BRITISH CHEMICAL ABSTRACTS

A.—PURE CHEMISTRY

AUGUST, 1929.

General, Physical, and Inorganic Chemistry.

Continuous spectrum of the hydrogen atom. P. S. Epstein and M. Muskat (Proc. Nat. Acad. Sci., 1929, **15**, 405—411).—Expressions are obtained suitable for numerical calculations of the intensities in the continuous spectrum of atomic hydrogen by means of a new integral representation for the wave function in this special case. The results are applied to the calculation of the absorption spectra of hydrogen beyond the limits of the Balmer and Lyman series, as well as certain limiting values of the absorption.

N. M. Bligh.

Helium band spectrum. II. S. Imanishi (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, **10**, 237—252; cf. *ibid.*, 193—209).—The green and orange regions of the helium band spectrum have been photographed in the first order of a 15-ft. concave grating. Two new bands, parhelium $2S(n{=}1)-3P(n{=}1)$ and $2S(n{=}2)-3P(n{=}2)$, were found and analysed. The band $2S(n{=}1)-3P(n{=}0)$ of Weizel and Füchtbauer is completed and the band $2S(n{=}0)-3P(n{=}0)$ much extended. Orthohelium $2s(n{=}2)-5p(n{=}2)$ were found in the ultra-violet. The Merton–Pilley–Fujioka bands at 4950 and 5350 Å. were re-investigated and are discussed. W. E. Downey.

Band spectrum of helium. W. Weizel and E. Pestel (Naturwiss., 1929, **17**, 390).—A preliminary communication. A series of hitherto unarranged bands has been analysed and arranged in series form.

J. W. Smith.

Series in the arc spectrum of chlorine. T. L. De Bruin and C. C. Kiess (Science, 1928, **68**, 356—357).—The arc spectrum of chlorine from 2300 to 3900 Å. has been photographed, and the new lines are classified as members of the doublet and quadruplet systems. The lowest term ^2P arises from the electron configuration s^2p^5, and other terms which have been established are ^2P and ^4P arising from $^2s^4p\times4s$, together with two sets of doublet and quadruplet S, P, and D terms from $s^2p^4\times4p$ and $s^2p^4\times5p$, respectively. Details will be communicated in a later paper. L. S. Theobald.

Spectrum of doubly-ionised magnesium. J. E. Mack and R. A. Sawyer (Science, 1928, **68**, 306).—The levels of the most stable three configurations of the doubly-ionised magnesium atom, isoelectronic with neon, have been revealed by an investigation of the condensed spark discharge in a vacuum using electrodes of pure magnesium. The relative values of the terms arising from the configurations $2p^6$, $2p^53s$, and $2p^53p$ are tabulated. The ionisation potential of Mg III—Mg IV is 80 ± 2 volts. L. S. Theobald.

Arc spectrum of germanium. K. R. Rao (Proc. Roy Soc., 1929, A, **124**, 465—477; cf. Rao and Narayan, A., 1928, 929).—Observations of the arc spectrum of germanium have been extended to 1630 Å., and the wave-lengths, intensities, wave-numbers, and classification of the lines from the visible region to 1630 Å. are tabulated. About 50 new lines are recorded. Gartlein's analysis (A., 1928, 679) is slightly modified to bring it into better agreement with that of C I, Si I, and Sn I. The absolute values of the terms have been calculated. From the largest term, $4p^3P_0=65558{\cdot}0$, the ionisation potential of Ge I is found to be 8·09 volts, approximately.

L. L. Bircumshaw.

Emission lines on the absorption bands of *H* and *K*. J. Evershed (Month. Not. Roy. Astron. Soc., 1929, **89**, 566—567).—Under favourable conditions close to the limb of the sun four emission lines can be detected near *K* and *H*: 1, 3931·54 (0); *K* 3933·684 (1000); 2, 3934·80 (2); 3, 3967·04 (0); *H*, 3968·494 (700); 4, 3969·40 X. (3); the figures in parentheses denoting intensity. The values for the emission lines are derived from solar iron lines in the limb spectra and are subject to a small positive correction for limb effect not exceeding 0·002—0·003 Å. The absorption line at 3931·590 (1) in the revised table of Rowland does not appear, nor does the 3967·057 (0) line attributed to Ce^+. A line at 3969·407 coinciding with emission 4 appears as a very faint absorption line in one of the spectra of the centre of the disc. R. A. Morton.

Stark effect in the second order for the Balmer series of hydrogen. H. R. von Traubenberg and R. Gebauer (Naturwiss., 1929, **17**, 442—443).—In recent papers (this vol., 224, 734) the authors record deviations from the Schrödinger theory for the higher components of H_γ. The theoretical values have been re-calculated and the discrepancies now disappear.

R. A. Morton.

Intensities of the Stark effect components of the Balmer series. W. Gordon and R. Minkovski (Naturwiss., 1929, **17**, 368).—Theoretical.

