J. W. LE FÈVRE (J.C.S., 1929, 733—738).—The malonylbenzidine of Remfry (*ibid.*, 1911, 99, 610) is shown to contain a free amino-group, since it furnishes a *salicylidene* derivative, m. p. 298—300°, and a *sulphate*; it is therefore probably 4-*amino*-4′-*malonylamidodiphenyl*. The carbonyl- and thiocarbonyl-dianisidines of Starke (A., 1899, i, 589) yield *salicylidene* derivatives as yellow, insoluble powders; the former substance is best prepared by heating 1 mol. of *o*-tolidine with 2 mols. of carbamide, and can also be obtained by mixing solutions of *o*-tolidine hydrochloride and potassium cyanate; it has therefore the structure I (R=NH_2, X=O), and the thio-compound has the analogous structure (with X=S). The oxalylbenzidine of Taussig (A., 1904, i, 663) does not react with salicylaldehyde and analysis indicates that it is 4 : 4′-*diethyloxamido*-3 : 3′-*dimethyldiphenyl* (I ; R=CO_2Et, X=O) (cf. A., 1928, 283). Attempted repetition of the preparation of *cyclo*formazyl methyl ketone (Wedekind, A., 1898, i, 454) proved unsuccessful.

$[R\cdot CX\cdot NH\cdot C_6H_3Me\cdot]_2$

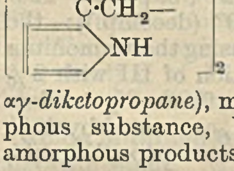
(I.)



(II.)

2 : 2′-Diaminodiphenyl (*disalicylidene* derivative, m. p. 153—154°; NN′-*thiocarbonyl* derivative, m. p. 243°), obtained by a modification of the method of Ullmann and Bielecki (A., 1901, i, 586), condenses with phenanthraquinone in acetic acid at 100° to yield 13 : 14 - (oo′ - *diphenylylene*)*dibenzoct* - 12 : 15 - *diazine*, m. p. 268—269° (II : X=H), and with chloro-2 : 4-dinitrobenzene to give 2 : 2′-*di*-(2″ : 4″-*dinitrophenylamino*)*diphenyl*, m. p. 177—178°, together with N-2′ : 4′-*dinitrophenylcarbazole*, m. p. 216—217°. Repetition of the preparation of di-*m*-nitrodi-*o*-aminodiphenyl (cf. Täuber, A., 1892, i, 480) yields a product which is probably a mixture of 5 : 5′-, 4 : 4′-, and 4 : 5′-dinitro-derivatives together with a little of 3 : 3′- and 3 : 5′-compounds; attempts to obtain dinitro-octdiazines from it were unsuccessful, as was also condensation of 2 : 2′-diaminodiphenyl with benzil-3 : 3′-disulphonic acid (cf. Kafka, A., 1891, i, 720). Definite compounds could not be isolated from the interaction of 2 : 2′-diaminodiphenyl with ethyl malonate, ethyl phthalate, or ethyl oxalate. 2 : 2′-Diacetamidodiphenyl, obtained by the process described by Brady and McHugh (J.C.S., 1923, **123**, 2047) for benzidine, is converted by bromine in acetic acid at 90—100° into 5 : 5′-*dibromo*-2 : 2′-*diacetamidodiphenyl*, m. p. 266—267°, hydrolysed by sodium hydroxide to 5 : 5′-*dibromo*-2 : 2′-*diaminodiphenyl*, m. p. 140—141° (*disalicylidene* derivative, m. p. 263—265°), which condenses with phenanthraquinone to yield 3 : 8-*dibromo*-13 : 14-(oo′-*diphenylylene*)*dibenzoct* - 12 : 15 - *diazine* (II : X=Br), m. p. above 280°. By contrast, 4 : 4′-*dibromo*-2 : 2′-*diaminodiphenyl*, m. p. 192—194° (*disalicylidene* derivative, m. p. 210—211°), obtained by reducing 4 : 4′ - dibromo - 2 : 2′ - dinitrodiphenyl (Ullmann and Bielecki, *loc. cit.*) with iron and water at 100°, does not yield an octdiazine under similar conditions. The following esters, prepared by heating the appropriate hydroxy-compound with diphenic anhydride at 160°, are described: *benzyl hydrogen diphenate*, m. p. 112—113°; α-*naphthyl hydrogen diphenate*, m. p. 202—203°, and β-*naphthyl hydrogen diphenate*, m. p. 178—179°. C. W. SHOPPEE.

αα′-Dipyrryl-pentadione and -butadione. T. N. GODNEV and N. A. NARYSCHKIN (J. pr. Chem., 1929, [ii], **121**, 369—373).—By the action of magnesium pyrryl iodide on ethyl succinate is obtained *s*-dipyrroylethane (2 : 2′dipyrrylglyoxal) (Oddo and Dainotti, A., 1912, i, 721) together with a *substance* to which the annexed formula is assigned. Similarly, with ethyl glutarate is obtained αγ-*dipyrroylpropane* (αγ-*dipyrryl*-αγ-*diketopropane*), m. p. 125°, together with an amorphous substance, but with ethyl malonate only amorphous products could be obtained.



J. W. BAKER.

Pyrimidines. CV. Test for thymine and 5-methylcytosine in presence of uracil and cytosine. H. H. HARKINS and T. B. JOHNSON (J. Amer. Chem. Soc., 1929, **51**, 1237—1242).—1 Mg. of thymine (prepared by an improved method) or

5-methylcytosine is detected by the formation of acetylcarbinol when its aqueous solution is treated with bromine, boiled to remove excess, and distilled with barium hydroxide (cf. Baudisch, A., 1918, ii, 412; 1925, i, 1100). Uracil and cytosine do not give acetylcarbinol, but are converted into the highly characteristic barium dialurate (A., 1907, ii, 826).

H. E. F. NOTTON.

Pyrimidines. CVI. Leuco-bases of dyes containing pyrimidine rings. T. B. JOHNSON (J. Amer. Chem. Soc., 1929, 51, 1274—1276).—2-Thio-4-aldehydothymine (A., 1916, i, 756) and dimethylaniline in presence of zinc chloride at 100° give *pp'-tetramethyldiaminodiphenyl-2-thio-4-thyminylmethane*, m. p. 212—214°. 2-Ethylthiol-4-aldehydothymine gives similarly *pp'-tetramethyldiaminodiphenyl-2-ethylthiol-4-thyminylmethane*, m. p. 218—219°, and 4-aldehydothymine gives *pp'-tetramethyldiaminodiphenyl-4-thyminylmethane*, m. p. 197—198°. These are oxidised in acid solution to dyes analogous to malachite-green, which are of interest as bactericides.

H. E. F. NOTTON.

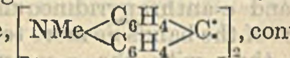
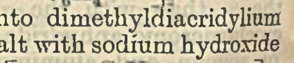
Action of *o*-phenylenediamines on dihydroxytartaric acid. F. D. CHATTAWAY and W. G. HUMPHREY (J.C.S., 1929, 645—651; cf. A., 1894, i, 624).—Interaction of sodium dihydroxytartrate and *o*-phenylenediamine in aqueous solution at 90° for 0·5 hr., followed by addition of 1 mol. of hydrochloric acid affords *quinoxaline-2 : 3-dicarboxy-o-phenylenediamide* (I), m. p. 184° (decomp.), readily soluble in sodium hydroxide solution and precipitated unchanged, and decomposing on attempted acetylation or benzoylation; I dissolves in hot dilute hydrochloric acid (1 : 50), but on cooling the *o-phenylenediamine* salt (II) of quinoxaline-2 : 3-dicarboxylic acid, m. p. 186° (decomp.), separates, whilst if hot concentrated hydrochloric acid (1 : 1) is employed *quinoxaline-2 : 3-dicarboxylic acid* (III), m. p. 190° (decomp.) [*dihydrate* (loses $2H_2O$ at 110°); *ethyl* ester, m. p. 83°; *ammonium* salt, m. p. 220—230° (decomp.)], is obtained on cooling; III condenses readily with *o*-phenylenediamine in aqueous or in alcoholic solution to yield II. When treated with acetic anhydride, III affords *quinoxaline-2 : 3-dicarboxylic anhydride*, m. p. 250—260° (decomp.), converted by treatment with dry ammonia in benzene suspension into the *ammonium* salt of quinoxaline-2 : 3-dicarboxylamic acid, which by acidification yields *quinoxaline-2 : 3-dicarboxylamic acid*, m. p. 190—195° (decomp.) (*compound* +1AcOH), with conversion into *quinoxalinedicarboxylimide*, m. p. 260° (decomp.) [*acetyl* derivative, m. p. 220° (decomp.)]. When heated above its m. p. III decomposes and gives a 10% yield of quinoxaline, m. p. 27°, b. p. 225—226° [*tetrachloroiodide*, m. p. 125—130° (decomp.)]; the yield may be increased to 30% by using the ammonium salt of III at 220—240°. Oxidation of III with 2% potassium permanganate at 100° affords *dipotassium dihydrogen pyrazinetetracarboxylate*, converted by 20% hydrochloric acid into *pyrazinetetracarboxylic acid*, m. p. 205° (decomp.) (*dihydrate*; *tetraethyl* ester, m. p. 104°).

p-Chloro-*o*-phenylenediamine reacts with sodium dihydroxytartrate in a similar manner to yield the following compounds, which exhibit reactions analogous to those above: *6-chloroquinoxaline-2 : 3-dicarboxy-p-chloro-o-phenylenediamide*, m. p. 207° (decomp.); *p-chlorophenylenediamine* salt of 6-chloroquinoxaline-3 : 2-dicarboxylic acid, m. p. 205° (decomp.); *6-chloroquinoxaline-2 : 3-dicarboxylic acid*, m. p. 175° (decomp.) [*dihydrate* (loses $2H_2O$ at 110°); *anhydride*, m. p. 235—240° (decomp.); *ethyl hydrogen* ester, m. p. 159°; *ethyl* ester, m. p. 60°; *ammonium* salt, m. p. 215—225° (decomp.)], which at 190° passes into *6-chloroquinoxaline*, m. p. 60° (yield 20%); an improved yield is obtained by employing the ammonium salt.

p-Bromo-*o*-phenylenediamine and sodium dihydroxytartrate yield a corresponding series of compounds: *6-bromoquinoxaline-2 : 3-dicarboxy-p-bromo-o-phenylenediamide*, m. p. 198° (decomp.); *p-bromophenylenediamine* salt of 6-bromoquinoxaline-2 : 3-dicarboxylic acid, m. p. 199° (decomp.); *6-bromoquinoxaline-2 : 3-dicarboxylic acid*, m. p. 172° (decomp.) [*dihydrate* (loses $2H_2O$ at 110°); *anhydride*, m. p. 235—245° (decomp.); *ethyl hydrogen* ester, m. p. 161°; *ethyl* ester, b. p. 69°; *ammonium* salt, m. p. 235—240° (decomp.)]; *6-bromoquinoxaline*, m. p. 56°.

Both 6-chloro- and 6-bromo-quinoxaline-2 : 3-dicarboxylic acids yield pyrazinetetracarboxylic acid when oxidised with 2% potassium permanganate at 100°.

C. W. SHOPPEE.

Acridine. IV. Formation of diacridyl derivatives from *N*-methylacridone. K. LEHMSTEDT and H. HUNDERTMARK (Ber., 1929, 62, [*B*], 1065—1067; cf. this vol., 454).—10-Methylacridine is reduced by zinc dust in boiling glacial acetic acid to 10 : 10'-dimethyl-5 : 5'-diacridine,  $\left[NMe{<}\begin{smallmatrix}C_6H_4\\C_6H_4\end{smallmatrix}{>}C\colon\right]_2$, converted by hot dilute nitric acid into dimethyldiacridylium nitrate. Treatment of the salt with sodium hydroxide precipitates the *carbinol base*,  $\left[NMe{<}\begin{smallmatrix}C_6H_4\\C_6H_4\end{smallmatrix}{>}C(OH)\cdot\right]_2$, m. p. above 300°, which, with potassium iodide, affords 10 : 10'-dimethyldiacridylium iodide (cf. Decker and Dunant, A., 1909, i, 433). The course of the action assumed by the latter authors thus receives confirmation (cf. Ehrlich and Benda, A., 1913, i, 904). Diacridyl (Decker and Dunant, *loc. cit.*) is conveniently prepared from 5-chloroacridine and copper powder at 140°.

H. WREN.

Manufacture of pharmaceutical products [quinazolines]. I. G. FARBENIND. A.-G.—See B., 1929, 377.

Polymerisation of pyrrole. A. K. PLISOV (Ukraine Chem. J., 1928, 3 [Sci.], 471—475, 477—480).—Tripyrrole is formed by the action at 100° of aqueous ethylene oxide on pyrrole. The catalytic agent is glycol formed from ethylene oxide during the reaction, since anhydrous ethylene oxide or water alone has no polymerising action. Aqueous trimethylethylene oxide has a similar, although feebler reaction.

Glycerol has a more intense polymerising action than ethylene glycol on pyrrole, whilst mannitol, erythritol, and dextrose have no action in this respect. A condensation *product*, m. p. 190°, is, however, formed in the reaction with dextrose. A resinous product is obtained in the reaction between pyrrole and acetaldehyde.

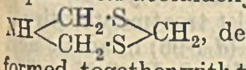
R. TRUSZKOWSKI.

Stability of diazonium salts of the triazole series. J. Reilly and D. Madden (J.C.S., 1929, 815—816).—The velocity of decomposition of triazole diazonium salts has been measured; the reaction is more rapid than in the pyrazole and pyrazolone series, and does not follow the unimolecular law. Substitution of alkyl groups in the 3 position confers increased stability in the sequence *iso*butyl>Pr^{β}>Et>Me>H, whilst the nature of the anion and the amount of acid present also influence the decomposition velocity; thus the nitrates are more stable than the chlorides. The following are described: 5-*amino*-3-*ethyl*-1 : 2 : 4-*triazole*, m. p. 152° (*nitrate*, m. p. 167°); 3-*ethyl*-1 : 2 : 4-*triazole*-5-*azo*-β-*naphthylamine*, m. p. 259°, -β-*naphthol*, m. p. 180—181°, and -*acetylacetone*, m. p. 236°; 5-*diazo*-3-*ethyl*-1 : 2 : 4-*triazole chloroaurate*; 5-*amino*-3-iso*butyl*-1 : 2 : 4-*triazole nitrate*, m. p. 171°.

C. W. Shoppee.

1 : 3 : 4-Oxdiazines. IV. J. van Alphen (Rec. trav. chim., 1929, 48, 417—421).—Chloroacetyl chloride reacts with benzoylhydrazine in benzene solution, forming β-*benzoyl*-α-*chloroacetylhydrazine*, m. p. 165°, which when treated with potassium carbonate in acetone yields Δ^2-5-*keto*-2-*phenyl*-1 : 3 : 4-*oxdiazine*, m. p. 161°. Diphenylchloroacetyl chloride (1 mol.) and benzoylhydrazine (3 mols.) give β-*benzoyl*-α-(β-*benzoylhydrazino*)*diphenylacetylhydrazine*, m. p. 217°, but with 1·35 mols. of the hydrazine, Δ^2-5-*keto*-2 : 6 : 6-*triphenyl*-1 : 3 : 4-*oxdiazine*, m. p. 185°, is obtained. β-*Cinnamoyl*-α-*chloroacetylhydrazine*, m. p. 185°, furnishes Δ^2-5-*keto*-2-*styryl*-1 : 3 : 4-*oxdiazine*, m. p. about 190° after sintering at 174° The 2-phenyl derivative is hydrolysed by 10% aqueous-alcoholic sulphuric acid to hydrazine, whilst the other oxdiazines are unaffected. The presence of two phenyl groups in positions 2 and 4 of the oxdiazine ring is necessary to prevent fission (cf. this vol., 334).

H. Burton.

1 : 3-Dithio-5-azine (formothialdine). T. G. Levi (Atti R. Accad. Lincei, 1929, [vi], 9, 424—427; cf. A., 1924, i, 964).—2 : 4 : 6-Trimethyl-1 : 3-dithio-5-azine (2 : 4 : 6-trimethylthioformaldine) may be readily prepared by the action of ammonium sulphide on acetaldehyde. Similarly, *thioformaldine*,  $NH<\begin{matrix}CH_2\cdot S\\CH_2\cdot S\end{matrix}>CH_2$, decomp. 75—90°, m. p. 115°, is formed, together with trithioformaldehyde, by treating aqueous formaldehyde with sulphur or preferably with ammonium hydrogen sulphide. Thioformaldine, which may also be obtained by saturating an ammoniacal solution of trioxymethylene with hydrogen sulphide, gives silver sulphide when treated with aqueous silver nitrate, and is decomposed by hot concentrated hydrochloric acid, yielding trithioformaldehyde, formaldehyde, and ammonium chloride.

T. H. Pope.

Caffeino-salicylic acid; a molecular compound. N. Schoorl (Pharm. Weekblad, 1929, 66, 317—358).—Following the preparation of the acid from molecular proportions of caffeine and salicylic acid (Schoorl and Regenbogen, *ibid.*, 1924, 34) the sodium salt $C_8H_{10}O_2N_4,C_7H_5O_3Na,5H_2O$ has been prepared by dissolving the theoretical quantities of caffeine and sodium salicylate in hot water, and allowing to crystallise. The salt loses its water of crystallisation slowly on the water-bath or in a vacuum.

S. I. Levy.

Carnegine. E. Späth [in part with J. Passl] (Ber., 1929, 62, [*B*], 1021—1024; cf. Heyl, this vol., 201).—*N*-Acetylhomoveratrylamine is converted by phosphoric oxide in toluene into 6 : 7-dimethoxy-1-methyl-3 : 4-dihydro*iso*quinoline, transformed by methyl iodide at 100° into the corresponding *methiodide*, m. p. 176—178° (vac.) [*trihydrate*, m. p. 100—102°]. Reduction of the hydrate with tin and hydrochloric acid affords 5 : 6-*dimethoxy*-1 : 2-*dimethyl*-1 : 2 : 3 : 4-*tetrahydro*isoquinoline, as a colourless, viscous oil, b. p. 170° (bath temp.)/1 mm., in which the position of the methoxyl groups is established by the formation of *m*-hemipinic acid on oxidation. The identity of the synthetic base with carnegine is established by direct comparison of the hydrochlorides, m. p. 210—211°, *picrate*, m. p. 212—213° (decomp.), 2 : 4 : 6-*trinitro*-m-*tolyloxide*, m. p. 169—170°, and *methiodide*, m. p. 210—211° (vac.).

H. Wren.

Alkaloids of Angostura bark. J. Tröger (Pharm. Zentr., 1929, 70, 213—222, 229—239, 245—252).—A critical survey of previous work.

S. Coffey.

Synthesis of coptisine. E. Späth and R. Posega (Ber., 1929, 62, [*B*], 1029—1033; cf. Kitasato, A., 1926, 1160).—Palmatine chloride is hydrolysed with fuming hydrochloric acid at 140° and the product is treated in an atmosphere of hydrogen with an excess of methylene iodide and alcoholic sodium ethoxide and then reduced with zinc dust in acid solution; small amounts of an amorphous, tertiary base, which does not contain tetrahydrocoptisine, are thus obtained; replacement of methylene iodide by methylene sulphate effects no improvement. Small amounts of tetrahydrocoptisine, m. p. 228—229° (vac.) (cf. *loc. cit.*), are obtained by heating tetrahydropalmatine with fuming hydrochloric acid and treatment of the product with methylene chloride and sodium methoxide under definite conditions. Protopine is converted by sodium amalgam into the corresponding carbinol base and thence by evaporation of the solution in hydrochloric acid into a quaternary salt from which tetrahydrocoptisine is derived by distillation in a high vacuum. Incidentally to their synthesis of protopine, Haworth and Perkin have prepared a base, m. p. 219°, of the constitution of tetrahydrocoptisine which they describe as 2 : 3 : 9 : 10-dimethylenedioxytetrahydroprotoberberine.

H. Wren.

Microchemical reactions of physostigmine. M. Wagenaar (Pharm. Weekblad, 1929, 66, 381—382).—The reactions with sodium salicylate and gold bromide are described; the former will detect 10 mg. at a dilution of 1 : 200 and the latter 5 mg. at a dilution of 1 : 500.