Spectra of Zn II, Cd II, In III, and Sn IV. R. J. Lang (Proc. Nat. Acad. Sci., 1929, **15**, 414—418).—In the spectrum of Zn II six new combinations between known terms are located. In Cd II three new combinations are given, and the $7S$ term is found. In In III one new multiplet $5P-6D$, based on known term values, is given and possible values for the $6F$ terms are obtained. In Sn IV four multiplets are located, all based on previously known term values. N. M. Bligh.

Fine structure of the high series doublets of cæsium. D. A. Jackson (Naturwiss., 1929, **17**, 364; cf. this vol., 1).—In reply to the criticisms of Filippov and Gross (this vol., 365) it is pointed out that the fine-structure doublets of cæsium previously reported were not due to reversal, since by variation of temperature and pressure conditions this spectrum could be obtained in the reversed state. J. W. Smith.

[Fine structure of the high series doublets of cæsium.] A. Filippov and E. Gross (Naturwiss., 1929, **17**, 364).—A reply to Jackson (preceding abstract). J. W. Smith.

Intensity relations in the spectra of titanium. II. Relative intensities of the stronger multiplets of Ti I. G. R. Harrison and H. Engwight (J. Opt. Soc. Amer., 1929, **18**, 287—301).—The relative intensities of sixteen of the more important multiplets of the normal titanium spectrum have been measured with a 10-metre concave grating and using a low-tension vacuum arc. The agreement between the relative intensities and those predicted by Kronig's formulæ is best when an effective temperature of 10,000° is assigned to the arc. The data are thought to support the view that the raie ultime of titanium is 3653·49 Å. R. W. Lunt.

Spectrum of trebly-ionised thallium. K. R. Rao (Proc. Physical Soc., 1929, **41**, 361—365).—Using Carroll's measurements (cf. A., 1926, 214) of the vacuum spark spectrum of thallium, combinations of the triad of triplet and singlet *F*, *D*, *P* terms of the d^9p configuration of Tl IV with the deeper ^3D and ^1D of the d^9s state are found and tabulated. The scheme is supported by comparison with similarly constituted spectra. N. M. Bligh.

Arc spectra in the region 1600—2100 Å. E. W. H. Selwyn (Proc. Physical Soc., 1929, **41**, 392—403).—A simple method, taking advantage of the transparency of nitrogen, of photographing ordinary arc spectra down to about 1600 Å. is described. Measurements were made and tabulated, together with the classification of lines between 1600 and 2100 Å., for the elements copper, gold, silver, beryllium, magnesium, calcium, strontium, barium, zinc, cadmium, mercury, boron, and aluminium. Impurity lines and their origins are also tabulated. A number of lines hitherto unobserved is recorded and additions are made to the analysis of the spectra of Mg I, Be I, and B I. N. M. Bligh.

Hg II spectrum in the infra-red. E. Rasmussen (Naturwiss., 1929, **17**, 389—390).—The first spark spectrum of mercury in the near infra-red has been investigated over the range 6000—10,600 Å. The results of Paschen (this vol., 365) have been confirmed and extended, about 100 new lines having been measured and classified. J. W. Smith.

Structure and significance of the mercury–inert gas bands. O. Oldenberg (Z. Physik, 1929, **55**, 1—15; cf. A., 1928, 346).—The fluorescence spectra obtained in mixtures of mercury vapour with argon and krypton show band series in the region 2540—2560 Å. which converge towards the long-wave side. These new bands are attributed to molecules HgA and HgKr. The energy of dissociation of these molecules in the normal state is calculated as 0·025 and 0·035 volt, respectively. It is pointed out, however, that these bands may bear other interpretations.

By correlating the data obtained with previous observations it is found that the lighter the inert gas atom the further does the resonance spectrum extend towards the short-wave side, the limit varying from 2513 Å. with helium to 2532 Å. for xenon. In the case of xenon only a diffuse maximum is observed at 2533 Å., corresponding with the maximum 2529 of HgKr. The previously reported observation that the extinguishing action of argon is strongly increased by heating is now explained as being due to increased pressure of mercury vapour. J. W. Smith.

Fluorescence bands and heat of dissociation of the mercury molecule. S. Mrozowski (Z. Physik, 1929, **55**, 338—357).—The intensities of the bands in the fluorescence spectrum of mercury vapour, and their dependence on temperature and density of the vapour, are investigated. It is shown that the fluorescence bands are emitted from the excited molecules which collide with atoms of a higher energy level. The effectiveness of the collision increases if the relative kinetic energy increases. Further, both the 3300 Å. and the 4850 Å. fluorescence bands have a common molecular origin, and apparently the first is due to spontaneous emission and the second to collisions of the second kind. The heat of vaporisation of the mercury molecule is derived from the relative change of the absorption coefficients of the bands of the saturated vapour with the temperature. It has the value 11 kg.-cal./mol. The heat of dissociation of the mercury molecule is about 17 kg.-cal./mol. This value agrees with the arrangement of absorption bands for the 2*P* state of the atom. An explanation of the intensity distribution in the mercury bands on the ground of Condon's theory is attempted, and a possible scheme of levels for the mercury molecule is derived. A. J. Mee.