S. I. Levy.

Acids obtained from brucine by oxidation with chromic acid. H. Wieland and W. Münster (Annalen, 1929, 469, 216—224).—Oxidation of brucine with chromic acid in dilute sulphuric acid solution first at 60—70° and then at 100° gives two monobasic *acids*, (*a*) $C_{17}H_{22}O_6N_2$ (+$5H_2O$), darkens at 250—280°, not melted at 345°, $[\alpha]_D^{24}$ +49·2° in water (*hydrochloride*,

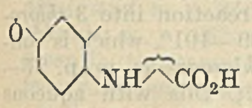
m. p. above 320°; *hydrobromide*; *hydriodide*; *chloroplatinate*), and (*b*) $C_{16}H_{20}O_4N_2$ (+2 or $4H_2O$), m. p. 311° (decomp.) after darkening at 250° and sintering at 307°, $[\alpha]_D^{24}$ −116·3° in water (*hydrobromide*, decomp. 286°; *chloroplatinate*). This last substance is identical with the acid, $C_{16}H_{18}O_4N_2$, described by Hanssen (A., 1885, 276, 1146), and is formed by degradation of the benzene nucleus. The original double linking is unaffected. H. BURTON.

Determination of brucine as silicotungstate and analysis of nux vomica. B. KLJATSCHKINA and M. STRUGADSKI (Arch. Pharm., 1929, **267**, 177—192).—Stuber and Kljatschkina (A., 1928, 532) showed that the composition of strychnine silicotungstate depended on the conditions of precipitation. It is now found that brucine silicotungstate is similarly of variable composition. When it is precipitated from neutral solution the molecular ratio of base to complex acid is as high as 4 : 1; this ratio falls with increase in the acid (hydrochloric or nitric, but not acetic) concentration of the solution, until in 20% hydrochloric acid it becomes 1·5 : 1. The ratio is also lowered when the solution contains salts of strong electrolytes or an excess of the precipitant, and it is further dependent on the temperature of precipitation. Precipitates with high ratio, as from neutral solution, are colloidal in nature. The precipitate, however, always has the same composition when the conditions of precipitation are the same. It is recommended that the precipitation be carried out at the ordinary temperature, in 1% hydrochloric acid, and that the exact amount of precipitant to use be determined by a preliminary series of titrations, in which the filtrates are tested for alkaloid or silicotungstic acid. The precipitate will then have the composition: 3·5 (brucine) + $12WO_3,SiO_2,2H_2O$ + $8H_2O$. Strychnine yields under the same conditions a precipitate of similar composition, so that the conversion factors (weight of ash : weight of alkaloid) become 0·4849 and 0·411, respectively. Brucine can be detected at a concentration of 1 in 160,000 and strychnine at a concentration of 1 in 220,000 by this method. Details are given for analysing nux vomica both gravimetrically and volumetrically. W. A. SILVESTER.

Synthesis of *r*-corydaline. E. SPÄTH and E. KRUTA (Ber., 1929, **62**, [*B*], 1024—1029).—Papaverine is converted by 40% aqueous formaldehyde at 125° into methylenepapaverine, m. p. 154—155°, hydrogenated in presence of palladised charcoal to methylpapaverine, m. p. 154°. Reduction of the last-named compound at a lead cathode gives *methyltetrahydropapaverine*, $(C_{21}H_{27}O_4N)_2,H_2O$, m. p. 93—95° (decomp.) (also *anhydrous*); the corresponding *picrate* has m. p. 215—216° (vac., decomp.). Treatment of the bases with fuming hydrochloric acid at 150—155° causes complete hydrolysis of the methoxyl groups and production of the *hydrochloride*, $C_{17}H_{20}O_4NCl$, m. p. 238—240° (also *monohydrate*). This is condensed with formaldehyde and the free base so produced is treated in methyl alcohol with diazomethane. The mixture of methylated products gives 10% of *meso*corydaline when crystallised from ether at 0°. Separation of the remaining material into its components could not be effected by fractional extraction with hydrochloric acid, crystallisation, or by means of salts. Separation of tertiary bases of the type of tetrahydropalmatine from other bases is effected by treatment with alcoholic iodine, giving yellow quaternary iodides which are transformed into the more readily separable tetrahydro-compounds by zinc and acetic acid. Fractional precipitation of the acid solution of these bases by potassium bromide yields precipitates from which *r*-corydaline can be extracted in small amount. H. WREN.

New strychnos alkaloid [vomicine]. I. H. WIELAND and G. OERTEL (Annalen, 1929, **469**, 193—215).—A new alkaloid has been obtained as a by-product in the isolation of strychnine and is named *vomicine* (I), $C_{22}H_{24}O_4N_2$, m. p. 282°, $[\alpha]_D^{23}$ +80·4° in alcohol [*monohydrochloride* (II), m. p. 245° (decomp.) after darkening and sintering at 210—215°; *benzoyl* derivative *hydrochloride*, m. p. 182° after darkening at 173°]. When heated with 20% methyl-alcoholic potassium hydroxide solution in absence of oxygen, I yields *vomicinic acid* (III), $C_{22}H_{26}O_5N_2$, sinters at 164° with loss of 1 mol. of water, giving I; in presence of air an intense green solution is obtained which gives a characteristic permanganate coloration with oxidising agents. This acid yields a stable *hydrochloride* in the cold, but in the hot regenerates I, indicating formation of a lactam grouping. When II is treated with bromine water below 20° a perbromide is produced which decomposes into *bromovomicine* (IV), m. p. 306° with darkening; this is converted as above into *bromovomicinic acid*. Methyl iodide has no action on I at 150°, but converts III in alcoholic alkaline solution into a mixture of N-*methylvomicinic acid*, m. p. 254° (*hydrochloride*, m. p. above 320°), and *vomicinic acid betaine*, m. p. about 210° after sintering at 175°, decomp. 230° (*hydrochloride*). The methylated acid is unaffected by hot hydrochloric acid. With methyl sulphate I yields an additive *compound* (1 : 1) which when crystallised from water loses methyl alcohol forming a *methosulphate* [I+$MeSO_4H$], m. p. 264° (decomp.); this gives the *hydriodide*, m. p. 260—270° (decomp.), of I with aqueous potassium iodide. Reduction of I with hydrogen in presence of platinum oxide and dilute acetic acid affords *dihydrovomicine*, m. p. 290° with darkening, whilst treatment with red phosphorus and hydriodic acid (*d* 1·96) in acetic acid solution yields *deoxyvomicine* (V), $C_{22}H_{24}O_3N_2$. The presence of a tertiary hydroxyl group is assumed to explain this last change. Catalytic reduction of IV gives *bromodihydrovomicine*, m. p. 280°, whilst V furnishes a mixture of two *bases*, $C_{22}H_{28}O_2N_2$, m. p. 213° [*methiodide*, m. p. 236° (decomp.)], and $C_{22}H_{30}O_2N_2$ (VI), m. p. 179°. The elimination of an oxygen atom during this last reduction indicates the presence of an oxide ring in I (cf. Fawcett, Perkin, and Robinson, this vol., 82). Fission of VI into the corresponding acid occurs only with concentrated alkali at 160°; the acid is then reconverted into VI by short heating with hydrochloric acid. Treatment of VI with bromine in dilute hydrochloric acid gives a *monobromo*-derivative, m. p. 159°. Treatment of dihydrovomicine with red phosphorus, hydriodic and acetic acids yields *iododihydrodeoxyvomicine*, $C_{22}H_{25}O_3N_2I$, decomp. 242°, which when boiled with alcoholic potassium hydroxide solution furnishes a halogen-free substance, and when treated with zinc dust and alcohol containing a small amount of acetic acid affords *dihydrodeoxyvomicine*, m. p. 210°.

Oxidation of I with chromic anhydride in 4*N*-sulphuric acid solution at 70° gives an *acid*, $C_{16}H_{20}O_3N_2$, m. p. 304° (decomp.) after sintering and colouring at 285°; when oxidation is carried out first in the cold and then successively at 50—90°, two *acids*, $C_{17}H_{22}O_7N_2$ and $C_{17}H_{22}O_5N_2$, m. p. 262° (decomp.) and 312—314° (decomp.), respectively, are obtained. The annexed grouping is probably present in III and when oxidised gives a coloured quinonoid oxonium salt. H. Burton.



Synthetical experiments on the aporphine alkaloids. V. Laurotetanine. Syntheses of 2 : 3 : 6 : 7- and 3 : 4 : 6 : 7-tetramethoxyaporphines. R. K. Callow, J. M. Gulland, and R. D. Haworth (J.C.S., 1929, 658—670).—The constitution assigned by Gorter (A., 1921, i, 587) to the (supposed) dimethyl derivative of laurotetanine, *iso*glaucine, as 2 : 3 : 6 : 7-tetramethoxyaporphine (cf. Späth and Strauhal, also Barger and Silberschmidt, this vol., 80) has been shown to be incorrect by synthesis of this compound. As the result of a comprehensive study of the colour reactions of the aporphines, on which Gorter partly based his suggestion, the isomeric 3 : 4 : 6 : 7-tetramethoxy-base was also synthesised; neither substance resembles *iso*glaucine.

β-2 : 3-Dimethoxyphenylpropionamide, m. p. 98—99°, b. p. 233—235°/16 mm., obtained in 95% yield from the corresponding acid chloride and ammonia (cf. Haworth, A., 1927, 1088) or from methyl β-2 : 3-dimethoxyphenylpropionate, b. p. 166—176°/15 mm., and ammonia, was converted into β-2 : 3-dimethoxyphenylethylamine (I), b. p. 158—159°/25 mm., as described by Haworth (*loc. cit.*). 6-Nitro-3 : 4-dimethoxyphenylacetic acid, m. p. 206—207°, was obtained by nitrating 3 : 4-dimethoxyphenylacetic acid in glacial acetic acid, and also from 6-nitrohomoveratrole by way of 6-nitro-3 : 4-dimethoxyphenylpyruvic acid by a modification of the method of Oxford and Raper (A., 1927, 365), improved yields, 77% and 83%, respectively, being recorded for both stages of the process. Greatly enhanced reactivity is displayed by derivatives of 6-nitrohomoveratrole as compared with those of 2-nitrohomoveratrole (cf. A., 1928, 532); thus 6-nitro-3 : 4-dimethoxyphenylacetyl chloride is very unstable (cf. A., 1928, 781) and a mixture of 6-nitro-3 : 4-dimethoxyphenylacetic acid and I at 130° gives pure 6-nitrohomoveratrole in theoretical yield, whilst no reaction occurs between 2-nitro-3 : 4-dimethoxyphenylacetic acid and I below 175°. 6′-*Nitro*-3′ : 4′-*dimethoxyphenylaceto*-β-2 : 3-*dimethoxyphenylethylamide*, m. p. 144·5—145·5°, obtained by addition of a chloroform solution of 6-*nitro*-3 : 4-*dimethoxyphenylacetyl chloride* to a mixture of a chloroform solution of I and a dilute solution of sodium hydroxide at 0°, was converted by phosphorus pentachloride in cold chloroform suspension into 6′-*nitro*-3′ : 4′ : 5 : 6-*tetramethoxy*-1-*benzyl*-3 : 4-*dihydro*iso*quinoline*, melting at 187·5—189·5° to a deep red liquid which became colourless on resolidification. This base yielded a *methiodide*, which appears to be dimorphous (*red* and *yellow* forms, m. p. variable), and by reduction with zinc dust and hydrochloric acid, followed by treatment of the product with dry hydrogen chloride in chloroform–ether solution, afforded 6′-*amino*-3′ : 4′ : 5 : 6-*tetramethoxy*-1-*benzyl*-2-*methyltetrahydro*iso*quinoline dihydrochloride*, m. p. 233·5—235° (decomp.), diazotised in methyl-alcoholic sulphuric acid to yield dl-2 : 3 : 6 : 7-*tetramethoxyaporphine*, m. p. 115·5—116·5° [*methiodide*, m. p. 204—208°; *hydriodide*, m. p. 227·5—230·5° (decomp.)]. The base could not be resolved by means of *d*- and *l*-tartaric acids, and gave colour reactions with sulphuric acid, nitric acid, Mandelin's, Fröhde's, and Erdmann's reagents which did not resemble those described by Gorter for *iso*glaucine.

2-Nitro-3 : 4-dimethoxyphenylacetyl chloride when condensed with I in cold dry benzene gave 2′-*nitro*-3′ : 4′-*dimethoxyphenylaceto*-β-2 : 3-*dimethoxyphenylethylamide*, m. p. 95—96°, converted by phosphorus pentachloride in chloroform suspension into 2′-*nitro*-3′ : 4′ : 5 : 6-*tetramethoxy*-1-*benzyl*-3 : 4-*dihydro*iso*quinoline*, melting at 152—156° to a red liquid [*methiodide*, m. p. 183—184° (decomp.) (*compound* +*n*MeI, m. p. 110—116°)]. The methiodide of the base was reduced with zinc and hydrochloric acid to 2′-*amino*-3′ : 4′ : 5 : 6-*tetramethoxy*-1-*benzyl*-2-*methyltetrahydro*iso*quinoline*, m. p. 117·5—119·5°, which when diazotised in methyl-alcoholic sulphuric acid yielded dl-3 : 4 : 6 : 7-*tetramethoxyaporphine*, m. p. 131—132° (*hydriodide*, m. p. 257—262°). Resolution of the *dl*-base with *d*- and *l*-tartaric acids gave d-3 : 4 : 6 : 7-*tetramethoxyaporphine hydrogen* d-*tartrate*, $[\alpha]_D^{21}$ +84·9°, as the hygroscopic *dihydrate*, m. p. 174—185°, and l-3 : 4 : 6 : 7-*tetramethoxyaporphine hydrogen* l-*tartrate*, $[\alpha]_D^{18\cdot5}$ −85·2°, as the *dihydrate*, m. p. 170—180°, from which d-3 : 4 : 6 : 7-*tetramethoxyaporphine*, m. p. 125—125·5°, $[\alpha]_D^{20}$ +168°, and l-3 : 4 : 6 : 7-*tetramethoxyaporphine*, m. p. 125·5—126°, $[\alpha]_D^{20}$ −167° (*methiodide*, m. p. 208—210°), were obtained respectively.

The colour reactions of the aporphine alkaloids with Mandelin's, ·Erdmann's, and Fröhde's reagents and with sulphuric acid and nitric acid are given in tabular form. C. W. Shoppee.

Trypanocidal activity and chemical constitution. I. New sulphur derivatives of aromatic organic arsenicals. J. G. Everett (J.C.S., 1929, 670—679).—Thiocarbonyl compounds described below have been compared with the analogous carbonyl compounds for trypanocidal action; substitution of sulphur for oxygen causes no appreciable difference in toxicity or therapeutic activity (cf. A., 1926, 1173), and permanence of cure is uninfluenced except in those compounds containing arsenic in the 5-position of a 2-thiolbenziminazole ring, which are outstandingly efficacious. *p*-Arsanilic acid boiled with alcoholic alkali and carbon disulphide affords pp′-*dithiocarbiminophenylarsenic sesquisulphide* (I), hydrolysed by boiling 25% sodium hydroxide to *diphenylthiocarbamide*-pp′-*arsenic sesquisulphide* (II); reduction of I by sodium hyposulphite at 55° yields pp′-*dithiocarbiminoarsenobenzene* (III), which is completely soluble in cold 5% sodium hydroxide solution, and by hydrolysis with this reagent affords pp′-*arseno*(*diphenylthiocarbamide*) (IV), also obtained by reduction with sodium hyposulphite from II (62% yield) or III, and by simultaneous hydrolysis and reduction of I with sodium hydroxide and sodium hyposulphite at 90°, as an orange, amorphous solid insoluble in sodium hydroxide. By treatment with iodine IV gives a 42% yield of *diphenylthiocarbamide*-pp′-*diarsinic acid* (V) (*calcium*, *magnesium*, and *barium* salts), also prepared by iodine oxidation of II (yield 31%), or by treatment of *p*-arsanilic acid with thiocarbonyl chloride (yield 69%); V is reduced by sodium hyposulphite, regenerating IV (yield 71%), and is further oxidised by iodine in the presence of sodium hydrogen carbonate to give a 43% yield of *diphenylcarbamide*-pp′-*diarsinic acid* (*calcium*, *magnesium*, and *barium* salts), also obtained from *p*-arsanilic acid and carbonyl chloride. Conversion analogous to the change III ⟶ IV also occurs among the non-arsenated compounds; thus phenylthiocarbimide is completely converted into thiocarbanilide by boiling 20% sodium hydroxide (1 hr.).

1-*Thiobenzoxazolone*-4-*arsenic disulphide* (VI) is obtained in 64% yield from 3-amino-4-hydroxyphenylarsinic acid by treatment with carbon disulphide and alcoholic sodium hydroxide. It is readily soluble in dilute sodium cyanide solution, and is reduced by sodium hyposulphite to 4 : 4′-*arseno*-(1-*thiobenzoxazolone*) (VII), a yellow, amorphous powder readily soluble in dilute sodium cyanide. Both VI and VII are oxidised by iodine to 1-*thiobenzoxazolone*-4-*arsinic acid* (VIII) (*mganesium* salt), also obtained from 3-amino-4-hydroxyphenylarsinic acid and thiocarbonyl chloride (yield 78%), and reconverted into VII by sodium hyposulphite. The acid VIII reacts further with iodine in the presence of sodium hydrogen carbonate giving benzoxazolone-4-arsinic acid (yield 77%), also prepared from 3-amino-4-hydroxyphenylarsinic acid and carbonyl chloride (Fargher, J.C.S., 1919, **115**, 991). Similarly, 3 : 4-diaminophenylarsinic acid affords 2-*thiolbenziminazole*-5-*arsenic disulphide* (yield 64%), reduced by sodium sulphite to 5 : 5′-*arseno*-(2-*thiolbenziminazole*) (IX) (72% yield); both these compounds by iodine oxidation give 2-*thiolbenziminazole*-5-*arsinic acid* (X) (*calcium*, *magnesium*, and *barium* salts), which is also obtained from 3 : 4-diaminophenylarsinic acid and thiocarbonyl chloride (yield 78%), and is reconverted by sodium hyposulphite into IX. Further oxidation of X with iodine and sodium hydrogen carbonate gives benziminazole-5-arsinic acid (yield 83%).

In order to compare the effects of oxygen and sulphur in analogous compounds, the following were prepared: pp′-*arseno*(*diphenylcarbamide*) by reduction of diphenylcarbamide-*pp*′-diarsinic acid with sodium hyposulphite; 2 : 3-dihydrobenziminazolone-5-arsinic acid (*calcium*, *magnesium*, and *barium* salts) (cf. Bertheim, A., 1911, i, 1055) giving 5 : 5′-*arseno*-(2 : 3-*dihydrobenziminazolone*) by reduction with sodium hyposulphite. C. W. SHOPPEE.

10-Chloro-5 : 10-dihydrophenarsazine and its derivatives. VII. Synthesis of the 1-methyl and 3-methyl homologues. C. S. GIBSON and J. D. A. JOHNSON (J.C.S., 1929, 767—787).—Attempts to differentiate between the alternative formation of 1- or 3-substituted isomerides by ring closure of *m*-substituted diphenylamines with arsenious chloride, or of substituted diphenylamine-*o*-arsinic acids by reduction, has led to inconclusive results, and a series of apparent identities is described.

3-Amino-*p*-tolylarsinic acid, m. p. 184—185°, obtained by a slight modification of the method of Jacobs, Heidelberger, and Rolf (A., 1919, i, 50), is converted by the Sandmeyer reaction into 3-*chloro*-p-*tolylarsinic acid* (I), m. p. 189—191°, which is convertible into 3-*chloro*-p-*tolyldichloroarsine*, m. p. 27—29°, b. p. 166—167°/17 mm.; this with aqueous ammonia gives 3-*chloro*-p-*tolylarsenious oxide*, m. p. 277°, soluble in sodium hydroxide and reprecipitated by carbon dioxide (distinction from I). 3-*Bromo*-p-*tolylarsinic acid* (II), m. p. 208—210° (decomp.) [*calcium*, *barium*, *mercurous*, *silver* (soluble in ammonia), and *mercuric* salts], is similarly prepared and converted into 3-*bromo*-p-*tolyldichloroarsine*, m. p. 47—49°, b. p. 176—177°/14 mm., which with aqueous ammonia affords 3-*bromo*-p-*tolylarsenious oxide*, m. p. 266—268°, soluble in sodium hydroxide but insoluble in sodium carbonate. By oxidation with boiling alkaline potassium permanganate, I yields 2-*chloro*-4-*carboxyphenylarsinic acid*, m. p. above 310° [*calcium*, *barium*, *mercurous*, *silver* (soluble in ammonia), and *mercuric* salts]; 2-*bromo*-4-*carboxyphenylarsinic acid*, m. p. above 317°, similarly obtained from II, condenses readily with aniline giving 3-*methyldiphenylamine*-6-*arsinic acid* (III), m. p. 158—159° [*sodium*, *potassium*, *ammonium*, *calcium*, *barium*, *magnesium*, *lead*, *mercurous*, *silver* (soluble in ammonia), and *mercuric* salts], which is very easily reduced by sulphur dioxide to 10-*chloro*-3-*methyl*-5 : 10-*dihydrophenarsazine* obtained as a homogeneous product, m. p. 216—216·5°, oxidised with hydrogen peroxide or "chloramine-*T*" to 3-*methylphenarsazinic acid*, decomposing slightly at 316° [*compound* +1AcOH; *sodium* salt; *hydrochloride*, m. p. 232—233° (decomp. turning emerald-green)]; the same hydrochloride appears to be obtained directly from III by boiling with excess of concentrated hydrochloric acid. When 3-methylphenarsazinic acid is reduced with sulphur dioxide in hydrobromic acid–alcoholic solution, 3-*methyl*-5 : 10-*dihydrophenarsazine*, m. p. 206—208°, is obtained.