Dependence of the intensity distribution in spectral lines broadened by gas pressure on the nature of the gas employed. R. Minkovski (Z. Physik, 1929, **55**, 16—27).—At small pressures of foreign gas the intensity distribution in the *D*-lines of sodium agrees with that calculated from the theory of collision damping. With increasing pressure of foreign gas deviations appear; in the case of gases of low mol. wt. such as hydrogen and helium the deviation is greater towards the short-wave side of the line, whilst with heavier molecules such as nitrogen and argon it is more pronounced on the long-wave side. These deviations are accounted for by the combined effect of radiation and collision. J. W. Smith.

Effect of gases and vapours on sparking voltage of small tubular electrodes. K. Honda and K. Otsuka (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, **8**, 319—334).—When gases or vapours other than air flow from a jet into the gap between a tubular and a disc electrode, the sparking potential is lower

than when the gas is stationary. The lowering effect increases with the molecular complexity of the gas, except for nitrogen compounds, which are irregular. A theory is advanced to explain the characteristics of glow and striated discharges, according to which the positive ions in the gap are in the molecular state in the glow discharge and in the atomic state in the striated discharge. The theory explains the appearance of pulsations in the striated discharge and leads to the conclusion that the frequency of the pulsations should be expressed by the formula v/g, where v is the velocity of the positive ions and g the length of gap in cm. The calculated values agree well with the observed frequencies. The vapours of anti-knocking materials such as carbon tetrachloride never lower the sparking potential, but always raise it.
E. S. HEDGES.

Absorption of Hertzian waves by ionised gases. H. DÄNZER (Ann. Physik, 1929, [v], 2, 27—62).—A new sensitive detector for Hertzian waves of any wave-length and resembling the bolometer in principle is described. The absorption and reflexion of wave-lengths near 4 cm. have been studied for intensely ionised neon, argon, nitrogen, hydrogen, oxygen, and air. The time between excitation and the complete disappearance of absorption is considered to correspond with the life period T of the electrons set free in the gases. The following values were obtained: argon, $2\times10^{-3}<T<10^{-1}$; hydrogen, 3×10^{-4}; nitrogen, 3×10^{-4}; oxygen, 1×10^{-4}; air, 1×10^{-4} sec. The experimental results are considered theoretically.
R. A. MORTON.

External photo-electric effects of silver halides and silver sulphide. F. KRÜGER and A. BALL (Z. Physik, 1929, 55, 28—43).—The external photo-electric effects of silver chloride, bromide, iodide, and sulphide have been measured at different wave-lengths. As the wave-length increases, the magnitude of the effect becomes asymptotic with the wave-length axis, the limiting values at which any effect could be measured being 407 mμ for silver iodide, 332 for silver bromide, and 312 for silver chloride. In each case this point lies at a wave-length rather below the maximum of the internal photo-electric effect, which coincides with the maximum photo-chemical action. It is concluded that in the external photo-electric effect the electron emitted from the surface does known work against an arresting surface film or against electrical forces. Similar observations are made in the case of silver sulphide, for which the absorption head in the infra-red lies at about 1·3 μ and the maximum internal photo-electric effect at 1·3—1·4 μ, whilst the external photo-electric effect can be detected only at 407 mμ.
J. W. SMITH.

Ratio of the mass of the proton to that of the electron. V. ROJANSKY (Nature, 1929, 123, 911—912).—In view of Eddington's conclusion (this vol., 231) that $ch/2\pi e^2=136$, it is thought that the relation $M/m=(136)^2/10=1849{\cdot}6$ (observed, approx. 1840) may not be a coincidence.
A. A. ELDRIDGE.

Diffraction of electrons by a copper crystal. H. E. FARNSWORTH (Nature, 1929, 123, 941—942).—The total secondary emission from a single copper crystal has been measured under the same conditions as the angular distribution of scattered electrons for bombarding potentials between 1 and 150 volts. The curve shows maxima at 3 and 10·5 volts, and several changes in slope between 10·5 and 150 volts. The results are discussed.
A. A. ELDRIDGE.

Scattering of fast electrons by atomic nuclei. N. F. MOTT (Proc. Roy. Soc., 1929, A, 124, 425—442).—Mathematical. A scattering formula is obtained by using the wave equation of Dirac, and it is found that the scattered beam is polarised. A method for detecting the polarisation is discussed.
L. L. BIRCUMSHAW.