3-Amino-*o*-tolylarsinic acid (IV), prepared according to the method of Jacobs, Heidelberger, and Rolf (*loc. cit.*), was accompanied by a *substance*, m. p. 117°, which was not identical with m-*toluidine arsenate*, m. p. 141—144°; IV (Sandmeyer reaction) furnishes 3-*chloro*-o-*tolylarsinic acid*, m. p. 236—239° (decomp.) (*silver*, *mercurous* salts), slowly reduced by sulphur dioxide in boiling hydrochloric acid solution to 3-*chloro*-o-*tolyldichloroarsine*, m. p. 37·5°, b. p. 156°/11 mm., which is converted by aqueous ammonia into 3-*chloro*-o-*tolylarsenious oxide*, melting at 234—237° to a turbid liquid which clears at 254°. 3-*Bromo*-o-*tolylarsinic acid* (V), melting below 260° with apparent conversion into an *anhydride*, m. p. above 306° (*calcium*, *barium* *magnesium*, *lead*, *silver*, and *mercurous* salts), is similarly obtained from IV, and is very slowly reduced by sulphur dioxide in boiling alcoholic hydrochloric acid to 3-*bromo*-o-*tolyldichloroarsine*, m. p. 25—27°, b. p. 170—171°/13 mm., which affords 3-*bromo*-o-*tolylarsenious oxide*, m. p. 214—219°, when treated with aqueous ammonia. Condensation of V with aniline yields 3-*methyldiphenylamine*-2-*arsinic acid* (VI), m. p. 170—171° (decomp.) (*ammonium, calcium, barium, magnesium, lead, mercurous, silver*, and *mercuric* salts), somewhat difficultly reduced by sulphur dioxide to 10-*chloro*-1-*methyl*-5 : 10-*dihydrophenarsazine*, m. p. 216—216·5°, which is oxidised by alkaline potassium permanganate to 1-*methylphenarsazinic acid*, m. p. 316° (decomp.) [*sodium* salt; *hydrochloride*, m. p. 231—232° (decomp. turning emerald-green)]; the same hydrochloride was also obtained from VI by boiling with concentrated hydrochloric acid.

o-Bromophenylarsinic acid condenses with *m*-toluidine to yield 3-*methyldiphenylamine*-6′-*arsinic acid* (VII), m. p. 141—142° (*sodium* salt), reduced by sulphur dioxide in hot alcoholic hydrochloric acid solution to 1- and/or 3-methyl-10-chloro-5 : 10-dihydrophenarsazine, m. p. 216—217°, obtained as a homogeneous product identical with the reduction product of III; the substance is oxidised by hydrogen peroxide or “ chloramine-*T* ” to a product indistinguishable from synthesised 1-methyl- or 3-methyl-phenarsazinic acids. The action of concentrated hydrochloric acid on VII affords a hydrochloride, m. p. 232—233° (decomp. turning emerald-green), indistinguishable from the hydrochloride of either 1-methyl- or 3-methyl-phenarsazinic acid. Hot 50% sulphuric acid appears to convert VII into 3-methylphenarsazinic acid. Reduction of 1- and/or 3-methylphenarsazinic acid with sulphur dioxide in boiling alcoholic hydrobromic acid gives 1- and/or 3-methyl-10-bromo-5 : 10-dihydrophenarsazine, apparently identical (direct comparison and mixed m. p.) with the genuine 3-methyl compound. The solubilities of 10-chloro-1-methyl- and -3-methyl-5 : 10-dihydrophenarsazines in benzene are approximately the same, viz., about 0·3% at the ordinary temperature and about 3% at the b. p.

3-*Nitro*-p-*tolyldichloroarsine*, m. p. 113°, may be obtained by sulphur dioxide reduction of 3-nitro-*p*-tolylarsinic acid. 3-Nitro-*o*-toluidine (cf. Gabriel and Thieme, A., 1919, i, 398) is converted by the method of Jacobs, Heidelberger, and Rolf (*loc. cit.*) into 3-*nitro*-o-*tolylarsinic acid*, m. p. above 300° (*sodium hydrogen* salt $+6H_2O$, m. p. 97°), which by reduction with sulphur dioxide affords 3-*nitro*-o-*tolyldichloroarsine*, m. p. 93°; the corresponding 3-*nitro*-o-*tolyldibromoarsine*, m. p. 116·5—117·5°, is obtained by reduction with hydrobromic acid (*d* 1·49) containing a trace of iodine.

C. W. SHOPPEE.

Organic compounds of mercury. I. Synthesis of aromatic organomercury salts. A. N. NESMEJANOV. **II. Preparation of symmetrical, aromatic, organomercury compounds.** A. N. NESMEJANOV and E. J. KAHN (Ber., 1929, 62, [*B*], 1010—1018, 1018—1020).—The double salts of diazonium compounds and mercuric halides decompose in the presence of copper powder with formation of mercuric aryl halides. If substituents are present in the benzene nucleus, the best yields are obtained when they are most positive in character, whereas strongly negative substituents inhibit more or less completely the production of mercury derivatives. The results depend also on the nature of the solvent used. Acetone is generally most useful. The change proceeds according to the equation $PhN_2Cl,HgCl_2+2Cu=HgPhCl+N_2+2CuCl$. The diazonium double salts are prepared (I) by mixing a diazotised solution of the amine in hydrochloric acid with a solution of mercuric chloride in the same solvent, (II) by adding a large excess of sodium nitrite to mercuric chloride dissolved in hydrochloric acid and shaking the solution with the amine in ether, and (III) by diazotising the amine hydrochloride with amyl nitrite in alcohol containing hydrochloric acid and pouring the resulting solution into ethereal mercuric chloride. The double salts, mixed with the requisite amount of copper powder, are decomposed by agitation at the ordinary temperature with a suitable solvent, generally ether. The following mercury compounds are described: the phenyl iodide, m. p. 269°; the phenyl chloride, m. p. 258°, and the parent *diazonium* compound, $PhN_2Cl,HgCl_2$: the *o*-tolyl chloride, m. p. 143°, and *salt*, $C_6H_4Me{\cdot}N_2Cl,HgCl_2$; the *p*-tolyl chloride, m. p. 238—239°, and *salt*, $C_6H_4Me{\cdot}N_2Cl,HgCl_2$, m. p. 107° (decomp.) when rapidly heated; the α-naphthyl chloride, m. p. 191, and *salt*, $C_{10}H_7N_2Cl_3Hg$, m. p. 120—121° (decomp.); the β-naphthyl chloride, m. p. 270°, and *salt*, $C_{10}H_7N_2Cl_3Hg$, m. p. 120—125° (decomp.); the *p*-hydroxyphenyl chloride, m. p. 226—227°, and *salt*, $C_6H_5ON_2Cl_3Hg$, m. p. 156°; the *o*-anisyl chloride, m. p. 180—181°, and *salt*, $C_7H_7ON_2Cl_3Hg$, m. p. 121·5°; the *p*-phenetyl chloride, m. p. 249—250°, and *salt*, $C_8H_9ON_2Cl_3Hg$, m. p. 109°; the *p*-chlorophenyl chloride, m. p. 240°, and *salt*, $C_6H_4N_2Cl_4Hg$, m. p. 124·5°; the *p*-bromophenyl chloride, m. p. 249·5°, and *salt*, $C_6H_4N_2Cl_3BrHg$, decomp. 119°; the p-*iodophenyl chloride*, m. p. 272·5°, and *salt*, $C_6H_4N_2Cl_3IHg$, m. p. 120—121·5° (decomp.); the 2 : 5-*dichlorophenyl chloride*, m. p. 208°, and *salt*, $C_6H_3N_2Cl_5Hg$, m. p. 147—148°. Methyl *o*-chloromercuribenzoate, m. p. 184—185°, and the *diazonium* salt, $C_8H_7O_2N_2Cl_3Hg$, m. p. 121°, are described. 2 : 4 : 6-Tribromoaniline gives a *diazonium* double compound, $C_6H_2Cl_3Br_3N_2Hg$, m. p. 146°, from which the mercury compound could not be obtained. Diazotised *p*-nitroaniline gives a double *salt*, $C_{12}H_{10}O_4N_6Cl_4Hg$, m. p. 106—107°, converted by ethereal mercuric chloride into the *compound*, $C_6H_4O_2N_3Cl_3Hg$, m. p. 102—103°; either compound in ether yields minute amounts of mercury *p*-nitrophenyl chloride, m. p. 267—269°. Diazotised *p*-aminobenzoic acid affords the double *salt*, $C_{14}H_{10}O_4N_4Cl_4Hg$, which does not yield a corresponding mercury compound.

II. The additive compounds of diazonium and mercuric chlorides, mixed with copper powder, are covered with cooled acetone or alcohol; when the first, energetic action has subsided, 25% aqueous ammonia is added and the mixture is preserved for 12—24 hrs. The change follows the course $2ArN_2HgCl_3+6Cu=Ar_2Hg+Hg+6CuCl+2N_2$. The following mercury compounds have been thus prepared in % yields shown in parentheses: diphenyl (65), m. p. 125°; di-α-naphthyl (53), m. p. 249°; di-*p*-tolyl (76), m. p. 243—244°; di-*p*-bromophenyl, m. p. 243—244°; *di*-p-*iodophenyl* (70), m. p. 270—272°; *di*-2 : 5-*dichlorophenyl*, (20), m. p. 237°; di-*o*-anisyl (60), m. p. 108°; *di*-p-*nitrophenyl* (10), decomp. 320°.

H. WREN.

Bases and mercurated anilines. F. C. Whitmore, E. R. Hanson, and F. L. Carnahan (J. Amer. Chem. Soc., 1929, **51**, 894—900).—Dialkylanilines are converted by mercuric acetate in aqueous alcohol into *p*-acetoxymercuri-derivatives. These yield in aqueous alcohol with calcium chloride and sodium bromide, respectively, *p*-chloromercuri- and *p*-bromomercuri-derivatives, and with sodium iodide (1 mol.) in cold acetone, *p*-iodomercuri-derivatives. Excess of sodium iodide yields the mercury tetra-alkyldiaminodiphenyls, which are also obtained with sodium thiosulphate. With potassium hydroxide (32 mols.) in boiling aqueous alcohol small amounts of the mercury diphenyls are again formed, together with dialkylaminophenylmercuric hydroxides and oxides, mercury and its oxides, and ethane hexamercarbide, but with sodium ethoxide or aqueous ammonia (cf. Pesci, A., 1898, i, 648) mercury diphenyls are not obtained. The following are described: p-*Acetoxymercuri*-derivatives of dimethyl-, m. p. 165°, diethyl-, m. p. 105°, di-*n*-propyl-, m. p. 99°, di-*n*-butyl-, m. p. 89—90°, methylethyl, m. p. 92—93°, and benzylethyl-, m. p. 92—94°, -aniline, and the corresponding *mercury tetra-alkyldiaminodiphenyls*, m. p. 168°, 161°, 86°, 79—80°, 139—142°, and 128°; p-*chloromercuri*-derivatives of diethyl-, m. p. 164°, di-*n*-propyl-, m. p. 170—172°, di-*n*-butyl-, m. p. 162—163°, methylethyl-, m. p. 162—166°; and benzylethyl-, m. p. 150—151°, -aniline; p-*bromomercuri*-derivatives of aniline, m. p. 181°, diethyl-, m. p. 158°, di-*n*-propyl-, m. p. 165—167°, di-*n*-butyl-, m. p. 164—165°, methylethyl-, m. p. 154—155°, and benzylethyl-, m. p. 155°, -aniline; p-*iodomercuri*-derivatives of aniline, m. p. 165°, diethyl-, m. p. 120—121°, di-*n*-propyl-, m. p. 150°, di-*n*-butyl-, m. p. 151°, methylethyl-, m. p. 137—138°, and benzylethyl-, m. p. 132—134°, -aniline; the *dialkylaminophenylmercuric hydroxides*, from dimethyl-, m. p. 152—156°, methylethyl-, m. p. 192—199°, and benzylethyl-, m. p. 158—167°, -aniline, and *oxides* from dimethyl-, m. p. 180°, diethyl-, m. p. 210—219°, di-*n*-propyl-, m. p. 184—185°, and di-*n*-butyl-, m. p. 170°, -aniline.

H. E. F. Notton.

Organo-metallic compounds. I. New class of tin aryl compounds: tin phenyl trihalides. K. A. Kozeschkov (Ber., 1929, **62**, [*B*], 996—999).—*Tin phenyl trichloride*, b. p. 142—143°/25 mm., is prepared in 80% yield by heating a mixture of 1 mol. of tin tetraphenyl with 3 mols. of tin tetrachloride for 1½—2 hrs. at 210—220°; at 190° for 1 hr. the yield of trichloride is diminished, whilst that of the dichloride is increased. The last-named compound, m. p. 42°, is formed almost quantitatively from tin tetraphenyl (1 mol.) and tin tetrachloride (1 mol.) at 220° and is converted by 1 mol. of tin tetrachloride at the same temperature into tin phenyl trichloride. In cold water, the trichloride dissolves without decomposition to a clear, acidic solution; it is partly hydrolysed by boiling water. Concentrated hydrochloric acid converts it into benzene and tin tetrachloride. Pyridine, ammonia, and other bases give the corresponding additive compounds. *Tin phenyl tribromide*, from the trichloride and hydrobromic acid (*d* 1·78), has b. p. 182—183°/29 mm. *Tin phenyl tri-iodide* appears to be formed as a heavy, unstable oil by the action of hydriodic acid on the bromide. H. Wren.

Racemisation. VIII. Action of alkali on proteins; racemisation and hydrolysis. P. A. Levene and L. W. Bass (J. Biol. Chem., 1929, **82**, 171—190).—The previous work on the action of alkali in varying concentrations on gelatin and caseinogen (A., 1928, 1043) has been repeated and extended to albumin, edestin, and fibrin. None of these proteins except gelatin exhibited the characteristic behaviour of diketopiperazines (*i.e.*, rapid racemisation by 0·1*N*- and rapid hydrolysis by 1·0*N*-alkali), but behaved rather as peptides; the apparent exception in the case of gelatin may be explained by the preponderance of lævorotatory amino-acids in this protein. The diketopiperazine theory of protein structure is further criticised on analytical grounds. In the light of experiments on simple peptides, the differences exhibited by different proteins in their rates of hydrolysis and of racemisation by alkali may be explained on the ground of differences in the nature of the constituent amino-acids and in the order in which they are combined. C. R. Harington.

Characterisations of small quantities of proteins by Van Slyke's method. N. Narayana and M. Sreenivasaya (J. Indian Inst. Sci., 1929, **12A**, 37—40).—The protein is digested with 20% hydrochloric acid, the product, freed from acid, is made up to a definite volume, and portions are analysed for amide-nitrogen by alkali distillation, for melanin-nitrogen by isolation of melanin and micro-Kjeldahl determination, for hexone bases by precipitation with phosphotungstic acid, and for arginine by the action of arginase. The method is applicable to quantities of about 0·125 g. Analyses of caseinogen and gelatin are given as examples.

R. J. W. Le Fèvre.

Determination of carbon and carbon dioxide. T. E. Friedemann and A. I. Kendall (J. Biol. Chem., 1929, **82**, 45—55).—Good results by the wet combustion method are obtainable only when the relative amount of water present is small. An apparatus is described in which organic material is oxidised with chromic acid in presence of a large excess of sulphuric and phosphoric acids, the carbon dioxide being swept by a stream of air into standard sodium hydroxide solution. The method gives practically quantitative results with compounds such as acetic acid and fats which are known to be oxidised only with difficulty.

C. R. Harington.

Analysis of thiazine eosinates. W. C. Holmes (Stain Tech., 1929, **4**, 49—52).—Moisture is determined by drying at 110°. The thiazine content is determined by dissolving 0·2 g. in 50 c.c. of glacial acetic acid, adding 100 c.c. of alcohol, heating to boiling, and titrating with *N*-titanous chloride in a current of carbon dioxide. The thiazine is thus reduced, whilst the eosin is unaffected. The disappearance of a bluish-green tint in the orange solution gives the end-point. The total dye content is determined by dissolving 0·2 g. in 100 c.c. of alcohol, adding 100 c.c. of water and 50 c.c. of 20% solution of sodium potassium tartrate, heating to boiling, and titrating as before. Under these conditions both the thiazine and the eosin are reduced. The disappearance of the pink tint gives the end-point.

H. W. Dudley.

Determination of tin in organic compounds. H. Gilman and W. B. King (J. Amer. Chem. Soc., 1929, 51, 1213—1215).—This extension of the method given for lead (A., 1928, 1041; cf. Krause and Becker, A., 1920, i, 340) is applicable to alkyl and aryl derivatives. Treatment in a large porcelain crucible with 4% bromine in carbon tetrachloride is followed by oxidation with graduated mixtures of sulphuric and nitric acids. H. E. F. Notton.

Methods. IX. L. Pincussen. Determination of halogens in organic substances. W. Roman (Biochem. Z., 1929, **207**, 416—425).—A method is outlined for the determination of the iodine, bromine, and chlorine contents of organic substances. The substance is fused with potassium hydroxide and the iodide separated from the bromide and chloride by extraction with alcohol. The iodide is then oxidised to iodate, potassium iodide added, and the iodine set free titrated with thiosulphate. The bromine liberated by oxidising the chloride–bromide mixture with hydrogen peroxide is extracted with chloroform and allowed to react with iodide, the equivalent amount of iodine being titrated. The chloride is then obtained by difference from the total halide of the bromide–chloride mixture.

P. W. Clutterbuck.

Van Slyke's method [for the determination of amino-acids]. L. Rosenthaler (Biochem. Z., 1929, **207**, 298—301).—The amounts of nitrogen liberated from a number of nitrogenous substances (substituted amines, amides, hydrazines, semicarbazones, pyrazolones, etc.) by the action of nitrous acid for varying lengths of time are tabulated.

P. W. Clutterbuck.

Biochemistry.

Resorption of carbon dioxide through the skin. S. Hediger (Klin. Woch., 1928, 7, 1553—1557; Chem. Zentr., 1928, ii, 2263).—The resorption of carbon dioxide and the so-called respiration of the skin depend on a diffusion phenomenon.

A. A. Eldridge.

Determination of blood volume in small animals. S. Went and C. K. Drinker (Amer. J. Physiol., 1929, 88, 468—478).—A method for the determination of blood volume after the injection of vital-red is detailed. Only 0·01 c.c. of heparinised blood is required. B. A. Eagles.

Rate of sinking of erythrocytes in relation to the Hofmeister ionic series. II. D. von Klobusitzky (Biochem. Z., 1929, **207**, 80—90; cf. A., 1925, i, 710).—In hypertonic solutions anions alter the electric charge, viscosity, and density of blood-plasma and the volume and density of the erythrocytes according to the Hofmeister salt series. There is complete agreement between the effects on these properties and that on the rate of sinking of the erythrocytes, the most important and dominating factor being the alteration in the electric charge. The cations have only a slight influence on the charge and hence the effects they produce are irregular.

W. McCartney.

Hæmoglobin and its biological significance. J. Barcroft (Naturwiss., 1929, **17**, 261—269).—A lecture. R. A. Morton.

Iron in the lungs of mammals and the formation of melanin pigments. F. Granel and L. Hédon (Compt. rend. Soc. Biol., 1928, **99**, 22—24; Chem. Zentr., 1928, ii, 2039).—A study of the effect of the injection of hæmoglobin into guinea-pigs.

A. A. Eldridge.

Blood pigments. IX. Linking between the protein and the prosthetic group in hæmoglobin. F. Haurowitz and H. Waelsch (Z. physiol. Chem., 1929, **182**, 82—96).—Globin prepared according to the method of Hill and Holden (A., 1927, 67), freed from salts by dialysis, contained 0·05% of an alcohol- or ether-soluble substance (sterol). When warmed to 47° the aqueous solution of the chloride-free dialysate became opalescent; in the presence of salt it coagulated at 47°. The isoelectric point measured by the cataphoresis method was p_H 7·0 in phosphate-buffered solution, 6·9—7·0 in cacodylic acid–sodium cacodylate solution. Dimethylmesohæmin dissolved in methyl alcohol yielded when treated with dialysed globin in the presence of ammonium sulphide first dimethylmeso-oxyhæmoglobin and then dimethylmesohæmoglobin. By the use of titanous tartrate in the Van Slyke gasometric apparatus the synthesised hæmoglobin has been shown to be able to form oxyhæmoglobin with molecular oxygen. The authors could not confirm the compound formation between globin and porphyrin observed by Hill and Holden (*loc. cit.*). Lipase after 24 hrs. caused no change in hæmoglobin which could be measured spectroscopically, whereas trypsin completely hydrolysed the protein portion. Whilst oxyhæmoglobin formed from hæmin and native globin coagulated at 47°, a specimen of the oxyhæmoglobin, from which the globin employed in the synthesis was prepared, coagulated at 63°.

C. C. N. Vass.

Normal bilirubin content in human sera. R. Sivò (Folia Clin. Chim. Micros., 1928, 3, 1—4; cf. Enriques and Sivó, A., 1926, 648).—In the great majority of normal cases the bilirubin content of human serum lies between 0·8 and 1·1 mg.-%, and cases showing more than 1·2 mg.-% are to be regarded as pathological, as also are some individual instances of values below 1·2. T. H. Pope.

Determination of serum-proteins. Comparison of results obtained by the gravimetric method and determination of nitrogen and of refactive index. C. O. Guillaumin, R. Wahl, and M. L. Laurencin (Bull. Soc. Chim. biol., 1929, **11**, 387—399).—The refractometric method gives results varying to some extent with the proportion of globulin present in the serum. The best method is that of Howe (A., 1922, ii, 171) in which the nitrogen in the various fractions is determined.

E. Boyland.

Molybdic acid as a precipitant for blood-proteins. S. R. Benedict and E. B. Newton (J. Biol. Chem., 1929, **82**, 5—10).—Molybdic acid may be utilised as a precipitant for blood-proteins under conditions closely analogous to those employed by Folin and Wu (A., 1919, ii, 308) in the case of tungstic acid. The use of molybdic acid is necessary in the determination of ergothioneine and is preferable in the determination of uric acid in blood.

C. R. Harington.

Occurrence and determination of ergothioneine in human blood. J. A. Behre and S. R. Benedict (J. Biol. Chem., 1929, **82**, 11—15).—Blood is freed from protein with molybdic acid, an aliquot portion of the filtrate is treated with silver lactate, the uric acid is extracted from the precipitate with sodium chloride and hydrochloric acid, and the residue dissolved in sodium cyanide; the resulting solution is treated with the uric acid reagent (A., 1922, ii, 405) and sodium hydroxide, in presence of which the colour given by uric acid is only 1·4 times as great as that given by the same weight of ergothioneine. The colour is compared with that given by a known solution of ergothioneine similarly treated. The average concentration of ergothioneine in human blood is 7·5 mg. per 100 c.c. C. R. Harington.

" Protein-sugar " of the blood. E. J. Bigwood and A. Wuillot (Compt. rend. Soc. Biol., 1928, **99**, 352—356; Chem. Zentr., 1928, ii, 2034).—The difference in reducing power of blood-serum before and after acid hydrolysis is no proof of the presence of a " protein-sugar." A. A. Eldridge.

Determination of true sugar in blood. E. S. West, F. H. Scharles, and V. L. Peterson (J. Biol. Chem., 1929, **82**, 137—153).—Blood is laked by dilution and treated with mercuric nitrate and the mixture shaken with excess of barium carbonate; the filtrate is freed from barium and mercury with sulphuric acid and hydrogen sulphide; or, better, the laked blood is treated with a solution of 30% mercuric sulphate in 10% sulphuric acid and shaken with barium carbonate, traces of barium and mercury being removed from the filtrate as above, or by treatment with sodium sulphate and zinc dust. Filtrates so prepared from human blood are apparently free from non-dextrose reducing substances, since their direct analysis with the reagent of Somogyi (A., 1927, 69, 1214) gave, except in one pathological case with a high non-protein-nitrogen concentration, figures for the sugar content in close agreement with those obtained by the yeast fermentation method of the latter author. Similar agreement by the two methods was obtained in various animal bloods, although discrepancies occurred with certain samples of pig's blood, which could not be accounted for by the presence of glutathione or of ergothioneine.

C. R. Harington.

Copper method of determining blood-sugar. O. Folin (J. Biol. Chem., 1929, **82**, 83—93).—The author's recent method (A., 1926, 648) for the determination of blood-sugar is discussed and certain modifications are suggested. C. R. Harington.

Lactic acid content of the blood. M. Hochrein and R. Meier (Deut. Arch. klin. Med., 1928, **161**, 59—83; Chem. Zentr., 1929, ii, 2101).—Human blood normally contains 6—10 mg.-% of lactic acid; higher values are found after febrile conditions and in certain pathological conditions of the heart and liver. A. A. Eldridge.

Calcium and inorganic phosphorus in the blood of rabbits. IV. Influence of light environment on normal rabbits. W. H. Brown and M. Howard (J. Exp. Med., 1929, **49**, 103—126).—The chemical equilibrium of the blood of rabbits, as indicated by the calcium and inorganic phosphorus content, is affected by exposure to neon light.

Chemical Abstracts.

Anticoagulant action of Witte's peptone. J. W. Pickering (Proc. Roy. Soc., 1929, **B**, **104**, 512—518).—Undisturbed plasma protects platelets against clumping and lysis. The principal influence of small amounts of peptone on blood freshly shed into paraffined vessels is the restraint of changes in the plasma. This reaction, by delaying the disintegration of platelets, assists in the inhibition of blood-clotting.

B. A. Eagles.

Fats of Japanese birds. I. R. Koyama (J. Soc. Chem. Ind. Japan, 1928, **31**, 292—296).—The fats obtained from Daurian tern (*Sterna longipennis*, Nordmann), Japanese snipe Mibuto (*Gallinago Mibuto*, Koyama), and Javan buzzard (*Butastur indicus*, Gmelin) have been studied. Males, females, chickens, and adults were examined separately. These fats had m. p. from 29·8° to 41·9°, d^{40} from 0·887 to 0·912, n^{40} from 1·464 to 1·471, saponification values from 179 to 196, acid values from 0·08 to 2·67, iodine values from 61 to 103, unsaponifiable matter from 0·53 to 7·94%, and insoluble bromine compounds from 1·88 to 31·08% (Br 52·51—71·53%). The fats of these birds contained some higher unsaturated fatty acids; the saturated fatty acids were apparently chiefly palmitic and stearic acids. The quantity of higher unsaturated fatty acids seemed to increase as the birds grew, and the properties of the fats varied during their breeding season. Y. Nagai.

Silkworm chrysalis oil. E. de'Conno and A. Quarto (Annali Chim. Appl., 1929, **19**, 91—97).—In comparison with oil obtained from the normal chrysalises, that obtained from chrysalises which have been killed with chloropicrin shows little difference in physical and chemical characters, but increased proneness to turn rancid. The lecithin undergoes hydrolysis, stearic acid being liberated; this action of chloropicrin is analogous to that of snake-poison, which causes loss of an oleic residue by the lecithin. T. H. Pope.

Action of bromine on insect oils. J. T. David (Compt. rend., 1929, **188**, 1122—1124).—The high iodine values of the oils from the larvæ of certain *Lepidoptera* and *Coleoptera* are given. The action of bromine on these oils was found to give in some cases a small precipitate (2—6%), in others a larger amount (14%), and in some cases none. The presence of linolenic acid in the oil from *Colaspidema atra* was proved by the isolation of hexabromostearic acid after the treatment with bromine.

B. W. Anderson.

Transmicroscopic structure of living bodies. III. Otoliths of *Rana esculenta*. S. Funaoka and S. Toyota (Folia anat. Jap., 1928, 6, 323—325; Chem. Zentr., 1928, ii, 2158).—The otoliths and the calcium salt in the lime sac consist of aragonite.

A. A. Eldridge.

Colorimetric method of determining guanine: application to determination of nucleo-cytoplasmic ratios. T. B. Robertson (Austral. J. Exp. Biol., 1929, 6, 33—58).—The oxidation of guanine to guanidine with potassium permanganate and hydrochloric acid and the colorimetric determination of the latter is used as a basis for the determination of guanine. The reagent used comprises 5 c.c. each of 10% solutions of sodium nitroprusside, potassium ferricyanide, and sodium hydroxide, diluted to 60 c.c. with distilled water. Certain oxidation products of guanine depress the colour value obtained; this depression is removed by treatment with alkaline hydrogen peroxide. The application of the method to the determination of nucleic acid in animal tissues is described and the ratio nucleic acid-nitrogen to coagulable protein-nitrogen is suggested as a measure of nucleo-cytoplasmic ratios. F. C. Happold.

Philothion. de Ray-Pailhade (Bull. Soc. Chim. biol., 1929, 11, 308—311).—Philothion is a complex protein which evolves hydrogen sulphide at 100° and reduces sulphur to hydrogen sulphide at 30°.

E. Boyland.

Seasonal variation in iodine percentage and dry weight of thyroid glands of sheep in Australia. M. C. Dawbarn (Austral. J. Exp. Biol., 1929, 6, 65—77).—A statistical examination of the results of determinations of dry weight and iodine content of 106 sheep's thyroid glands reveals a seasonal variation in the iodine percentage which is 25% less on the average in the early summer months than in the winter. The sex of the animal affects the dry weight but not the percentage iodine content of the thyroids. F. C. Happold.

Carbohydrate of rabbit's skeletal muscle. H. Handovsky and K. Westphal (Pflüger's Archiv, 1928, 220, 399—409; Chem. Zentr., 1928, ii, 2039).—Values are: total carbohydrate 509—568, glycogen 377—493, lower sugars 39—165 (30% reducing sugar), lactose 123—153 mg.-%. A. A. Eldridge.

Glycogen content of the liver. I. Determination of the glycogen and carbohydrate content of the liver. E. Burghard and H. Paffrath (Z. Kinderheilk., 1927, 45, 68—77; Chem. Zentr., 1928, ii, 2174—2175).—On account of post-mortem decomposition of glycogen in muscle and liver it is recommended that the total carbohydrate content should be determined and the liver-glycogen calculated from this, the constant difference being 0·23.

A. A. Eldridge.

Chemical examination of a mummy. A. Tulli (Atti R. Accad. Lincei, 1929, [vi], 9, 233—237).—Examination of a mummy from the Vatican Museum showed absence of nitre, arsenic, heavy metals, and bitumen. Probably natural balsams were used in the mummifying process. T. H. Pope.

Regulation of respiration. XXVII. Effect on salivary secretion of varying carbon dioxide and oxygen content of inspired air. N. B. Eddy (Amer. J. Physiol., 1929, 88, 534—545).—The submaxillary gland of the dog was made to secrete at a constant rate by continuous intravenous administration of pilocarpine. Under these conditions, an increased carbon dioxide content of the inspired air produced an increased rate of secretion of saliva and decreased oxygen content a decreased rate of secretion.

B. A. Eagles.

Regulation of respiration. XXVIII. Lymph acidity and lymph flow during administration of sodium hydrogen carbonate and carbon dioxide. XXIX. Lymph acidity and lymph flow during impaired oxidations produced by cyanide. R. Gesell (Amer. J. Physiol., 1929, 88, 546—553, 554—561).—XXVIII. Intravenous injections of sodium hydrogen carbonate solution decreased the hydrogen-ion concentration of the lymph and blood. Administration of carbon dioxide increased the acidity of the lymph and blood.

XXIX. Cyanide markedly increased the flow of lymph. B. A. Eagles.

Mechanism of lymph-formation. G. Quagliariello (Atti R. Accad. Lincei, 1929, [vi], 9, 243—249).—The differences in chemical constitution and chemico-physical properties between lymph and plasma are explainable in some degree on the assumption that, when the two liquids are separated by a membrane more readily permeable by electrolytes than by colloids, a membrane equilibrium either is established or tends to become established.

T. H. Pope.

Acid-base composition of gastric secretions. J. L. Gamble and M. A. McIver (J. Exp. Med., 1928, 48, 837—847).—A study of the secretion of isolated pouches constructed in the fundus and in the pyloric antrum of the cat's stomach.

Chemical Abstracts.

Acid-base composition of pancreatic juice and bile. J. L. Gamble and M. A. McIver (J. Exp. Med., 1928, 48, 849—857).—The concentration of fixed base in the pancreatic juice is approximately equal to that in the blood-plasma; the concentration of chlorine ion is 25—50% of the fixed base value. In bile as delivered by the liver the concentrations of fixed base and chlorine ion correspond with those in the blood-plasma, whilst in gall-bladder bile the concentration of fixed base is double that of hepatic duct bile and the chlorine ion has almost entirely disappeared. Chemical Abstracts.

Physical decolorisation of bile. H. Wit (Biochem. Z., 1929, 207, 141—145).—Of adsorbents which are in the form of powders animal charcoal is the best for decolorising bile; kaolin, talc, and kieselguhr are much less active. The efficiency of these powdered adsorbents is increased by the presence of acid and decreased by that of bile acids or of protein. It is chiefly on the electrochemical nature of the adsorbent that the removal of colouring matter depends, but the reaction of the bile also has an important influence on the process. W. McCartney.

Iodine as a biogenic element. XVIII. Method of combination of iodine in milk. K. Scharrer and J. Schwaibold (Biochem. Z., 1929, 207, 332—

340).—Under normal conditions only a small part of the iodine of milk is present as inorganic salts. It is mostly combined with organic substances of the serum. Feeding iodised protein alters the proportions a little, whilst administration of moderate amounts of alkali iodides causes a considerable increase in the inorganic fraction. By feeding di-iodostearolic acid, the chief portion of the iodine carried over into the milk is iodised fatty acid or glyceride.
P. W. CLUTTERBUCK.

Composition of liquor folliculi. M. TESTA (Arch. Farm. sperim., 1929, **46**, 174—176).—Analysis of two samples of liquor folliculi gave the following results in mg. per 100 g.: free cholesterol, 28·57, 30·07; cholesteryl esters, 27·96, 29·44; neutral fats, 13·46, 12·65; fatty acids, 36·90, 32·42; phosphatides, 34·90, 26·50. About 0·907% of the protein present is precipitable by alcohol but not coagulable by heat and appears to be a mucoid (cf. Testa and Tafuri, Boll. Soc. Biol. sperim., 1927, **2**, 893). When isolated by the method used by Needham for the mucoid of hen's eggs (A., 1927, 787) and hydrolysed by means of 20% hydrochloric acid solution, it yields 9·192% of total, 0·392% of melaninic, 3·721% of basic, and 5·075% of amino-nitrogen, and when dissolved in a solution of potassium chloride and hydrochloric acid, it gives 16·49% of reducing substance calculated as dextrose.
T. H. POPE.

Composition of the body fluids of the goosefish (*Lophius piscatorius*). H. W. SMITH (J. Biol. Chem., 1929, **82**, 71—75).—The goosefish differs from other teleosteans in that its pericardial and perivisceral cavities contain considerable quantities of fluid; these fluids are slightly more alkaline than the blood-serum, but in other respects neither they nor the spinal fluid show marked difference in composition from the serum.
C. R. HARINGTON.

Determination of organic acids in small amounts of urine and of the basic equivalents combined with the acids. F. MAINZER and A. JOFFE (Biochem. Z., 1929, **207**, 167—176).—By means of a modification of the method of Van Slyke and Palmer (A., 1920, i, 459) the organic acids of urine can be determined in a volume of 10 c.c. A process for the titration of the bases combined (at the p_H of the urine) with these acids is also described. The extent of combination of the bases in urine shows no detectable dependence on the p_H.
W. MCCARTNEY.

Acetone and acetoacetic acid in urine. C. OTTO (Pharm. Ztg., **74**, 499).—The ethylenediamine test gives with acetone a pale to deep violet colour and with acetoacetic acid an orange to brown colour. In the presence of both substances, the latter is masked by the former. Proof of the presence of acetoacetic acid depends on the sensitiveness of the Jack test, which is not given by acetone. Results obtained from the application of the tests show that the presence of small amounts of acetone in urine can be considered normal.
B. A. EAGLES.

Acetone and acetoacetic acid in urine. P. HORKHEIMER (Pharm. Ztg., **74**, 499—500).—A reply to the criticisms of Otto (preceding abstract). In urines containing small amounts of acetone substances a positive acetone test is due to acetoacetic acid rather than to acetone. Both the Lang and Legal test and the ethylenediamine test are more sensitive to acetoacetic acid than they are to acetone.
B. A. EAGLES.

Determination of lævulose in urine. C. I. KRUISHEER (Biochem. Z., 1929, **207**, 441—446).—Lævulose can be determined in urine (after destruction of aldehyde sugars and urinary reducing substances by treatment with alkaline iodine) by determining the reducing power to Fehling's solution with an accuracy of 0·05%.
P. W. CLUTTERBUCK.

Colouring matters of urine. VII. Spectrometric determination of urobilin. M. WEISS (Biochem. Z., 1929, **207**, 151—158).—By means of a method described previously (cf. this vol., 91) the urobilin content of urine, fæces, or bile can be quantitatively determined. A spectrometer and a urobilin solution of known concentration are employed. The amount of urobilin which can be determined in 1 day's urine is not less than 0·5 mg.
W. MCCARTNEY.

Upper limit of hydrogen-ion and hydrogen carbonate concentrations of urine. F. MAINZER (Biochem. Z., 1929, **207**, 159—166).—Determinations made with urine from women to whom large amounts of hydrogen carbonate had been orally administered and with that from a dog into which sufficient sodium carbonate to produce alkali poisoning had been intravenously injected show that the p_H of urine cannot exceed 8·3. The amount of hydrogen carbonate excreted in the urine is simply related (at constant carbon dioxide tension) to the p_H. The maximum possible concentration of hydrogen carbonate in urine is 536 millimol.-%, but this concentration is influenced by other factors than the p_H.
W. MCCARTNEY.

Anæmia as an avitaminosis. O. STINER (Mitt. Lebensm. Hyg., 1928, **19**, 79—84; Chem. Zentr., 1928, ii, 2261).

Metabolism in pernicious anæmia. H. L. ALT (Arch. Int. Med., 1929, **43**, 488—503).—Patients with pernicious anæmia showed negative nitrogen balance. Positive nitrogen balances occurred shortly after treatment with liver extract was begun. The output of nitrogen decreased definitely about the time of the rise in the number of reticulocytes.
B. A. EAGLES.

Analysis of the liquid from a splenic cyst. S. GRILLON (J. Pharm. Chim., 1929, [viii], **9**, 23—25).—See this vol., 342.

Diabetes insipidus. III. The diuretic substance. H. BOURQUIN (Amer. J. Physiol., 1929, **88**, 519—528).—Experimental diabetes insipidus in dogs gives rise to a greatly increased amount of diuretic substance in the urine. This substance has also been demonstrated in extracts of the mammillary bodies and thalamus of the brains of normal animals.
B. A. EAGLES.

Microchemistry of the nervous system. II. Cerebral water, nitrogen, sulphur, and phosphorus in experimental traumatic encephalitis. R. M. MAY (Bull. Soc. Chim. biol., 1929, **11**, 312—332).—On degeneration after trauma of the cerebral hemisphere, the sulphur, nitrogen, and water contents of the nervous tissue increased, whilst the amount of total phosphorus decreased. The increased sulphur may be due to the increased oxidation in the degenerating cells, the nitrogen may be due to blood, whilst the decrease in phosphorus is probably caused by decomposition of phosphatides. E. Boyland.

Ehrmann's alcohol test for examining the gastric functions. P. Introzzi (Folia Clin. Chim. Micros., 1928, 3, 44—64).—This test possesses distinct practical advantages over others, the alcohol furnishing an adequate stimulus for developing the maximum secretory capacity of the gastric mucous membrane. The test renders possible the study of all the gastric functions, and, to some extent, of the mobility of the stomach itself. It serves also indirectly for the examination of the function of the liver (bile) and pancreas and of the effect of duodenal reflux in the stomach. Chemical, histological, and, since the alcohol administered is readily sterilised, bacteriological investigations are also possible with its help. T. H. Pope.