Recombination of ions in atmospheric air. I. Investigation of the decay coefficient by Schweidler's method. P. J. NOLAN and C. O'BROLCHAIN (Proc. Roy. Irish Acad., 1929, 38*A*, 40—48; cf. Schweidler, Wien Ber., 1918, 127, 953; 1919, 128, 947, etc.).—The linear recombination law, $i+iH/E=S$ (i being the current in an ionisation chamber, E the *P.D.* between the electrodes, S the saturation current, and H the *P.D.* for $S/2$), for small ions in atmospheric air has been shown to be approximately true. The value of η_2, the recombination coefficient between charged nuclei and small ions, is not constant; the variation does not appear to be associated with variation in the dust content measured by an Owens dust-counter.
R. A. MORTON.

Recombination of ions in atmospheric air. II. Law of recombination of ions and nuclei. P. J. NOLAN (Proc. Roy. Irish Acad., 1929, 38*A*, 49—59).—Experiments with air in a closed vessel show that the recombination coefficient between small ions and nuclei increases as the concentration of nuclei decreases. The coefficient varies inversely as the square root of the nucleus concentration. The equation $q=\alpha n^2+\zeta n(N)^{\frac{1}{2}}$ (n being the number of positive or negative ions per c.c., q the number of pairs of ions formed per c.c. per sec., N the sum of the numbers of the oppositely-charged large ions and the uncharged nuclei, α is given by $dn/dt=q-\alpha n^2$, and the probable value of ζ is 55×10^{-5} cm.$^{3/2}$/sec.) represents the relation between the rate of production of ions in atmospheric air and the equilibrium concentrations of ions and nuclei. The equation has been tested with good results by measurements of ionic concentrations at different places and of the equilibrium of ionisation over the sea (assuming a nucleus concentration for sea air based on Aitken's observations).
R. A. MORTON.

"Mechanical" ionisation of gases under extreme pressure at any low temperature. W. ANDERSON (Physikal. Z., 1929, 30, 360—364).—Any gas can be ionised at low temperatures by means of pressure alone, provided only that the pressure is sufficiently great (cf. Bridgman, A., 1927, 183; Frenkel, Z. Physik, 1924, 29, 214). Under such conditions atomic hydrogen can be regarded as a mixture of electron-gas and proton-gas. The complete breakdown of ordinary ideas concerning ionisation potentials is demonstrated by calculations based on the ordinary Bohr theory of the hydrogen atom (and not requiring the Bose quantum statistics or the Pauli principle). The behaviour of mechanically ionised hydrogen at 0° Abs. is calculated in terms of density, pressure, and electron velocity. Eddington's views ("Internal Constitution of the Stars," p. 172) are criticised. The density inside some stars must be extraordinarily great and Eddington's paradoxical result is arrived at by omitting from consideration the possibility of mechanical ionisation.

R. A. Morton.

New regularities in the series of the elementary ionic radii. V. M. Goldschmidt (Z. physikal. Chem., 1929, **141**, 451—452; cf. this vol., 487).—The attempt by Berkenheim to establish numerical relations between the ionic radii of the elements, or a proportionality between the latter and certain simple whole numbers, on the basis of similar relationships among at. wts., is not justified in view of the fact that these have no simple physical meaning. Neither is it appropriate to make use of ionic radii calculated in this manner to maintain the accuracy of the author's empirical values in preference to those derived by Pauling on the principles of wave mechanics.

F. L. Usher.

Transmission and reflexion of slow-moving electrons by metals. E. Rupp (Naturwiss., 1929, **17**, 365).—Characteristic absorption maxima have been found for the transmission of slow-moving electrons (4—40 volts) through thin metallic films, transmitted electrons being here defined as such as pass through the film without considerable loss of velocity. Similar metallic surfaces show maxima at the same voltage for absorption and reflexion, the small differences observed (up to 1 volt) being explained by the difference in the contact potential in the two cases. Calculation of the maximum from known atomic magnitudes has not yet been found possible.

J. W. Smith.

Dependence of the mobility of ions in air on the relative humidity. E. Griffiths and J. H. Awbery (Proc. Physical Soc., 1929, **41**, 240—247).—The relationship between relative humidity and the mobility of negative ions in air at atmospheric pressure was examined in order to provide a means of following fairly rapid changes of humidity. The principle of the method was to balance the movement of the ions under an electric field by an opposing air stream of definite humidity, the mobility being deduced from the critical potential required to produce a balance. Ionisation was obtained by a small quantity of polonium on a gauze sheet in the air stream. The relative humidity plotted against potential gradient is approximately linear.

N. M. Bligh.

Mobility of gaseous ions. A. M. Tyndall (Proc. Physical Soc., 1929, **41**, 248—257).—There is no satisfactory quantitative theory of the motion of an ion through a gaseous medium. The ion may, however, be regarded as a charged core surrounded by a cluster of neutral molecules which may be treated as a dynamic or as a static cluster, as by Langevin (cf. Hassé, A., 1926, 219). The difference between positive and negative mobilities is discussed on these two theories. The effect of vapours with a marked dipole in lowering the mobility of the negative ion is found to be a direct result of the dynamic cluster theory (cf. A., 1926, 877). In pure gases, in absence of polar impurities, many negative ions do not take on a cluster, but remain in the electronic state. Various explanations of the transformation with age of positive ions from the initial to the final type found by Erikson are discussed.

N. M. Bligh.

Elastic scattering of electrons in argon and the Ramsauer effect. J. Holtsmark (Naturwiss., 1929, 20, 365—366).—The effective target area in argon may be calculated as a function of the velocity of the colliding electrons of the mean potential field if the argon atoms and the polarisation produced by the colliding electron are known. The curve calculated in this way gives values about 15% too high, but the agreement between the actual and predicted positions of the minimum at $0{\cdot}7\sqrt{\text{volt}}$ and of the maximum at $3{\cdot}6\sqrt{\text{volt}}$ is good.

R. W. Lunt.

Recombination of gaseous ions. L. B. Loeb (Amer. Electrochem. Soc., May, 1929. Advance copy. 16 pp.).—Previous work is reviewed and preliminary results of unpublished experimental work by Marshall are discussed in relation to the theoretical conclusions of Sommerfeld and the author. It is shown that the recombination is primarily a process of random drifting together of the ions, the attractive forces playing a part only in the last free path or two between the ions. The coefficient of recombination, α, depends on the duration of the ionising *X*-ray flash period as well as of the recombination period, and apparent variations in α are due to the non-random distribution of ions following their generation in pairs close together. The true value of α for air is probably about $0{\cdot}9\times10^{-6}$ instead of $1{\cdot}6\times10^{-6}$ as usually assumed. From a comparison of results with air and argon it is concluded that free electrons play no direct rôle in the recombination of ions and can act only by first attaching themselves to neutral molecules. With argon this attachment does not occur readily, but negative ions may be formed by attachment of electrons to molecules of an impurity. In such cases the apparent value of α is determined essentially by this rate of ion formation and depends on the molecules of impurity present. The fact that the velocity of thermal agitation determines the recombination prevents satisfactory comparison between theory and observation as to the relative values of α for different gases until the true masses of the ions in a given gas are known, as well as their mean free paths.

H. J. T. Ellingham.

Different magnetic states of an ion. G. Foex (Amer. Electrochem. Soc., May, 1929. Advance copy. 7 pp.).—Previously determined values of the constant θ in the Weiss equation $\kappa(T-\theta)=C$, where κ is the magnetic susceptibility and C a constant, and of the magnetic moment, μ, for the ferrous and nickelous ions are discussed. For the cobaltous ion varying values of θ and μ are obtained under different conditions and it is concluded that the ion in solution is not the same as the ion in a crystal. The possible nature of these differences is discussed.

H. J. T. Ellingham.

[Optical] concentration determination of atoms and ions. W. de Groot (Z. Physik, 1929, **55**, 52—55; cf. A., 1928, 1294).—Mathematical. The broadening of emission lines by self-absorption may have quite a considerable effect on optical concentration measurements. Such complications cause the curve of log I/I_0 against concentration never to reach an inflexion point. J. W. Smith.

At. wt. of arsenic. H. Křepelka (Nature, 1929, **123**, 944).—Analysis of arsenic trichloride gives the value 74·937 for the at. wt. of arsenic. A. A. Eldridge.

At. wt. of nitrogen occluded in fergusonite. H. P. Cady and H. U. Beecher (Science, 1928, **68**, 594—596).—Nitrogen was removed from the crude gas obtained from Norwegian fergusonite by hot metallic calcium, converted into ammonia by careful addition of water, and then absorbed in hydrochloric acid. The chlorine in the ammonium chloride was determined gravimetrically and the at. wt. of the nitrogen calculated to be only 0·02% greater than the value obtained for a control sample of nitrogen from liquid ammonia. The existence of an isotope of nitrogen of at. wt. 15, a possible decomposition product of potassium, is therefore negatived. The crude gas from the fergusonite contained 12·67% He. L. S. Theobald.

At. wts. of terrestrial and meteoric nickel. III. Analysis of nickelous bromide. G. P. Baxter and S. Ishimaru (J. Amer. Chem. Soc., 1929, **51**, 1729—1735).—Terrestrial and meteoric nickel have identical isotopic compositions. The value found for the at. wt. of nickel was 58·694. S. K. Tweedy.