"Haff disease." G. Lockemann (Biochem. Z., 1929, **207**, 194—216).—A previously unknown disease ("Haffkrankheit") which broke out in the Frische Haff region in 1924 was believed to have been caused by the presence of a volatile arsenic compound in the atmosphere. The belief is erroneous. The disease was probably caused by products of putrefaction derived from sewage and consumed by eels which were used as food. W. McCartney.

Lactic acid of the blood in hepatic disease. H. Schumacher (Klin. Woch., 1928, 7, 1733—1737; Chem. Zentr., 1928, ii, 2161).—In severe hepatic disease the blood-lactic acid value is high, and falls only slowly after intravenous administration of sodium lactate. A. A. Eldridge.

Hypertension and blood-sugar. E. Wiechmann (Deut. Arch. klin. Med., 1928, **61**, 92—109; Chem. Zentr., 1928, ii, 2161).

Variations of blood-sugar in disease. Effect of potassium iodide and thyroid preparations on the blood-sugar curve. O. Holsti (Acta Med. Scand., 1927, **66**, 443—446; Chem. Zentr., 1928, ii, 2161).—In most acute diseases the blood-sugar level is higher than the normal; after administration of dextrose (10 g.) the curve falls more slowly than normally. In chronic diseases the relation is not simple. Potassium iodide has no influence on the blood-sugar level. Thyroid gland preparations raise the blood-sugar. A. A. Eldridge.

Changes in the mineral constituents of the blood in experimental nephritis. Serum-potassium and -calcium. A. Bolliger and F. Breh (Zentr. inn. Med., 1928, 49, 825—831; Chem. Zentr., 1928, ii, 2161).—In interstitial nephritis caused by irradiation of the kidneys with *X*-rays, the blood-potassium and inorganic phosphate are increased, the alkali reserve is frequently markedly diminished, whilst the blood-calcium may be increased or decreased. A. A. Eldridge.

Distribution of the globulin and albumin fractions in the blood and urine [of children] in nephrosis. F. W. Schultz and M. R. Ziegler (Amer. J. Dis. Children, 1928, **36**, 756—763).—The total plasma-protein is decreased, and the cholesterol increased; the albumin : globulin ratio is lowered or inverted. During nephrosis the non-protein-nitrogen of the blood varies from 19·6 to 43·2 mg. per 100 c.c. The urine may contain fat and globulin as well as albumin, the concentration of the globulin eventually exceeding that of the albumin. Chemical Abstracts.

Chloride, sugar, and calcium content of the cerebrospinal fluid in children. A. V. Neale and M. S. Esslemont (Arch. Dis. Childhood, 1928, **3**, 243—256).—A study of pathological conditions of the nervous system and of the meninges.
Chemical Abstracts.

Porphyrin. A. A. H. van den Bergh and A. J. Hyman (Deut. med. Woch., 1928, **54**, 1492—1494; Chem. Zentr., 1928, ii, 2046).—In congenital porphyrinuria large quantities of porphyrin were detected in the urine and fæces, from which methyl esters differing in the absorption spectra from those of uro- and copro-porphyrin (Fischer) were isolated. Four carboxyl groups were present. Lead poisoning leads to the presence of porphyrin in the urine; porphyrin was never found in the serum but was present in considerable amount in the red blood-corpuscles.
A. A. Eldridge.

Metabolic changes in rickets. I. Phosphate metabolism in the musculature in experimental rickets in rats. H. Hentschel and E. Zoeller (Z. Kinderheilk., 1927, **44**, 146—162; Chem. Zentr., 1928, ii, 2037).—In rachitic rats the synthetic phase of the lactacidogen metabolism in the musculature suffered injury, whilst the splitting-power for lactacidogen was conserved. Values for the total phosphoric acid content of the musculature varied around 0·812 g.-%. The inorganic phosphoric acid is chiefly reduced, and the organic fraction after 14 days. The former increased on irradiation. A. A. Eldridge.

Metabolic changes in rickets. II. Carbohydrate metabolism. E. Ayrer and H. Hentschel (Z. Kinderheilk., 1928, 45, 289—295; Chem. Zentr., 1928, ii, 2037).—Large variations in the glycogen content of both normal and rachitic rats were observed. A. A. Eldridge.

Behaviour of lactic acid in the blood. I. Typhoid and tuberculous infections. G. Margreth (Folia Clin. Chim. Micros., 1928, 3, 5—43).—A review is given. In patients suffering from slowly-progressing phthisis and in good nutritional condition, the lactic acid content of the blood does not differ from the normal, even when there is a temperature rise. Where there is cachexia, values slightly higher than the normal are observed. High proportions of lactic acid were, however, found with two patients in which tubercular infection was developing rapidly. Slightly raised values, comparable with those accompanying pulmonary lesions, exist in cases of marked malnutrition. T. H. Pope.

Influence of high altitude on the catalase content of blood. A. I. Alexeeff (Biochem. Z., 1929, 207, 28—38).—The catalase content of, and amount of erythrocytes in, blood from tubercular patients resident in the plains at Tashkent decrease after two months' sojourn in the hills (at 1500 m.). The fall in the catalase content occurs rapidly and almost entirely in the first week after return from the hills, but the decrease in the amount of erythrocytes proceeds regularly during four months. In the blood of healthy persons the same changes take place except that a pronounced decrease both in catalase content and amount of erythrocytes occurs in the first two weeks after return. The curve of the colour index of the blood runs almost parallel with that showing the changes in the amount of erythrocytes.

W. McCartney.

Influence of cations on the fermenting power of tumour cells. I. A. Lasnitzki and O. Rosenthal (Biochem. Z., 1929, **207**, 120—140).—The fermenting power of tissue from tumours decreases when the Ringer solution used as a medium in which fermentation takes place contains neither potassium nor calcium ions. The extent of the decrease, in the case of tumours from rats, is from 25 to 40%.

W. McCartney.

Non-consumption of vitamin-*B* by growing chicken sarcoma. W. Nakahara and E. Somekawa (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, **10**, 211—220).—The vitamin-*B* content of the liver of chickens fed on a diet lacking in vitamin-*B* is not reduced as the result of the inoculation of the bird with a rapidly growing Rous sarcoma no. 1. It therefore appears that the tumour may not require vitamin-*B* for its growth. W. O. Kermack.

Vital staining of normal and malignant cells. II. Staining of malignant tumours with trypan-blue. R. J. Ludford (Proc. Roy. Soc., 1929, **B**, **104**, 493—511).—It is possible that most malignant cells fail to stain like their normal prototypes because their greater acidity prevents the flocculation of acid dyes.

B. A. Eagles.

Calcium and phosphorus metabolism. V. Bone trabeculæ as a readily available reserve supply of calcium. W. Bauer, J. C. Aub, and F. Albright (J. Exp. Med., 1929, **49**, 145—161).—Easily mobilisable calcium is not deposited in the shafts of adult animals, but in the trabeculæ of bone. The shafts show a slow progressive exchange of inorganic salts. Chemical Abstracts.

Ionic mobility as a factor in influencing the distribution of potassium in living matter. A. B. Macallum (Proc. Roy. Soc., 1929, **B**, **104**, 440—458).—From solutions containing equimolecular quantities of potassium and sodium chlorides or potassium and lithium chlorides considerable quantities of potassium and very little of sodium or lithium are adsorbed by a naturally occurring quartz sand, the exact quantity of potassium adsorbed depending on the rate of percolation of the solution through the sand and on the quantity of sand used. With a solution containing 0·7614% of sodium chloride and 0·0381% of potassium chloride, the quantity of potassium adsorbed was about double that of the sodium adsorbed. It is suggested that the preferential adsorption of potassium depends on the higher ionic mobility of this ion which results in its reaching first and so occupying the interfacial surfaces. The bearing of these results on the rôle of potassium in living cells is discussed. W. O. Kermack.

Ion content of mother and embyro. S. Hayashi (Biochem. Z., 1929, **207**, 432—436).—The potassium, calcium, magnesium, and phosphorus contents of the liver, heart, and bones of female rats on a sufficient diet are carefully preserved during the period of growth of the embryo, the ratio of K/Ca for liver increasing slightly (at the most by 10%) and for heart decreasing slightly owing to increase in calcium. The bones preserve the calcium and magnesium contents absolutely. The ratio Ca/Mg for pregnant is somewhat less than for normal animals. The potassium and magnesium contents of the embryo scarcely change after the twelfth day, the values being rather higher in the earlier stages. The calcium and phosphorus contents increase with the formation of bone and attain the highest values just before birth.

P. W. Clutterbuck.

Metabolism following anoxæmia. I. Oxygen consumption and blood-lactates after exercise. E. G. Martin, J. Field, and V. E. Hall (Amer. J. Physiol., 1929, **88**, 407—419).—In dogs under certain conditions of exercise, the excess oxygen consumption following exercise is not determined by the amount of lactate disappearing from the body.

B. A. Eagles.

Lactic acid metabolism in athletics. I. Snapper and A. Grünbaum (Deut. med. Woch., 1928, **54**, 1494—1495; Chem. Zentr., 1928, ii, 2263).—Football does not usually lead to marked increase of blood-lactic acid; on warm days the urinary excretion of lactic acid does not exceed 60 mg., but on cold days it may reach 290 mg. Excretion of lactic acid through the skin may amount to 1·1—2·5 g.

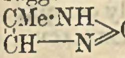
A. A. Eldridge.

Muscle contraction. II. Distribution of phosphorus in frog muscle during delayed relaxation. H. H. Dixon, H. A. Davenport, and S. W. Ranson (J. Biol. Chem., 1929, **82**, 61—70).—The gastrocnemii of frogs which had received intraperitoneal injections of hypertonic solutions of various substances showed an increase of 500% in the relaxation time over that of muscles from normal animals and a distribution of phosphorus similar to that found in fatigued muscles. The effect is ascribed to dehydration. C. R. Harington.

Purine metabolism of muscle, and the parent substance of muscle-ammonia. J. K. Parnas (Klin. Woch., 1928, **7**, 1423—1424; Chem. Zentr., 1928, ii, 2038).—The chief purine base of (frog's) muscle is adenine, present probably as the nucleotide. Processes which lead to elimination of ammonia convert the adenine into hypoxanthine. Hypoxanthine and inosic acid are related to adenine and adenine nucleotide as is lactic acid to glycogen. Conversion of adenine nucleotide into inosic acid is the source of traumatic ammonia formation in muscle.

A. A. Eldridge.

Possible origin of uric acid. L. Bernard (Compt. rend. Soc. Biol., 1928, **99**, 314—315; Chem. Zentr., 1928, ii, 2166).—The following scheme is

suggested: (i) $COMe\cdot CHO+2NH_3+H\cdot CHO \longrightarrow$

$\begin{array}{l}CMe\cdot NH \\ CH—N\end{array}\!\!>\!CH+3H_2O$; (ii) $CO(NH_2)_2+C_4H_6N_2+5O \longrightarrow C_5H_4O_3N_3+3H_2O$. A. A. ELDRIDGE.

Nucleoprotamine and its components in animal metabolism. H. HENSCHEL (Z. Biol., 1929, 88, 594—603).—The effect of the ingestion by dogs of clupeine sulphate, nucleic acid, and clupeine nucleinate (in the form of dried fish sperm) has been determined on the nitrogen, uric acid, and phosphoric acid output in the urine and the nitrogen and phosphoric acid output in the fæces.
W. O. KERMACK.

Amino-acid catabolism. III. Fate of ω-hydroxy-derivatives of propionic, butyric, valeric, and hexoic acids in the phloridzinised dog. R. C. CORLEY and C. S. MARVEL (J. Biol. Chem., 1929, 82, 77—82).—Extra dextrose is excreted by the phloridzinised dog following administration of γ-hydroxybutyric acid, but not of hydracrylic, δ-hydroxyvaleric, or ε-hydroxyhexoic acids; since ornithine, but not lysine, gives rise to extra dextrose formation in the phloridzinised animal, further evidence is thus afforded for the view (A., 1926, 1171) that catabolism of the diamino-acids proceeds through the stages of the ω-amino- and ω-hydroxy-acids with one carbon atom less. C. R. HARINGTON.

Derivative of dextrose concerned in the oxidation–reduction equilibrium of cells. R. WURMSER and J. GELOSO (Compt. rend., 1929, 188, 1186—1188).—Dextrose in alkaline solution under vaseline generates a substance (probably a dienolic form, the time required varying with temperature and p_H value) which is rapidly oxidised either by dehydrogenation in the presence of methylene-blue as an acceptor or by molecular oxygen, and which is regenerated on keeping. Electrometric titration shows that this solution has an oxidation–reduction potential similar to that in the interior of living cells and a mechanism of the regulation of intracellular potential based on the presence of this intermediate substance (derived from glucosides) is suggested. J. W. BAKER.

Carbohydrate metabolism of the normal, phloridzinised and diabetic viviperfused stomach. R. K. S. LIM, T. G. NI, H. NECHELES, and H. C. CHANG (Chinese J. Physiol., 1929, 3, 123—155).—In a non-secreting dog's stomach subjected to viviperfusion according to the authors' method (cf. Ni and Lim, A., 1928, 442) the uptake of dextrose is reduced when phloridzin is administered or insulin is deficient. Under these conditions stimulation of secretion by histamine results in no increase but sometimes in a decrease in the uptake of dextrose, whereas an increase frequently occurs in the case of a non-phloridzinised stomach supplied with insulin. Neither the presence of phloridzin nor the deficiency of insulin affects the uptake of oxygen, and this is increased when secretion is stimulated. It is concluded that some substance other than carbohydrate is probably oxidised during secretion.
W. O. KERMACK.

Changes of metabolism during irradiation. IV. L. PINOUSSEN. **Fat content of organs.** E. ZUCKERSTEIN (Biochem. Z., 1929, 207, 426—431).—During irradiation the fat content of the serum of guinea-pigs increases considerably but the cholesterol content is scarcely affected; the fat content of the heart decreases considerably with and without the presence of eosin as sensitiser, whereas the cholesterol content without sensitiser decreases slightly but with sensitiser increases considerably; the fat content of the liver decreases considerably without and to an even greater extent with sensitiser, whilst the cholesterol content is slightly increased; in the kidney a small decrease of fat and increase of cholesterol is obtained, whilst in muscle the fat content is decreased and the cholesterol content is unchanged.
P. W. CLUTTERBUCK.

Cholesterol. IV. Relation of ovaries and testes to cholesterol metabolism. F. S. RANDLES and A. KNUDSON (J. Biol. Chem., 1929, 82, 57—59).—Removal of the ovaries or testes from rats has no effect on the cholesterol content of the blood.
C. R. HARINGTON.

Rôle of phospholipins of intestinal mucosa in fat absorption. Phospholipins of liver and muscle. R. G. SINCLAIR (J. Biol. Chem., 1929, 82, 117—136).—The composition, but not the total amount, of the phospholipins of the intestinal mucosa is influenced by changes in the nature of the fat of the diet; such changes are without effect on the composition or total amount of the phospholipins of plain or striated muscle. It is thought that the phospholipins of the intestinal mucosa represent an intermediate stage in the re-synthesis of neutral fat from the absorbed fatty acids. C. R. HARINGTON.

Effect of gestation and lactation on the growth and composition of swine. D. J. GRISWOLD, P. F. TROWBRIDGE, A. G. HOGAN, and L. D. HAIGH (Missouri Agric. Exp. Sta. Res. Bull., 1928, No. 114, 6 pp.).—The ash of pre-natal and new-born pigs contains more sodium, chlorine, and sulphur, and less magnesium, potassium, and silicon than that of older animals. The percentage of iron is low and constant. The ash at all ages contains about 75% $CaH_4(PO_4)_2$. Results of experiments on digestion are recorded.
CHEMICAL ABSTRACTS.

Action of chalybeate waters on metabolism. M. KOCHMANN and H. SEEL (Deut. med. Woch., 1928, 54, 1321—1322; Chem. Zentr., 1928, ii, 2263).—Ferrous hydrogen carbonate in a natural water had a favourable action on the metabolism of young growing rats, possibly owing to an increase of plasma-iron.
A. A. ELDRIDGE.

Relationship between chemical constitution and physiological action. E. MAMELI (Boll. Chim. farm., 1929, 58, 299—308, 351—356, 399—402).

Aluminium toxicity. F. T. MCLEAN and B. E. GILBERT (Plant Physiol., 1928, 3, 293—302).—Low concentrations (3—13 in 10^6) of aluminium are stimulating, and higher concentrations toxic, to plants. Aluminium in combination with organic acids (citric, tartaric) is toxic at low acidities (p_H 6·5). Non-dialysable aluminium is toxic when placed in contact with the roots of barley. At equivalent concentration, phosphate prevents toxic action by aluminium compounds. CHEMICAL ABSTRACTS.

Relation of arsenicals to the glutathione content of animal tissues. H. Brown and J. A. Kolmer (J. Pharm. Exp. Ther., 1929, **35**, 417—424).—The reduced glutathione content of the blood and various organs of rats, rabbits, guinea-pigs, and dogs has been determined. No relation appears to exist between the susceptibility of the animal species to salvarsan poisoning and the content of its organs in reduced glutathione. The administration of numerous therapeutic doses of salvarsan or neosalvarsan to rabbits is without significant effect on the reduced glutathione content of its organs but a single very large dose brings about a decrease.

W. O. Kermack.

Pharmacological significance of reactions between arsenious acid and thiol compounds. R. Labes (Arch. exp. Path. Pharm., 1929, **141**, 148—160).—The toxic effect of injected arsenious acid on mice is greatly delayed if cysteine is administered at the same time. Mixture of solutions of these two compounds results in the rapid precipitation of a compound containing 1 mol. of arsenious acid and 3 mols. of cysteine, the solubility of which is less than 8×10^{-12}. It is suggested that the delayed toxic effect is due to the catabolism of the cysteine portion of the compound in the animal body. The influence of cysteine on the tone of smooth muscle preparations is compared with that of adrenaline; both reduce the muscle tone of frog-stomach preparations, but with the former there is frequently a marked increase in the excitability of the preparation. With the rabbit's uterus there is a differentiation in action; cysteine again reduces muscle tone, adrenaline increases it.

F. C. Happold.

Action of rubidium on the serum. A. H. Roffo and H. de Giorgi (Bol. Inst. Med. exp., 1926, No. 14, 14 pp.; Chem. Zentr., 1928, ii, 2259).—Intravenous administration of rubidium chloride or sulphate to guinea-pigs or man causes a slight diminution of the p_H and surface tension of the blood. Apparently the colloid equilibrium in the serum is altered. A. A. Eldridge.

Absorption and excretion of magnesium. W. F. Taylor and J. E. Winter (J. Pharm. Exp. Ther., 1929, **35**, 435—439).—In rabbits, light and deep narcosis occur when the blood-magnesium level exceeds 7—11 and 18—21 mg. per 100 c.c., respectively. In the dog even light narcosis is not produced when the blood-magnesium level is 10·44 mg. per 100 c.c. In dog and man approximately 7·5—11% Mg ingested as magnesium chloride is excreted in the urine. The temperature of dogs with fever is reduced approximately 1° for each rise of 2 mg. in the blood-magnesium content. W. O. Kermack.

Distribution of mercury in the organism and its elimination after injection of "salyrgan." J. Müller (Arch. exp. Path. Pharm., 1929, **141**, 1—18).—After intravenous injection of "salyrgan" into dogs the highest concentrations of mercury are found in the bile and the wall of the gall bladder followed by the adrenals and then the kidneys and large intestine. Most of the other organs contain small quantities of mercury. Both in man and in animals after salyrgan injection elimination of the mercury takes place chiefly in the urine and only to a small extent in the fæces and is practically complete within 24 hrs. W. O. Kermack.

Pharmacology and toxicology of some new organo-mercury compounds. S. J. Cohen (J. Pharm. exp. Ther., 1929, **35**, 343—350).—The sodium or potassium salts of methyl-, ethyl-, and butylmercurithioglycollic acids, which are strongly bactericidal towards the tubercle bacillus, are also highly toxic to animals, causing paralysis of the hind-limbs. W. O. Kermack.

[Biological] action of certain metals. K. Waltner (Arch. exp. Path. Pharm., 1929, **141**, 123—128).—The effect has been determined of the administration to animals in their food of considerable quantities of metallic magnesium, nickel, cobalt, copper, zinc, molybdenum, cadmium, tin, tungsten, and bismuth, particularly on growth, bone formation, fertility, and serum-phosphorus.

W. O. Kermack.

Colloidal metals and glycolysis. A. Franciaviglia (Arch. Farm. sperim., 1929, **46**, 201—206).—Incubation of blood containing colloidal silver causes a marked increase in the proportion of combined sugar, the silver either accelerating the action of the enzyme which determines glucoprotein synthesis or retarding that of the enzyme effecting true glycolysis. A similar mechanism is suggested for the action of colloidal metals *in vivo*. T. H. Pope.

Pharmacology of stabilised colloidal lead sulphide. A. Chistoni and E. Milanesi (Arch. Farm. sperim., 1929, **46**, 147—173).—Colloidal lead sulphide, when prepared as a suspensoid in presence of a denatured protein, which acts as a protecting colloid, is far more stable than any colloidal lead preparation previously described. This colloid is rapidly absorbed even by subcutaneous tissue and, in consequence of its ready oxidisability, easily undergoes further transformations; it is eliminated by the intestine and kidney like other lead salts. The minimum fatal dose is 0·016 g. per kg. body-weight (rabbit). The changes produced in the different organs by the colloid are described. T. H. Pope.

Chemistry and therapeutic action of dextrose. F. Fischer (Münch. med. Woch., 1928, **75**, 1541—1544; Chem. Zentr., 1928, ii, 2260).—A discussion.

A. A. Eldridge.

Action of decamethylenediguanidine (synthalin) on the blood-sugar of normal and depancreatised dogs. F. Rathery, R. Kourilsky, and S. Gibert (Compt. rend. Soc. Biol., 1928, **99**, 282—284, 284—287; Chem. Zentr., 1928, ii, 2034).—Small doses of synthalin cause glycosuria in the depancreatised dog. Its action on the normal dog is variable. A. A. Eldridge.

Nephropathogenic action of cystine. G. J. Cox, C. V. Smythe, and C. F. Fishback (J. Biol. Chem., 1929, **82**, 95—103).—Young rats develop an acute nephrosis when kept on synthetic diets containing 0·3% or more of free cystine; restoration to normal diet usually results in recovery, and some spontaneous recoveries occur even when the cystine diet is continued. C. R. Harington.

Cellular toxicity of gaseous and volatile poisons. S. Lallemand (J. Pharm. Chim., 1929, [viii], 9, 380—390).—Hen's eggs were placed in an atmosphere of the gas for varying periods of time, then exposed to room air for 24 hrs. and incubated for 48 hrs., and the development of the embryo was noted. Hydrogen, nitrogen, oxygen, and carbon dioxide are non-toxic. Embryonic development is slightly retarded by nitrous oxide. Hydrogen chloride, sulphur dioxide, and chlorine are more toxic. Exposure to ammonia or hydrogen sulphide for 3 min. prevents development of the embryo. B. A. Eagles.

Use and elimination of water-soluble camphor derivatives. M. Pichon (J. Pharm. Chim., 1929, [viii], 9, 369—371).—The taking of sodium camphor-sulphonate does not lead to an increased excretion of conjugated glycuronates, as is the case after the ingestion of camphor. B. A. Eagles.

Promoting action of saponin on resorption and the action of cholesterol. L. Kofler and R. Fischer (Arch. exp. Path. Pharm., 1929, **141**, 105—115).—Various types of saponin very strongly increase the rate of absorption of curare from the intestine of the frog, the quantities required being less than one hundredth of the toxic dose. When the saponin is combined with cholesterol, this action, like most of its other biological activities, is largely or entirely inhibited, but the mere presence of cholesterol as distinct from combination is not sufficient to cause this inhibition. W. O. Kermack.

Determination of the potency of digitalis : (A) Pigeon-emesis. P. J. Hanzlik. **(B) Results with the pigeon-emesis method of estimating the probable therapeutic dose of digitalis.** P. J. Hanzlik and A. B. Stockton (J. Pharm. Exp. Ther., 1929, 35, 363—391, 393—407).—(A) Digitalis preparations may be conveniently assayed by determining the minimum dose necessary to produce vomiting in pigeons. (B) From observations on human subjects it is found that the therapeutic dose for man can be satisfactorily determined from assay by the pigeon-emesis method. W. O. Kermack.

Pharmacological action of some tertiary amines related to ephedrine. F. R. Curtis (J. Pharm. Exp. Ther., 1929, 35, 321—332).—Tertiary amines of the type $CHPh(OH)\cdot CHMe\cdot NMeR$, in which R=Me, Et, $(CH_2)_2OH$, Pr^α, Pr^β, or Bu, as well as the amine $CHPh(OH)\cdot CHMe\cdot NEt_2$, possess little power to raise the blood-pressure of a pithed cat, but on the isolated uterus they produce contraction and act more strongly than ephedrine itself (R=H). The compounds containing R=Me and Et and also the diethyl compound dilate the bronchi of a cat as efficiently as does ephedrine, and this property associated with their small action on the blood-pressure may render them capable of clinical application. W. O. Kermack.

Phytopharmacological examination of adrenaline and ephedrine. D. I. Macht (J. Amer. Pharm. Assoc., 1929, 18, 335—337).—Adrenaline is much more toxic to living seedlings of *Lupinus albus* than is ephedrine. This method enables the activity of different samples of adrenaline to be evaluated and distinguishes them from ephedrine. E. H. Sharples.

Antipyretic action and toxicity of combinations of magnesium with phenylcinchonic acid. H. G. Barbour and J. E. Winter (J. Pharm. Exp. Ther., 1929, 35, 425—434).—The antipyretic action of phenylcinchonic acid on dogs or rabbits with fever is increased by the simultaneous administration of salts of magnesium. W. O. Kermack.

Antitoxic properties of calcium in respect of sparteine sulphate. P. L. Violle and A. Giberton (Compt. rend., 1929, **188**, 1181—1182; cf. this vol., 348).—Subcutaneous or intracardiac injections of an isotonic solution of calcium chloride (4 g. calcium/litre) into a guinea-pig have an antitoxic effect on a simultaneous injection of a lethal dose (0·01 g./100 g. body-weight) of sparteine sulphate, the animal usually surviving indefinitely. A similar effect (survival for 4 days) is produced by frequent injections of calcium prior to the injection of sparteine sulphate. Similar experiments using diphtheria toxin, however, give negative results, showing that the antitoxic effect is specific to certain poisons. J. W. Baker.

[Respiratory enzymes.] O. Warburg (Biochem. Z., 1929, **207**, 494—495).—A criticism of Keilin's paper (this vol., 470). P. W. Clutterbuck.

Malt amylase. V. Determination of the power of amylase to convert starch into dextrins and sugars and a comparison of the two reactions. T. Sabalitschka and R. Weidlich (Biochem. Z., 1929, **207**, 476—493).—A method is described for the determination colorimetrically of the velocity of dextrin formation and breakdown during the hydrolysis of starch by amylase. The dextrination constant so obtained permits the comparison of the dextrin-forming and hydrolysing actions of different amylases. The ratio of the dextrination constant to the saccharification constant (obtained simultaneously by iodometric determination of the maltose formed) in seven experiments with different amounts of amylase gave a quotient of 1·12±0·14. P. W. Clutterbuck.

Takadiastase. Inactivation and reactivation ; importance of these processes in the therapeutic use of the enzyme. E. Ohlsson and T. Swaetichin (Bull. Soc. Chim. biol., 1929, **11**, 333—386).—Takadiastase loses its power to hydrolyse starch in acid or alkaline solution (below p_H 2·0 or above p_H 11·5), but on neutralisation the activity slowly returns. The enzyme has maximum stability between p_H 5 and 9. Reactivation in neutral solution (p_H 6—7) is generally almost complete in an hour, but both inactivation and reactivation are delayed by the presence of starch and accelerated by phosphate. Takadiastase acts between p_H 2·5 and 8·0 with an optimum zone between p_H 4·5 and 6·5. Inactivation experiments indicate that takadiastase is a simple dextrinase. Although takadiastase is inactivated in the acid of the stomach it is slightly more effective than malt diastase, and under normal conditions the enzyme will become reactivated in the intestine. It is suggested that the reversible activation is due to a change in dispersion of the enzyme. E. Boyland.

Enzymes and light. XIV. L. Pincussen. **Effect of temperature on the action of light.** T. Oya (Biochem. Z., 1927, 207, 410—415).—Comparison of the theoretical amounts with the amounts of maltose actually formed by the action of taka-diastase on starch at varying temperature and p_H and after the enzyme had been irradiated or heated shows that the mechanism of the injury brought about by light and by heat is different. Diastase solutions after injury by irradiation can be reactivated by addition of a small amount of unirradiated solution, but reactivation does not occur when the enzyme is injured by heat. P. W. Clutterbuck.

Specificity and mechanism of action of the sugar-hydrolysing enzymes. R. Weidenhagen (Z. Ver. deut. Zucker-Ind., 1929, 79, 115—154).—From a detailed review of recent work it is concluded that there is no evidence for the existence of specific disaccharases. The hydrolyses described can be referred to the action of glucosidases (cf. Oppenheimer, A., 1923, i, 495). These exhibit structural specificity, *e.g.*, glucosidases, galactosidases, stereo-specificity as regards the glucoside carbon atom, *e.g.*, α- and β-glucosidases, and ring-specificity depending on the oxygen linking in the hexose molecule, *e.g.*, *n*- and *h*-fructosidases. Conclusions as to specificity based on the inhibiting effect of added hexoses are unsound, since the effects of impurities are obscure.

F. E. Day.

Action of invertase : free water, viscosity, and rate of reaction. H. Colin and A. Chaudun (Bull. Soc. Chim. biol., 1929, 11, 258—267).—With low concentrations of sucrose the rate of hydrolysis varies logarithmically with the concentration of sugar, but high concentrations reduce the rate of hydrolysis. Additions of gelatin or of agar, which increase the viscosity, produce proportional decreases in the rate of hydrolysis, although a mixture of agar and gelatin seemed to have less effect on the hydrolysis than either agar or gelatin alone. Solutions of sucrose and of mixtures of sucrose and lactose having equal viscosities are hydrolysed at the same rate, but the addition of glycerol affected the hydrolysis more than the viscosity. The rate of hydrolysis of concentrated sucrose solutions cannot be completely explained either by viscosity or by retention of water.

E. Boyland.

Fermentation of lactic acid by the tissues of warm-blooded animals. I. Conditions for obtaining "extra" fermentation with liver tissue. O. Rosenthal (Biochem. Z., 1929, 207, 263—297; cf. A., 1928, 916).—The amount of fermentation with glandular tissue depends on whether the tissue is asphyxiated immediately after removal from the organ or some time subsequently, the fermentation being 50—150% higher after aërobiosis for 1 hr. at 37·5°. This extra fermentation with liver tissue is due to fermentation of lactic acid, some carbohydrate specific to the cell being the substrate. Extra fermentation never occurs with tissues of starving rats nor with fœtal livers. Nourishment of the animal is one condition for obtaining extra fermentation. The maximal effect is obtained with an aërobic period of 15 min., and body temperature is also necessary. Extra fermentation is not obtained when, during the aërobic period, potassium- and calcium-free Ringer's solution is used as medium. Replacement of Ringer's solution by fresh serum does not affect the intensity of fermentation.

P. W. Clutterbuck.

Isolation of methylglyoxal in lactic acid fermentation. C. Neuberg and M. Kobel (Biochem. Z., 1929, 207, 232—262).—From the dried sterile material extracted by alcohol–ether from cultures of *B. Delbrücki* water (or 1% sodium chloride solution) extracts an enzyme, "glycolase," which produces methylglyoxal from magnesium hexosediphosphate. The yields of this substance are the higher the greater is the concentration of the substrate and in some cases are equivalent to 100% of the hexose decomposed. Very little co-enzyme is present in the aqueous extracts. The residue from them only gives methylglyoxal with high concentrations of hexosediphosphate, and with low concentrations converts it quantitatively into lactic acid. The methylglyoxal is isolated as the bisdinitrophenylhydrazone and also as the dioxime. Glycolase is found also in animal tissues and in higher plants and may be expected to occur wherever glyoxalase is found. W. McCartney.

Dehydrogenation of malic acid. II. A. Hahn, W. Haarmann, and E. Fischbach (Z. Biol., 1929, 88, 587—593).—A mixture of frog-muscle pulp, methylene-blue, and malic acid containing semicarbazide was incubated at 38° and the deproteinised filtrate evaporated to dryness. The residue was treated with 50% sulphuric acid at 50° to decompose the oxalacetic acid semicarbazide, and the pyruvic acid formed was finally isolated as the phenylhydrazone. The quantity of phenylhydrazone obtained was greater than when no malic acid was present, the pyruvic acid in the latter case being formed from lactic acid as the result of the treatment. The above result confirms the view that oxalacetic acid is the first product formed from malic acid during dehydrogenation by muscle pulp in presence of methylene-blue (cf. A., 1928, 1281).

W. O. Kermack.

Barley-malt catalase. II and III. M. O. Charmandarjan (Biochem. Z., 1929, 207, 462—471, 472—475).—II. The amount of hydrogen peroxide decomposed by malt extract varies with the volume of fluid and the concentration of peroxide. Addition of toluene increases slightly the amount of decomposition. Prolonged exposure to water decreases the decomposing power.

III. Malt on keeping loses its power to decompose peroxide, more quickly in ground than in whole grain, more quickly in air than in carbon dioxide, and very quickly over sulphuric acid in a desiccator.

P. W. Clutterbuck.

Peroxidase nature of "active" iron. H. Ucko (Klin. Woch., 1928, 7, 1515—1517; Chem. Zentr., 1928, ii, 2155).—The effect of vegetable and animal peroxidases and iron compounds on peroxide systems (hydrogen peroxide and benzidine, pyrogallol, and potassium iodide) has been studied. Aqueous and alcoholic benzidine solutions give with most iron compounds, and with compounds of other heavy metals, a bluish-green product; there is a group of complex iron compounds which, in acid solution, like true peroxidases and oxyhæmoglobin, give a positive reaction. The catalytic oxidation of pyrogallol to purpurogallin by hydrogen peroxide is effected by peroxidase, oxyhæmoglobin, complex iron salts, and copper ions; ferric and ferrous ions give a violet compound which rapidly becomes brown. The reaction between potassium iodide and hydrogen peroxide is not catalysed by the "active" iron compounds or by other complex iron salts, whilst ferric and ferrous ions have a certain stoicheiometric effect. Thus for testing peroxidase activity the effect on potassium iodide and hydrogen peroxide, as well as on the benzidine reaction, must be examined.

A. A. ELDRIDGE.

Activation of pancreatic lipases in serum by leucylglycylglycine. Modification of Rona's test. A ROSENO (Klin. Woch., 1928, 7, 1693—1694; Chem. Zentr., 1928, ii, 2155).—The presence of active lipase in the serum after treatment with atoxyl is a proof of the transition of pancreas lipase into the blood, since atoxyl is toxic to the serum lipases. Pancreatic lipases are strongly activated by leucylglycylglycine.

A. A. ELDRIDGE.

Molecular constitution and accessibility to enzymes. Effect of various substances on the velocity of hydrolyses by pancreatic lipase. D. R. P. MURRAY (Biochem. J., 1929, 23, 292—308).—Ketones and aldehydes produce an inhibition of the velocity of hydrolysis out of proportion to that produced by the chemically related compounds investigated. This power is lost by the ketone when converted into its oximes. Secondary alcohols also produce an inhibition which may be due to reversal of hydrolysis. The former inhibition is due to the specific affinity between the carbonyl group and the active centre of the enzyme and to the consequent influence on the normal adsorption of esters preparatory to their hydrolysis by the enzyme.

S. S. ZILVA.

Disaggregating action of pepsin. M. FRANKEL (Biochem. Z., 1929, 207, 53—65).—The optical rotatory powers of gelatin solutions containing pepsin and the amounts of amino-nitrogen present in them remain practically unchanged at temperatures from 10° to 37° during the period of induction before hydrolytic action sets in. It follows that the pepsin has no disaggregating effect during this interval.

W. MCCARTNEY.

Relationship between chemical properties of a series of pepsin preparations and their activity towards different proteins. J. A. SMORODINCEV and A. N. ADOVA (Z. physiol. Chem., 1929, 182, 1—7).—A series of pepsin preparations, the activities of which were determined by the method outlined (A., 1928, 1282), showed relatively corresponding proteoclastic action on caseinogen, edestin, gelatin, egg-white, and myosin.

C. C. N. VASS.

Relation of structure to rate of hydrolysis of peptides. V. Enzymic hydrolysis of dipeptides. P. A. LEVENE, R. E. STEIGER, and L. W. BASS. **VI. Hydrolysis of dipeptides by alkali.** P. A. LEVENE, L. W. BASS, and R. E. STEIGER (J. Biol. Chem., 1929, 82, 155—166, 167—170).—V. The results of earlier experiments (this vol., 301) together with those now recorded show that dipeptides of which one component is the enantiomorph of the naturally occurring amino-acid, and those in which the free amino- or carboxyl group is attached to a tertiary carbon atom, are not attacked by erepsin; those in which one component is a *dl*-amino-acid are hydrolysed to the extent of 50%. As in the case of acid hydrolysis, the intrinsic dissociation constants of the groups involved play a part in determining the velocity of the reaction. *Glycyl-α-amino*iso*butyric acid* was obtained by conversion of α-amino*iso*butyric acid into the *chloroacetyl* derivative, followed by treatment of the latter with ammonia. l-*Phenylglycine*, $[\alpha]_D^{25}$ −111·7° in water, was treated with bromoacetyl bromide, and the product, with ammonia, yielded *glycyl*-l-*phenylglycine*, $[\alpha]_D^{25}$ −173·9° in water. *Glycyl*-dl-*phenylmethylglycine* was prepared similarly.

VI. The rate of hydrolysis of dipeptides by alkali bears no relationship to the intrinsic dissociation constants of the groups involved in the peptide linking, and is possibly determined by the dissociation constants of the enolic forms of the peptides. As in the cases of acid and ereptic hydrolysis, those peptides in which the free acidic or basic group is attached to a tertiary carbon atom show the greatest resistance.

C. R. HARINGTON.

Specificity of animal proteases. XVI. Dipeptidase and polypeptidase from the mucous membrane of the intestine. E. WALDSCHMIDT-LEITZ, A. K. BALLS, and J. WALDSCHMIDT-GRASER (Ber., 1929, 62, [*B*], 956—962; cf. A., 1928, 1401).—The separation of the mixture of peptidases into di- and poly-peptidase, which cannot be effected by aluminium hydroxide C_γ, is relatively easily brought about by ferric hydroxide. The bulk of the polypeptidase remains in the mother-liquor from the adsorption and is obtained free from dipeptidase after three treatments. The dipeptidase is concentrated in the adsorbates, from which it is obtained by elution with alkali phosphate in poor yield. It is less stable than the polypeptidase, particularly in acid solution.

H. WREN.

Arginase. VII. Ureotelic character of the nitrogen metabolism of Chelonia. A. CLEMENTI (Atti R. Accad. Lincei, 1929, [vi], 9, 505—509).—Like that of *Bufo*, the urine of *Testudo græca* and *Emys europæa* contains uric acid in proportions almost too small to be determined. In the summer, the urine of these two animals contains about 0·5 part of urea per 1000, which is approximately the same as in the urine of *Bufo* at the same period. Contrary to what is observed with uricotelic animals (birds), oral administration of ammonia to *Testudo* and *Emys* produces marked increase in the urea content *per diem* and per 1000 of the urine, so that the nitrogen metabolism of the Chelonia is not uricotelic, as with other reptiles and with birds, but ureotelic.

T. H. POPE.

Isoelectric point of crystalline urease. J. B. SUMNER and D. B. HAND (J. Amer. Chem. Soc., 1929, 51, 1255—1260; cf. A., 1928, 329, 1401).—In phosphate, phthalate, and acetate buffers of

p_H 7—5·5, crystalline urease migrates towards the anode, but in more acid solutions no electrophoresis occurs. Urease is precipitated by (*a*) 0·02*M*-phthalate ion, (*b*) 0·008*M*-lead ion in acetate buffer, precipitation beginning at p_H (*a*) 5·3, (*b*) 4·7, and being complete at p_H (*a*) 4·6, (*b*) 5·6. Precipitation causes no separation of urease from protein and, near the isoelectric point, very little loss of activity. Mercuric and cupric ions precipitate urease over a much wider range and almost completely inactivate it. It is soluble in excess of phosphate, acetate, and hydrogen carbonate buffers at all p_H values, but in very dilute solutions the isoelectric point is given by a precipitation maximum at p_H 5·0—5·1. The solubility relations of crystalline urease are those of a typical globulin. It is active on both sides of the isoelectric point. H. E. F. Notton.