Fine structure of the magnetic spectrum of α-rays. S. Rosenblum (Compt. rend., 1929, **188**, 1549—1550; cf. this vol., 738).—An α-ray of radium-*A* and a new ray (α_1-ray) were obtained on the same plate as the α-rays of thorium-*C*, equidistant from the strongest of the latter and having a difference in velocity of about ±0·003. With the α-ray of radium-*C′*, slowed down to the extent of 10% by a gold screen, the focalisation method produces a large band with maximum blackening in the middle. Sources of radium-*A* and radium-*C′* are conveniently prepared without loss of radon by introducing glass or platinum threads into a capillary tube containing a gaseous mixture rich in radon, and sealed at atmospheric pressure by a column of mercury. An activation yield of 50% is obtained with 500 millicuries of radon. J. Grant.

Speed of volatilisation of tungsten in presence of salt vapours. H. Alterthum (Z. tech. Physik, 1928, **9**, 285—288; Chem. Zentr., 1929, i, 27).—The volatility of tungsten in a vacuum lamp is increased by spraying the metal with various salts, particularly halogen compounds. Skaupy's view, that with sufficiently volatile addenda reaction takes place in the space between the filament and the wall, as well as at the filament itself, is supported. Interaction at the wall also occurs. A. A. Eldridge.

Penetrating radiation and de Broglie waves. F. T. Holmes (Nature, 1929, **123**, 943).

Active nitrogen. Z. Bay and W. Steiner (Naturwiss., 1929, **17**, 442).—Active nitrogen, apart from the complications arising from the nature of the walls, is not properly described unless the conditions of excitation are accurately specified. Generally, it consists of a mixture of ordinary and metastable (8-volt) nitrogen molecules, with ordinary and metastable (2·37- and 3·56-volt) nitrogen atoms. Its properties are determined by the mixture ratio. The presence of atoms is essential for the afterglow. R. A. Morton.

Reflexion of molecular rays by the lattice of a crystal cleavage plane. O. Stern (Naturwiss., 1929, **17**, 391).—Improvements have been made on the apparatus previously described (this vol., 490), permitting the rotation of the reflecting plane during the progress of the experiment. Using this modification further experiments have been carried out on the reflexion of molecular streams from hydrogen and helium. J. W. Smith.

Paths of charged particles in electric and magnetic fields. W. Bartky and A. J. Dempster (Physical Rev., 1929, [ii], **33**, 1019—1022).

Interpretation of the relativity wave equation for two electrons. N. F. Mott (Proc. Roy. Soc., 1929, **A**, **124**, 422—425).—Mathematical. Although two times (one for each electron) occur in the relativity wave equation for two electrons, all results of physical importance can be obtained by using one time only, putting t_1—t_2 in the wave equation. L. L. Bircumshaw.

Collision problem in the wave mechanics. C. G. Darwin (Proc. Roy. Soc., 1929, **A**, **124**, 375—394).—With the object of determining whether a sharper line of demarcation could be drawn between the particle-like and the wave-like properties of matter, a problem is discussed which is at first sight irreconcilable with a pure wave theory but typical of the behaviour of particles, and it is shown how the correct result does in fact arise naturally from the consideration of waves alone. Certain fundamental questions of the quantum theory are discussed. L. L. Bircumshaw.

Velocity in Dirac's theory of electrons. V. Fock (Z. Physik, 1929, **55**, 127—140).—Mathematical. W. E. Downey.

Velocity in quantum mechanics. D. Iwanenko (Z. Physik, 1929, **55**, 141—144).—The author comments on the views of Fock (cf. preceding abstract). W. E. Downey.

Quantity allowing a new classification of atoms. G. Fournier (Compt. rend., 1929, **188**, 1553—1555).—From a consideration of the α- and β-transformations corresponding with a change in atomic number (*N*), at. wt. (*A*), and Harkins' isotopic number (*A*—2*N*), it is suggested that an atom may be defined by its "filiation capacity" $U=(3A/4—N)$ which decreases by unity with the passage from a radioactive atom to its direct descendant by α- or β-emission. *U*, which is the sum of the α- and β-transformation capacities, *i.e.*, $A/4$ and $(A/2—N)$, respectively, has the same value for those radioactive atoms produced from the same parent atom, and also for an isotope of zinc and one of krypton. J. Grant.

Quantum mechanics of the molecule. H. Ludloff (Z. Physik, 1929, **55**, 304—326).—Mathematical. A. J. Mee.

Displacement of spectra of praseodymium compounds. V. F. Ephraim and P. Rây (Ber., 1929, **62**, [*B*], 1509—1519; cf. A., 1927, 121; 1928, 217).—The displacement of the spectra of praseodymium compounds, previously explained on the basis of the volume factor of the metallic atom, is also interpreted by consideration of the energy relationships of the shared electrons. If a negative atom by attraction of electrons can render strongly positive the atom of a rare-earth metal with which it is combined, the removal of further electrons from its 4_4 zone which conditions the absorption spectrum is rendered more difficult and the greater energy required corresponds with the shorter wave-length of the absorbed light. The violet displacement of the spectra of the rare-earths is the more pronounced as the metallic atom becomes more positive relative to its partner. The hypothesis is considered in detail with respect to a large series of praseodymium salts. The following praseodymium compounds are described: anhydrous *ammonium nitrate*, $(NH_4)_2Pr(NO_3)_5$, decomp. 160°; *nitrate ammonate*, $Pr(NO_3)_3,5NH_3$; *phosphite trihydrate*; anhydrous *hypophosphite*; *naphthalene-2-sulphonate pentahydrate*; *acetylacetonate*; *succinate pentahydrate*, *dihydrate*, and *anhydrous*; *perchlorate*; *chlorate*; *iodate tetrahydrate*; *periodate*, $2Pr_2O_3,3I_2O_7,24H_2O$; *bromide nona-ammonate* and *sesquiammonate*. H. Wren.

Displacement of spectra of neodymium compounds. F. Ephraim and P. Rây (Ber., 1929, **62**, [*B*], 1520—1525).—The displacement of the spectra of neodymium compounds is analogous to that of praseodymium salts, but the spectra are so much more complex that the selection of comparison lines is rendered more difficult. The band at about 430 mμ is most suitable. The following observations are new: *neodymium fluoride*, in reddish-blue and pink varieties which give almost identical spectra, by precipitation of the chloride with hydrofluoric acid; the *nitrate*, $(NH_4)_2Nd(NO_3)_5,4H_2O$ (also anhydrous); *phosphite*, $Nd_2(HPO_3)_3,4{\cdot}5H_2O$; *iodide*; *bromide octa-*, *hexa-*, *tri-*, and *nona-ammonate*. H. Wren.

Lanthanide contraction and spectrum displacement during formation of compounds. Alterations of the samarium spectrum. F. Ephraim and P. Rây (Ber., 1929, **62**, [*B*], 1639—1650; cf. preceding abstracts).—The volume of the equivalent ions of the rare-earth metals diminishes with increasing atomic number, so that in the later members the electrons are more firmly retained by the nuclear charge and consequently their displacement towards the acid residue becomes more difficult. Since the displacement of the spectrum in salts of the rare earths is due to change in the energy of the anion of the electrons of the 4_4 group with the metallic atom, the effect of the change of anion must be less marked with increasing firmness of retention of the electrons to the nucleus. Observations with samarium salts appear to confirm this conclusion. The spectra of praseodymium and, particularly, of samarium salts are unexpectedly sensitive to external influences. Thus very marked lines in the bromide spectrum are found at about 430 mμ which find no analogy in the chloride or other compound and cannot be regarded as due to displacement of the chloride line. Cooling of samarium sulphate octahydrate from the ordinary temperature to −180° alters the spectrum "almost beyond recognition." Most certain comparison is afforded by use of the lines between 400 and 410 mμ and the band in the ultra-violet between 360 and 370 mμ. The course of the displacement with samarium compounds is very similar to that of praseodymium and neodymium compounds.

The stability of the ammonates of the rare-earth metals may be expected to increase with increasing atomic number. This is fulfilled by samarium chloride decammine, which, unlike the ammines of the other rare earths, is stable below 31·5°.

Contrary to Klemm and Rockstroh (this vol., 38) samarium chloride and bromide are colourless or yellowish-white. *Samarium iodide nonahydrate* has been prepared. The degradation of the ammines of samarium chloride and bromide is described in detail. H. Wren.

New ultra-violet band spectrum of hydrogen chloride. B. A. Brice and F. A. Jenkins (Nature, 1929, **123**, 944).—An extended band system observed in the region 2830—3966 Å. from a low-pressure discharge in hydrogen chloride with platinum electrodes, or a discharge in hydrogen with electrodes carrying silver chloride or cuprous chloride, is probably emitted by the HCl^+ ion. The intensity distribution is unusual. A. A. Eldridge.

Absorption spectrum and decomposition of hydrogen peroxide by light. H. C. Urey, L. H. Dawsey, and F. O. Rice (J. Amer. Chem. Soc., 1929, **51**, 1371—1383).—The absorption spectrum of hydrogen peroxide in the ultra-violet is continuous, possibly because, as in the case of the alkali and hydrogen halides, the main intensity of absorption lies towards the violet side of a limiting wave-length separating the continuous and discontinuous spectra. The absorption coefficients appear to be the same for hydrogen peroxide in solution and in the gaseous state. The continuous spectrum shows that the molecule is broken up into two parts; the most probable reaction is $H_2O_2+h\nu=OH(^2P_{1/2})+OH(^2P_{3/2})$, indicating that hydrogen peroxide is a pseudohalogen. This is supported by the fact that water bands due to hydroxyl predominate in the emission spectrum of hydrogen peroxide streaming rapidly through a cool discharge tube. Illumination by the zinc spark spectrum causes water bands to appear in the fluorescence of hydrogen peroxide, indicating that under these conditions the molecules $OH(^2P)$ and $OH(^2S)$ are formed. S. K. Tweedy.