Kinetics of the formation of acetaldehyde in alcoholic fermentation with dried yeast. B. Kisch and J. Leibowitz (Biochem. Z., 1929, **207**, 384—394).—Under optimal conditions (concentration of sulphate 2—5%, and of sugar 1—3%) the amount of aldehyde formed is almost a linear function of the time, the linear course of the aldehyde–time curve being unaffected by changes of temperature over the optimal zone, 31—38°. P. W. Clutterbuck.

Alcoholic fermentation. XIX. Fermentative bacteria in maceration juice. S. Kostytschev and O. Schulgina (Z. physiol. Chem., 1929, **182**, 50—56).—Cell-free fermentation is not yet established. Invisible forms of fermentative bacteria play an important part in the processes occurring in maceration juices. Intensive fermentation in the presence of powerful stimulators can be brought about by a very small quantity of living cells contained in a large quantity of dead yeast-cells.

C. C. N. Vass.

Production of starch in moulds (*Penicillium*, Link); its relation to acid production. T. Chrzaszcz and D. Tiukov (Biochem. Z., 1929, **207**, 39—52).—The formation of starch-like substances in moulds is a normal process requiring special conditions for particular species of moulds. These species form two groups: starch producers, which are older evolutionary forms and produce less organic acid than the others; and acid producers. The acid and the starch-like substances play the part of reserve materials. The production of starch-like substances by those moulds which normally accumulate other materials is an atavistic phenomenon. Normally, the starches, in varying amounts, are deposited in layers in the mould, but their nature and localisation are dependent on external conditions and on the species of the mould.

W. McCartney.

Coloration of *Aspergillus niger* grown on fatty media. C. Pontillon (Compt. rend., 1929, **188**, 1184—1185).—By cultivation on media both with and without fatty constituents prepared in different ways it is shown that the yellow pigment sometimes observed in the cultures of *A. niger* (Roussy, *ibid.*, 1909, **149**, 482; 1911, **151**, 884) is due, not to the presence of fats, but to the disturbance of the equilibrium composition of the media by the removal of various salts consequent on filtration after prolonged boiling. J. W. Baker.

Conversion of acetic acid by *Mucor stolonifer* into succinic and fumaric acids and a method of separation and quantitative determination of these acids. W. S. Butkevitsch and M. W. Fedorov (Biochem. Z., 1929, **207**, 302—318).—Fumaric acid does not accumulate when *Mucor stolonifer* is grown on solutions of succinic, malic, lactic, or tartaric acid in presence of calcium carbonate, but is formed in considerable amounts when the organism is grown on solutions of glycerol under the same conditions. Acetic acid in presence of calcium carbonate is converted into succinic and fumaric acids, 15—30% being so converted. In these experiments the succinic acid constitutes 80—90% of the mixed acids, whereas in experiments with sugar it formed only 10% of the mixture.

P. W. Clutterbuck.

Metabolism of *Ustulina vulgaris*, L. H. Wünschendorff and C. Killian (Compt. rend., 1929, **188**, 1124—1126).—Cultures of *U. vulgaris* were maintained at 25° in a medium containing 1% of peptone. After 3 weeks the medium answered faintly or not at all to the biuret reaction. The amount of ammonia evolved is dependent on the surface area of the fungus and not on its dry weight. However, a constant ratio exists between the amount of nitrogen fixed by the fungus and its weight; this ratio is not maintained when the concentration of peptone in the medium is lowered or raised. As the weight of the fungus increases, the acidity of the medium decreases. B. W. Anderson.

Oxidases of wood-destroying moulds. I. W. Bavendamm (Z. Pflanzenkrankh., 1928, **38**, 257—276; Chem. Zentr., 1928, ii, 2154—2155).—For the plate method for the detection of oxidases the use of tannin or gallic acid is preferred.

A. A. Eldridge.

Three new species of sulphur-oxidising bacteria. Y. Emoto (Proc. Imp. Acad. Tokyo, 1929, 5, 148—151). C. C. N. Vass.

Metabolism of *Bacillus tetani*. II. Bases of the culture medium. H. Sievers and E. Müller (Z. Biol., 1929, **88**, 553—560).—From culture media on which tetanus bacilli have been grown, the following compounds have been isolated after removal of the ether-soluble constituents: hypoxanthine, ammonia, histidine, carnitine, γ-butyrobetaine, β-homobetaine, and methylamine. W. O. Kermack.

Tetanus toxin, ricin, and some alkaloids and their detoxication. J. Schubert (Z. Immunitäts., 1928, **57**, 261—284; Chem. Zentr., 1928, ii, 2259).—*In vitro*, tetanus toxin is detoxicated by tyrosine, cholesterol, or ethereal alcoholic extracts of human bone marrow, cod-liver oil, octoic or oleic acid, certain vegetable oils, and solutions of cocaine, morphine, and "heroin." Ricin poisoning is prevented by previous treatment of the poison with cholesterol or "heroin." Aconitine is not detoxicated by alkaloids.

A. A. Eldridge.

Relationship between the physical properties of chemical substances and their action on

micro-organisms. T. Sabalitschka (Arch. Pharm., 1929, 267, 272—290).—The antiseptic and germicidal properties of various phenolic substances are connected with their adsorptive powers.

S. Coffey.

Germicidal and hæmolytic action of α-bromo-soaps. A. H. Eggerth (J. Exp. Med., 1929, 49, 53—62).—The soaps of the α-bromo-fatty acids are (except for *Bacillus typhosus*) usually more germicidal than the unsubstituted soaps and are most active when the reaction is acid. The germicidal and hæmolytic action at first increases rapidly with increasing mol. wt. and then diminishes.

Chemical Abstracts.

Mercuric oxycyanide compounds of organic acids and their sterilising action on *Gonococcus*. H. Takaoka (Bull. Osaka Inst. Ind. Res., 1928, 4, 1—8).—The *compound* $HgC_4H_4O_6,Hg(CN)_2,H_2O$ (from tartaric acid and $HgO,3Hg(CN)_2$ in 90% alcohol) has an immediate sterilising effect on *Gonococcus* at a dilution of 1 in 5×10^4. The corresponding *salicylate* (+2EtOH) and *citrate* were also prepared.

Chemical Abstracts.

Adrenaline content of the suprarenal capsule in the hen embryo. M. Okuda (Endocrinol., 1928, 12, 342—348).—Adrenaline appears at about the eighth day; a close relation with tyrosine and with the chromic reaction in the cells is indicated.

Chemical Abstracts.

Effect of pituitary extract and adrenaline on ketonuria and liver-glycogen. J. H. Burn and H. W. Ling (Quart. J. Pharm., 1929, 2, 1—16).—Injections of pituitary extract into rats fed on butter fat cause an inhibition of the output of acetone substances; with adrenaline a seemingly inhibitory as well as the augmentor effect observed by Anderson and Anderson (A., 1928, 90) is recorded. During the spring there is a steady rise in the glycogen content of the liver as also observed in the winter (*ibid.*, 925) which bears no relationship to the ketonuria. Injections of pituitary extract during the first 5 days of the fat diet reduce the liver-glycogen to a negligible quantity, whilst administration of adrenaline causes the rise in the liver-glycogen to occur more slowly.

C. C. N. Vass.

Oxytocin and vasopressin. Examination of separated principles of pituitary (posterior lobe) extract. J. H. Burn (Quart. J. Pharm. 1928, 1, 509—512).—The antidiuretic activity of oxytocin and vasopressin has been tested on man. Oxytocin is devoid of activity; vasopressin has an activity which is equal, per unit pressor activity, to that of a sample of pituitrin. The power of pituitrin to inhibit the hypoglycæmic effect of insulin is possessed by vasopressin but not by oxytocin.

F. C. Happold.

Oxytocic, pressor, and antidiuretic activities of commercial samples of pituitary extract. U. G. Bijlsma, J. H. Burn, and J. H. Gaddum (Quart. J. Pharm., 1928, 1, 493—508).—Four commercial preparations of pituitary extract have been tested independently by the authors and compared with the international standard for oxytocic and pressor power. A new method of testing the antidiuretic power on the human is described; this factor has been measured in the unanæsthetised dog. The antidiuretic activity is due neither to the pressor nor to the oxytocic principle, consequently the test for any one of these three active principles does not provide an index of the concentration of either of the others in a commercial extract.

F. C. Happold.

Use of rabbits in insulin assay. K. Culhane (Quart. J. Pharm., 1928, 1, 517—533).—Marks' "cross test" used on ten or more selected rabbits in an insulin assay gives an error of less than 5%. The variability of response to insulin is affected by weight and season, heavier animals give a higher percentage reduction than light ones and all are more sensitive in summer. Rabbits used in cross tests have been grouped according to the accuracy of the results to which they have contributed; certain rabbits are consequently designated as unsuitable for insulin testing.

F. C. Happold.

Activation of insulin by yeast juice. E. Glaser and G. Halpern (Biochem. Z., 1929, 207, 377—383).—Yeast juice after boiling for 8 hrs. does not, on injection, cause a decrease in blood-sugar, but if allowed to remain with insulin in solution at p_H 7·8 and then injected, it increases the effect of the insulin. It is suggested that a portion of the insulin, present in an inactive form, is activated.

P. W. Clutterbuck.

Pancreatic hormone and mineral metabolism. II. Influence of the pancreatic hormone on the blood constituents. S. Takeuchi (Tohoku J. Exp. Med., 1928, 11, 327—343).—With normal dogs the pancreatic hormone causes a decrease in blood-sugar, inorganic phosphorus, potassium, and calcium, and tends to increase the chlorine and serum-albumin, whilst the sodium and magnesium are unchanged. In dogs with pancreatic diabetes, in addition to the above changes the sodium, but not the magnesium, tends to increase.

Chemical Abstracts.

Effect of insulin and thyroxine on autolysis in liver. A. Simon and P. Weiner (Biochem. Z., 1929, 207, 319—331).—After administration of large doses of insulin to starving and normal cats, liver autolysis at p_H 6·04—6·24 proceeds more slowly than with the liver of normal cats. The inhibitory action of insulin and of thyroxine on autolysis is not obtained in experiments *in vitro*.

P. W. Clutterbuck.

Method of action of the thyroid hormone. R. Weil and M. Landsberg (Biochem. Z., 1929, 207, 186—193).—Thyroxine, in concentrations as low as 1 in 4×10^5, quantitatively promotes the autolysis of tissue at neutral reaction. The effects of the hormone on metabolism are explained on a physico-chemical basis.

W. McCartney.

Lipoid-soluble and -insoluble forms of the ovarian hormone. E. Glimm and F. Wadehn (Biochem. Z., 1929, 207, 361—367).—Ether-soluble and -insoluble œstrus-producing substances occur in urine, the former in predominating amount. The former is converted into a form insoluble in ether by heating in alkaline solution and this on heating with hydrochloric acid is partly reconverted into an ether-soluble substance.

P. W. Clutterbuck.

Vitamin content of meadow and pasture grass. A. SCHEUNERT (Biochem. Z., 1929, 207, 447—457).—In experiments with rats, the vitamin-*A* and -*B* contents of the second crop of nine different kinds of mowing and pasture grasses are investigated. The differences in vitamin-*A* and -*B* content were small, but whereas pasture grass contained less vitamin-*A* than mowing grass no difference in vitamin-*B* content was detected. The grasses had a high vitamin-*A* and a low vitamin-*B* content. P. W. CLUTTERBUCK.

Vitamin-*A*. I. Vitamin-*A*-choleic acid. T. SHIMIZU and T. HATAKEYAMA (Z. physiol. Chem., 1929, 182, 57—71).—The view that vitamin-*A* (biosterin) is related to both sterol and the bile acids has led to the adoption of the choleic acid method of Wieland and Sorge (A., 1916, i, 710) in order to prepare a water-soluble vitamin-*A* compound. Vitamin-*A*, from egg-yolk, dissolved in 100 parts of alcohol was treated with four to five times its weight of deoxycholic acid and evaporated to dryness on a water-bath. The residue was extracted with warm alcohol and water added until the fluorescence disappeared. On keeping, *vitamin*-A-*choleic acid* (*gallosterin*) crystallised as yellow needles which were freed from excess of vitamin-*A* and cholesterol by repeated extraction with dry ether or chloroform and were recrystallised from aqueous alcohol; m. p. 179°. Gallosterin is insoluble in chloroform or ether, but readily soluble in acetone or alcohol. Titration with 0·01*N*-sodium hydroxide gave equivalent weight 468 [$(C_{24}H_{40}O_4)_5,C_{27}H_{24}O_2,2H_2O$ requires 476], $[\alpha]_D^{18}$ +45°. Treatment of gallosterin with ten times its weight of xylene under reflux in an atmosphere of carbon dioxide under reduced pressure for 1 hr. caused a precipitation of xylenecholeic acid, m. p. 183°, the vitamin remaining in solution. Removal of the xylene under diminished pressure in carbon dioxide gave a residue from which after treatment with a little alcohol the vitamin crystallised as needles. Distillation of gallosterin in a high vacuum in nitrogen at 200—260° removed the vitamin, which was crystallised from alcohol, m. p. 187°. Palladium–hydrogen reduction of gallosterin corresponded with four atoms of hydrogen; its iodine value was 20·2 (95% of theory). Mice fed on vitamin-*A*-free diet to which gallosterin was added showed normal growth; without gallosterin, avitaminosis set in which disappeared on adding gallosterin. Whilst deoxycholic acid showed no difference when added to a normal diet, when added to a vitamin-*A*-free diet the animals died within four to six days. C. C. N. VASS.

Detection of vitamin-*A*. H. STEUDEL (Biochem. Z., 1929, 207, 437—440).—The author claims the isolation of a substance which gives no blue colour reaction with antimony chloride but contains sufficient vitamin-*A*, as shown by feeding experiments, to maintain young rats in normal growth.

P. W. CLUTTERBUCK.

The Rosenheim–Drummond colour tests of vitamin-*A* in cod-liver oil. E. C. TOWLE and E. C. MERRILL (J. Amer. Pharm. Assoc., 1929, 18, 357—359).—In the antimony chloride test for vitamin-*A* according to the method of Carr and Price, the development of the blue colour and its change to red are positively influenced by the temperature of the reaction mixture. At 10° or below, the rate of change is about one twentieth of that at 25° and a definite working temperature should be specified. The addition of small quantities of alcohol tends to accelerate the reaction and the change from blue to red, and the presence of varying amounts of water influences the reaction in a very uncertain manner. The development of the red coloration may be associated with an oxidation process.

E. H. SHARPLES.

Chemistry of fat-soluble vitamins in cod-liver oil. A. L. BACHARACH and E. L. SMITH (Quart. J. Pharm., 1928, 1, 539—545).—Zucker's claim to have separated vitamins-*A* and -*D* is confirmed. Vitamin-*D* is present in cod-liver oil mainly in a form soluble in ethyl alcohol, in which vitamin-*A* is insoluble; it is rendered soluble by saponification without affecting its vitamin or chromogen activities.

F. C. HAPPOLD.

Vitamin-*A* in the liver. E. LAQUEUR, L. K. WOLFF, and E. DINGEMANSE (Deut. med. Woch., 1928, 54, 1495—1497; Chem. Zentr., 1928, ii, 2035—2036).—As determined colorimetrically, the vitamin-*A* content of liver-oils of different origin varies between 34 and 187 (biological) units. Human liver contains 0—160 units per g. Animal liver contained 30—50 units in autumn, and 10—20 units in winter and spring. A. A. ELDRIDGE.

Vitamin colour reactions. N. BEZSSONOFF (Bull. Soc. Chim. biol., 1929, 11, 294—307).—The colour reaction of Jendrassik (A., 1923, ii, 892) for vitamin-*B*, although given by phenols, is much more sensitive to vitamin-*B* than to phenols. It is suggested that determination of oxidation–reduction potential and the colour reactions given by many reagents would be useful in the determination of vitamins. E. BOYLAND.

Fundamental rôle of the alimentary equilibrium in the utilisation of lactose. (MME.) L. RANDOIN and R. LECOQ (Compt. rend., 1929, 188, 1188—1190; cf. A., 1928, 92).—Pigeons fed on a balanced artificial diet containing 66% of lactose to which varying daily doses of brewer's yeast have been added all develop polyneuritis, the yeast not having any retarding effect on the development of this condition. Death occurred after 18—30 days. Similar results are obtained when hydrolysed lactose, or an artificial mixture of 33% of dextrose and 33% of galactose, was used in place of lactose. On giving an artificial diet of composition analogous to that of cow's milk, but deficient in vitamins-*B*, polyneuritis develops and death occurs after 35—50 days, but in this case addition of large daily doses (0·5 g.) of brewer's yeast prolongs life for 150 days. Thus modification of the composition of the diet enables a better utilisation of lactose by the pigeon, but such utilisation is not entirely conditioned by the presence of sufficient vitamins-*B* but by a very rigid alimentary equilibrium. J. W. BAKER.

Formation of vitamin-*B* by *B. vulgatus* (Flügge) Migula. M. SCHIEBLICH (Biochem. Z., 1929, 207, 458—461).—The formation of vitamin-*B* by *B. vulgatus* is demonstrated by growing the organism on a medium devoid of the vitamin and feeding the resulting material to young rats.

P. W. CLUTTERBUCK.

Vitamin-*C* content of fresh and frozen winter cow's milk. W. SALECK (Milchwirt. Forsch., 1928, 6, 464—486; Chem. Zentr., 1928, ii, 2301).—The vitamin-*C* content of cow's milk is diminished only slightly by freezing for 3 days. A. A. ELDRIDGE.

Antirachitic principle of irradiated food. A. HOTTINGER (Z. Kinderheilk., 1927, **43**, 8—23; Chem. Zentr., 1928, ii, 2036).—Cholesterol, olive oil, cholesteryl oleate, and bile salts have no antirachitic action, but after irradiation with ultra-violet light all except bile salts are antirachitic. Active cholesterol preparations gradually lose their activity, the loss with olive oil being less rapid. Cholesterol is inactivated by heating at 150—200°, and partly at 100—120°. Irradiation for several hours inactivates active olive oil or cholesterol. A. A. ELDRIDGE.

Influence of changes in body-weight of the test rats on the accuracy of the assay of vitamin-*D* by means of the line test. K. H. COWARD and M. R. CAMBDEN (Quart. J. Pharm., 1929, **2**, 44—47). —Rats fed on a rachitogenic diet showed at the best only slight evidence of healing due to a more or less temporary loss of weight (cf. Bills, Honeywell, and MacNair, A., 1928, 332). C. C. N. VASS.

Chemical reaction for antirachitic vitamin. W. STOELTZNER (Münch. med. Woch., 1928, **75**, 1584; Chem. Zentr., 1928, ii, 2036).—Addition of phosphorus pentoxide to the oil containing antirachitic vitamin produces a reddish-brown coloration, gradually darkening, finally becoming almost black.

A. A. ELDRIDGE.

Irradiation of ergosterol: action of quartz [lamp] ultra-violet rays and of soft *X*-rays. R. DELAPLACE and G. REBIÈRE (Compt. rend., 1929, **188**, 1169—1172).—The absorption of an alcoholic solution of ergosterol irradiated by the quartz lamp showed an absorption maximum and minimum during the first minutes of irradiation. After about 7—10 min. it attained its maximum (vitamin-*D*) activity, though 40 min. exposure was required for the full production of the absorption band attributed to this vitamin. Analogous results were obtained with soft *X*-rays. J. GRANT.

Absorption spectrum of vitamin-*D*. R. B. BOURDILLON, C. FISCHMANN, R. G. C. JENKINS, and T. A. WEBSTER (Proc. Roy. Soc., 1929, **B**, **104**, 561—583).—The action of ultra-violet radiation on ergosterol has been studied by comparing the absorption spectra and antirachitic activity of the products formed. It is concluded that three substances are produced in succession of which the first shows an absorption band similar to that of ergosterol (maximum 280 μμ), but more than twice as intense. Evidence is given showing that this substance is probably vitamin-*D*. The second product, which is formed by further irradiation of the first, shows a strong absorption band with maximum at 240 μμ and has no antirachitic activity. The third substance is formed by further irradiation of the second, and shows neither antirachitic activity nor marked absorption.

B. A. EAGLES.

Origin of chlorophyll and its relation to blood pigments. K. NOACK and W. KIESSLING (Z. physiol. Chem., 1929, **182**, 13—49).—Protochlorophyll was obtained as a dark green non-crystalline powder, m. p. 80—129°, by extraction of the inner skin of cucumber seeds, after removal of fat, with 80% acetone and precipitation with light petroleum. It has not yet been obtained pure. The absorption spectra agree with those found by Monteverde and Lubimenko (A., 1912, ii, 800) and differ from that of chlorophyll in diminished absorption in the red, a displacement towards the violet, and a more intense green band. It is more basic than chlorophyll. Acid treatment of its ethereal solution yields the magnesium-free pigment protophæophytin, precipitated by light petroleum as a dark green, non-crystalline substance which could not be purified. Protophæophytin on treatment with the Grignard reagent yields a magnesium-containing pigment the spectrum of which is identical with that of protochlorophyll. Comparision of the absorption spectra of protophæophytin and phylloerythrin obtained from the bile of animals shows a complete agreement in the intensities of the series, whilst the single bands of the latter were removed 50—70 Å. towards the violet. The magnesium Grignard reagent yields with phylloerythrin a pigment the absorption spectrum of which shows an analogous agreement with that of protochlorophyll. Treatment of phylloerythrin in *iso*propyl alcohol with a minimal quantity of aqueous potassium hydroxide at 25° gives a substance containing a free carboxyl group the absorption spectrum of which is fundamentally the same as that of blood-protoporphyrin. The free carboxylic acid is extremely labile, reverting to a less acid substance the spectrum of which is of the same type as that of phylloerythrin. When boiled with methyl-alcoholic hydrogen chloride it yields an alkali-insoluble anhydrous compound. Light converts the free carboxylic acid and its methyl ester into a chlorophyll-green substance with the characteristic red band of chlorophyll (670—653 μμ). Hydrolysis of protophæophytin with methyl-alcoholic potassium hydroxide yields an alkali-insoluble compound spectroscopically identical with the anhydrous compound derived from the carboxylic acid obtained from phylloerythrin. Hydrolysis of protophæophytin with methyl-alcoholic hydrogen chloride yields a pigment which crystallises in brownish-red plates or olive-green prisms and having a spectrum identical with that of the carboxylic acid from phylloerythrin. A pigment having the same spectrum may also be obtained by alkaline hydrolysis of protophæophytin. Chlorophyll in *iso*propyl-alcoholic solution on treatment with iron powder and hydrochloric acid yields, on subsequent extraction with ether and treatment with hydrochloric acid, on addition of light petroleum a dark red powder the absorption spectrum of which agrees with that of natural protophæophytin. Reduction of chlorophyll in glacial acetic acid by hydrogen iodide and red phosphorus gives an olive-green substance almost identical spectroscopically with phylloerythrin. Natural and synthetic protophæophytin have the same ester characteristics as chlorophyll, hence the absence of the well-defined crystalline property found in phylloerythrin. It has not been possible to confirm the analogy between chlorophyll and protochlorophyll by the separation of the latter into the *a* and *b* forms. Hydrolysis of synthetic protophæophytin with methyl-alcoholic potassium hydroxide yields a free carboxylic acid the absorption spectrum of which is identical with that of the acid derived from phylloerythrin.

C. C. N. Vass.

Chlorophyll content and rate of photosynthesis. R. Emerson (Proc. Nat. Acad. Sci., 1929, 15, 281—284).—An internal factor, the chlorophyll content, affecting the rate of photosynthesis, was controlled in *Chlorella vulgaris*, and the rate of photosynthesis was determined at high light intensity and plotted against relative chlorophyll concentration, and also for two different values of the latter, as a function of the temperature. It is shown that the rate of photosynthesis is a function of the chlorophyll content, and is the same function of the temperature, independent of the chlorophyll concentration. The inhibition of photosynthesis by hydrocyanic acid is discussed. N. M. Bligh.

Absorption of carbon dioxide by roots and its utilisation in chlorophyllic photosynthesis. (Signa.) M. Bergamaschi (Atti R. Accad. Lincei, 1929, [vi], 9, 238—242).—Maize and other plants grown in an atmosphere free from carbon dioxide form starch in their leaves from carbon dioxide absorbed by the roots from either the soil or the nutrient solution in which they are grown, and, since the plants contain a greater quantity of carbon than the original seeds, the contention that the organic material is formed solely at the expense of carbon dioxide of respiration is refuted.

T. H. Pope.

Growth of the tomato as correlated with organic nitrogen and carbohydrates in roots, stems, and leaves. G. T. Nightingale, L. G. Schermerhorn, and W. R. Robbins (N. J. Agric. Exp. Sta. Bull., 1928, No. 461, 1—38).—The roots contain little carbohydrate, but much protein-nitrogen. In vigorously growing plants the assimilated nitrogen is high in the stem, but the protein-nitrogen is low except at or near the growing point. Sucrose, starch, and dextrin do not in general accumulate unless the reducing sugar is high. Petioles and veins correspond with stems as regards carbohydrates and nitrate-free nitrogen. In general, proteose, basic-, amino-, amide-, and ammonia-nitrogen increase during darkness, but in the upper stems the proteose, protein, and basic nitrogen decreased, whilst the amino-, amide-, and ammonia-nitrogen increased. On return to light, carbohydrates and protein increased, and all forms of nitrate-free soluble nitrogen decreased. Chemical Abstracts.

Behaviour of the olive under the influence of uranium radiations and of the ionisation of the air. L. Petri (Atti R. Accad. Lincei, 1929, [vi], 9, 188—189).—The stimulating effect produced on the growth of the olive by ionised air is completely annulled by radiations emitted by green uranium oxide when these exceed a certain limiting intensity. Plants thus treated stopped growing entirely when cold weather set in, whereas the control plants continued to grow, even at temperatures between 5° and 15°; the functional activity of the former, indicated by the quantity of water used up, was only about one half of that of the controls.

T. H. Pope.

Influence of the nitrate-ion concentration of nutrient solutions on the growth of summer wheat. M. A. J. Goedewaagen (Proc. K. Akad. Wetensch. Amsterdam, 1929, 32, 135—150).—Nitrate-ion concentrations were used which it may be assumed occur in the soil solution. Solutions of sodium nitrate were employed, but as the sodium-ion concentration alters with the nitrate-ion concentration, experiments were made in such a way that the effect of the former could be judged separately. As a general result of the experiments it is shown that good growth of wheat plants is possible with nutrient solutions having widely divergent nitrate content. The maximum nitrogen concentration for good growth is between 182 and 238 parts per million. The lowest concentration permitting fairly good growth lies below 5 parts per million. A. J. Mee.

Nutrition of higher plants with ammonia. D. Prianischnikov (Biochem. Z., 1929, 207, 341—349).—In neutral reaction ammonia, and in acid reaction nitrate, is the better source of nitrogen. Optimal development can be obtained by administration of either ammonia or nitrate by suitably adjusting either the p_H or the content of cation associated with ammonium in the nutritive mixture.

P. W. Clutterbuck.

Nitrogen metabolism of forest soil. D. Fehér (Biochem. Z., 1929, 207, 350—360).—Tables and curves show the changes of total nitrogen, nitrate-nitrogen, and humus contents, of the protozoal and bacterial counts, of the p_H, and air- and ground-temperatures of the soil of three types of pine wood during a period of 12 months. The total nitrogen content is maximal in June and July, rapidly decreasing in autumn, and is minimal in September. The nitrate-nitrogen follows a similar course, but the maximal values are obtained in April and May. The bacterial count is also maximal in the spring and summer months. There does not appear to be the same causal connexion between the changes in number of nitrifying and fixing organisms and the changes of nitrate- and total nitrogen as was observed between the bacterial count and carbon dioxide production (A., 1928, 558, 1406; B., 1928, 381), the chief factor being the intensity of the activity of the organisms rather than their number.

P. W. Clutterbuck.

Nucleo-cytoplasmic ratio in plant tissues. F. E. Huelin (Austral. J. Exp. Biol., 1929, 6, 59—63).—Nucleo-cytoplasmic ratios have been determined for young wheat plants by the method of Robertson (this vol., 715). The ratio diminishes rapidly with age at a comparatively early stage of growth. F. C. Happold.

Effects of the waxy gene in maize on fat metabolism. F. A. Abegg (J. Agric. Res., 1929, 38, 183—193).—The differences in acid value and saponification value of the ether-soluble oils from non-waxy and waxy maize grains are shown to be due to the high acid value and saponification value of the fat from the endosperm tissue in the waxy gene.

E. A. Lunt.

Isolation of methyl alcohol from tobacco smoke. C. Neuberg and M. Kobel (Biochem. Z., 1929, **206**, 240—244).—The presence of methyl alcohol in tobacco smoke was demonstrated by the isolation of the pure substance in a yield of 0·24% on tobacco. J. H. Birkinshaw.

Microanalytical tobacco determinations. II. Determinations of nicotine in fresh green tobacco. J. Bodnár and V. L. Nagy (Biochem. Z., 1929, **206**, 410—415).—Drying of the fresh green leaves at 95—97° caused no loss in nicotine content. The dried leaves after powdering are extracted with a mixture of ether and light petroleum under faintly alkaline conditions. The extract is freed from ammonia by means of a current of air, an equal volume of water added, and a known amount of 0·01*N*-hydrochloric acid. The excess of hydrochloric acid is determined by titration with 0·01*N*-sodium hydroxide, using methyl-red as indicator. One c.c. of 0·01*N*-hydrochloric acid corresponds with 1·62 mg. of nicotine. This method compares favourably with the gravimetric method of Rasmussen (A., 1916, ii, 359).

C. C. N. Vass.

[Non-]occurrence of fatty acids with an uneven number of carbon atoms in natural fats, oils, and waxes. I. Oil from *Datura stramonium*, L. P. E. Verkade and J. Coops, jun. (Biochem. Z., 1929, **206**, 468—481).—Fractionation of the methyl esters of the saturated fatty acids obtained from the oil of *D. stramonium*, and a comparison of their m. p. with those of the m.-p. diagram of a mixture of methyl palmitate and methyl stearate, show the so-called margaric or daturic acid to be a mixture of palmitic and stearic acids in the ratio 5 : 1. Pure methyl stearate has m. p. 38·70°, methyl palmitate 29·70°. *X*-Ray analysis shows that the spectrum of the methyl ester of the supposed heptadecoic acid is identical with the spectrum of a synthetic mixture of methyl palmitate and stearate having the same m. p.

C. C. N. Vass.

Seeds of *Monarda punctata*. A. A. Harwood (J. Amer. Pharm. Assoc., 1929, **18**, 228—231).—Light petroleum extraction of the seeds (3·6% water, 7·5% ash) of *M. punctata* gave 20·5—25·2% of oil having d^{25} 0·9100 and saponif. value 173·3. Ether extraction gave 29·7% of oil having d^{25} 0·9217, n^{23} 1·4840, saponif. value 206 and 207·8, iodine value 207.

E. H. Sharples.

Ether-soluble substances of cabbage-leaf cytoplasm. V. Isolation of *n*-nonacosane and di-*n*-tetradecyl ketone. H. J. Channon and A. C. Chibnall (Biochem. J., 1928, **23**, 168—175).—These two compounds are precipitated in the so-called phosphatide fraction obtained by the addition of cold acetone to the ethereal extract of cabbage leaf (A., 1927, 1227). They were removed from this fraction by extraction with boiling acetone. The paraffin was obtained by crystallising the lower-boiling fractions of the mixture from alcoholic benzene. The ketone, m. p. 80·5—81°, was separated by taking advantage of the greater solubility of the ketoxime in a mixture of light petroleum and acetone. The number of carbon atoms and the purity of the paraffin were determined by *X*-ray analysis. The ketone gave the same m. p. when mixed with the synthetic compound, but a depressed m. p. when mixed with synthetic palmitone. *Di-n-tetradecyl ketone* was synthesised by Kipping's method (J.C.S., 1890, **57**, 980) for the preparation of palmitone. *Palmityl myristyl ketone*, m. p. 74—74·5°, was synthesised as follows. *Ethyl α-dodecylacetoacetate* was prepared by treating dodecyl iodide with alcoholic sodium and ethyl acetoacetate and extracting with ether. It was then treated in dry ether with sodium and palmityl chloride and the resulting *ethyl αα-dodecylpalmitylacetoacetate* was saponified with potassium hydroxide. The palmityl myristyl ketone was finally extracted with ether and precipitated with acetone from the ethereal solution.

S. S. Zilva.

Ether-soluble substances of cabbage-leaf cytoplasm. VI. Summary and general conclusions. A. C. Chibnall and H. J. Channon (Biochem. J., 1929, **23**, 176—184).—A summary and discussion of results previously obtained (cf. A., 1927, 386, 799, 1227). The chlorophyll content of the acetone–ether fraction of one of the batches was 9·3%, the carotin 0·86%, and the xanthophyll 0·62%. The chemical character of the unsaturated fraction of the unsaponifiable fraction which consists of sterols and unidentified products, probably alcohols and hydrocarbons, is described. S. S. Zilva.

Nature of the pectic substances of flax. F. W. Norris (Biochem. J., 1929, **23**, 195—198).—Pectic substances were prepared from flax by Clayson, Norris, and Schryver's method (A., 1922, i, 206). The ash content, and furfuraldehyde and carbon dioxide produced on hydrolysis with 12% hydrochloric acid were determined for each product and in the case of the soluble pectin methoxyl groups were also determined. The results obtained are in accordance with expectations based on the ring formula of Nanji, Paton, and Ling (J.S.C.I., 1925, **44**, 253T) and do not support Henderson's simpler galactose-tetragalacturonic acid formula (A., 1928, 1119).

S. S. Zilva.

Sarmentocymarin and sarmentogenin. W. A. Jacobs and M. Heidelberger (J. Biol. Chem., 1929, **81**, 765—779).—By the usual direct methods of extraction *Strophanthus sarmentosus* seeds yielded small amounts of *sarmentocymarin*, $C_{30}H_{46}O_8,2H_2O$, m. p. 130°, $[\alpha]_D^{20}$ −12·5° in methyl alcohol; further larger amounts of the same compound, together with dextrose, were obtained by digestion of the crude residual glucosides with an enzyme prepared from the seeds. When hydrolysed with hydrochloric acid the compound yielded *sarmentogenin*, $C_{23}H_{34}O_5$, m. p. 265—266°, $[\alpha]_D^{20}$ +21·5° in 95% alcohol, forming, when crystallised from pyridine, a *compound*, $C_{23}H_{35}O_5,C_5H_5N$, m. p. 258°); sarmentogenin gave a *dibenzoate*, m. p. 281°, $[\alpha]_D^{20}$ +14°, and, with hydrogen and platinum, yielded *dihydrosarmentogenin*, $C_{23}H_{36}O_5$,EtOH, m. p. 142°; when oxidised with chromic acid it gave *sarmentogenone*, $C_{23}H_{32}O_5$, m. p. 226° (*semicarbazone*, m. p. 200°). With methyl-alcoholic potassium hydroxide, sarmentogenin gave iso*sarmentogenin*,

$C_{23}H_{34}O_5$,EtOH, m. p. 248° (*dibenzoate*, m. p. 297°), which, when treated with sodium hydroxide, yielded the lactone acid, iso*sarmentogenic acid*, $C_{23}H_{34}O_6$, m. p. 212° (*methyl* ester, m. p. 274°). Sarmentogenin is thus isomeric with periplogenin and gitoxigenin and shares with these the general chemical characteristics of the strophanthidin series. It is probably identical with the "strophanthidin" described by Kohn and Kulisch (A., 1898, i, 329).
C. R. HARINGTON.

Two phloroglucinol drugs. W. PEYER and W. LIEBISCH (Pharm. Zentr., 1929, 70, 197—200).—Phloroglucinol has been detected in the drugs obtained from *Albizzia anthelminthica* and *Combretum raumbaultii*; the first contains 8·2% of saponin and the second 2·25% of saponin and considerable quantities of a tannin. W. O. KERMACK.

Occurrence of euxanthone in heart-wood of *Platonia insignis*, Mart ("Geelhart" or "Pakoeli"). D. B. SPOELSTRA and M. J. VAN ROYEN (Rec. trav. chim., 1929, 48, 370—371).—Extraction of 2 kg. of the wood with benzene gave 1·3% of euxanthone, m. p. 239° (acetyl derivative, m. p. 185°; bromo-derivative, m. p. 278°). Further extraction of the wood with alcohol yielded a dark-coloured, brittle residue, m. p. 205—225° (decomp.), completely soluble in alkali, but insoluble in water. No definite product was isolated by fusion with potassium hydroxide or distillation with zinc dust.
H. BURTON.

Proteins of the avocado (*Persea americana*, Mill). D. B. JONES and C. E. F. GERSDORFF (J. Biol. Chem., 1929, 81, 533—539).—The finely-divided fruit was extracted with 10% sodium chloride solution; when the extract was heated to 68° there was obtained a globulin in a yield of 0·44% of the original fruit; the same protein could be obtained by treating the extract with ammonium sulphate to 67% saturation, or by acidifying to p_H 3·9 with acetic acid. The residue left after extraction with sodium chloride was boiled with 60% alcoholic 0·1*N*-sodium hydroxide and the filtrate acidified with acetic acid; this yielded a second protein. A third protein was obtained by dilution of the mother-liquor with water. Figures are given for the nitrogen distribution of the various proteins. C. R. HARINGTON.

Similarity between physico-chemical and biological reactions. C. P. SIDERIS (Plant Physiol., 1928, 3, 79—83).—The isoelectric points of two proteins, *A* and *B*, isolated from the stem of the pineapple, are, respectively, p_H 6·4 and 4·8. Various organisms were unable to grow in the protein-*A* at the isoelectric point. CHEMICAL ABSTRACTS.

Modification of f.-p. determinations for small quantities of biological fluids. E. FROMM and T. LEIPERT (Biochem. Z., 1929, 206, 314—318).—Details of the method and apparatus used to determine f. p. and the depression of m. p. in 3 c.c. of a fluid by means of an ordinary thermometer graduated in hundredths of a degree are given. C. C. N. VASS.

Determination of cysteine, cystine, and their derivatives in tissues and biological fluids. Y. OKUDA (J. Dept. Agric. Kyushu, 1929, 2, 133—148).—The proteins of biological tissues or fluids are coagulated by means of a solution of sulphosalicylic acid and the cysteine in the filtrate is determined by titration with a standard iodate solution containing iodide. Cystine is similarly determined after reduction to cysteine. For precipitation of proteins, sulphosalicylic acid possesses advantages over trichloroacetic acid, since in presence of the latter acid the iodine titration is untrustworthy.
W. O. KERMACK.

Purification of picric acid. S. R. BENEDICT (J. Biol. Chem., 1929, 82, 1—3).—Picric acid, for the purpose of the colorimetric determination of creatinine, is best purified by crystallisation from glacial acetic acid, or by solution in sodium carbonate, separation of the sodium salt, and decomposition of the latter with dilute hydrochloric acid.
C. R. HARINGTON.

Ergosterol-digitonin complex. H. PÉNAU and Z. HARDY (J. Pharm. Chim., 1929, [viii], 9, 145—151, and Bull. Soc. Chim. biol., 1929, 11, 437—442).—The influence of time, temperature, and the presence of water on the formation of ergosterol-digitonide from alcoholic solutions of its constituents has been studied. The following procedure for its preparation is described. Ten c.c. of a 0·175% solution of ergosterol in 99% alcohol are introduced into a dried and weighed centrifuge tube; 9 c.c. of a 1% solution digitonin in 99% alcohol are added, and then 2 c.c. of water. The mixture is shaken and kept for 18 hrs. at about 18°, then centrifuged for 15 min. and the supernatant liquor decanted. The solid is stirred with 3 c.c. of a mixture of acetone 73 c.c., water 18 c.c., and alcohol 9 c.c., the stirrer washed with 1 c.c. of the same mixture and, after centrifuging and decanting the supernatant wash-liquor, the tube and contents are dried for 18—24 hrs. over phosphorus pentoxide. 1 G. of the ergosterol-digitonide complex is equivalent to 250 mg. of ergosterol. E. H. SHARPLES.

Micro-determination of phosphorus in tissue. Y. NAITO (J. Biochem. Japan, 1928, 9, 45—69).—The method depends on the production of a precipitate of ammonium phosphomolybdate of definite composition when a phosphate solution containing ammonium nitrate is treated at 80° with ammonium molybdate at a definite acidity; the compound is then decomposed by sodium hydroxide, and the residual alkali titrated. Accurate results can be obtained with 0·03 mg. of phosphorus. The tissue, containing 0·1—0·005 mg. of phosphorus, is digested with 3 c.c. of 20% sulphuric acid, the digestion being completed with nitric acid or redistilled hydrogen peroxide; 3 c.c. of ammonium nitrate solution (30 g. in 100 c.c.) are added, and water to 9 c.c. At 80°, 1 c.c. of 10% ammonium molybdate solution is added, and the precipitate, after being kept overnight, is washed with 20% alcohol and decomposed with 0·04*N*-sodium hydroxide. CHEMICAL ABSTRACTS.

Determination of halogens in organic substances. W. ROMAN.—See this vol., 713.

Van Slyke's method. L. ROSENTHALER.—See this vol., 713.