Near infra-red absorption spectra of some aldehydes, ketones, esters, and ethers. J. W. Ellis (J. Amer. Chem. Soc., 1929, **51**, 1384—1394).—Absorption curves for light below 2·5 μ are recorded for a series of carbonyl compounds (cf. A., 1928, 1071). The band at 5·8 μ due to the carbonyl group exhibits a second overtone at 1·9—2 μ; indications of the existence of other overtones up to the fifth were obtained. S. K. Tweedy.

Shift in the 1·14 μ absorption band of some benzene derivatives. J. Barnes and W. H. Fulweiler (J. Amer. Chem. Soc., 1929, **51**, 1750—

1752).—The wave-lengths of the benzene absorption band at 1·14 μ are shifted towards higher values with the progressive introduction of methyl groups into the molecule. Absorption curves are given for toluene, *p*-xylene, and mesitylene in the neighbourhood of 1·14 μ (cf. A., 1927, 918). S. K. TWEEDY.

Infra-red investigations of molecular structure. I. Apparatus and technique. C. P. SNOW and A. M. TAYLOR. **II. Molecule of nitric oxide.** C. P. SNOW, F. I. G. RAWLINS, and E. K. RIDEAL (Proc. Roy. Soc., 1929, **A**, **124**, 442—452, 453—464).—I. Full details are given of the construction and use of a grating spectrometer (a modified form of that used by Sleator and Imes; Astrophys. J., 1919, **50**, 251), designed to give dispersion and resolution sufficient to analyse a fine structure with a frequency difference of one or two wave-numbers. The apparatus is efficient from 2 to 6 μ, and gives accurate results when used for the determination of absolute coefficients of absorption (cf. Robertson and Fox, A., 1928, 1073).

II. The vibration-rotation band spectrum of nitric oxide proves to be a fundamental, the transition being $n''=0\longrightarrow n'=1$, with a definite Q branch with its head at the wave-number 1882·9, and at least 42 rotation bands in each of the P and R branches. No overtone, which should fall in the region of 2·7 μ, has yet been detected. The molecular constants, $I=1{\cdot}64\times10^{-39}$ g.-cm.^{2}, $r_0=1{\cdot}15\times10^{-8}$ cm., and $\omega=1882{\cdot}9$, derived from the separation of the fine-structure bands (3·35 cm.$^{-1}$), correspond almost exactly with those obtained from electronic band spectral data (cf. Jenkins, Barton, and Mulliken, A., 1927, 916). The presence of a Q branch is to be attributed to the gyroscopic motion of the molecule, which is the only common diatomic molecule with an odd number of electrons, and the absence of alternating intensities in bands of low rotational quantum number is also in accordance with theoretical predictions for the gyroscopic diatomic molecule. L. L. BIRCUMSHAW.

Third positive carbon and associated bands. R. K. ASUNDI (Proc. Roy. Soc., 1929, **A**, **124**, 277—296).—The third positive carbon bands, the 3*A* bands (cf. Duffendack and Fox, A., 1926, 777), and the so-called Wolter spurious bands (Z. wiss. Phot., 1911, **9**, 361), now regarded as forming a new system of bands "5*B*"), have been photographed in the first order of a 21-foot grating. In addition, a second new system consisting of bands degraded towards the red has been photographed under small dispersion. A vibrational analysis of these four systems is given, showing that they all have the same final electronic level and that the initial state of the last system is identical with the new level at $\nu=58927$ found by Hopfield and Birge (A., 1928, 1307). The fine structure analysis of the 0—0 and 0—1 bands of the third positive system is given and the usual molecular constants are evaluated. Each band consists of five sub-bands, each with a P, Q, and R branch; the transition involved is ${}^5S\longrightarrow{}^5P$, and for the 3*A* bands it is probably $5P\longrightarrow5P$. L. L. BIRCUMSHAW.

Formation of absorption lines [in stellar spectra]. A. S. EDDINGTON (Month. Not. Roy. Astron. Soc., 1929, **89**, 620—636).—Theoretical.

Effect of temperature of radiation on its photographic action. R. A. HOUSTON (Phil. Mag., 1929, **7**, [vii], 1139—1143).—Negative results were obtained in attempts to detect differences in the photographic action of radiation of different temperatures on photographic plates of different types. F. G. TRYHORN.

Raman effect. A. PETRIKALN and J. HOCHBERG (Z. Physikal. Chem., 1929, **B**, **3**, 405; cf. this vol., 741).—A correction for the previously determined wave-lengths of the Raman lines of some compounds is given. The reference line should be 4046·6 Å. instead of 4358·3 Å., and for five compounds it should be 4077·8 Å. A. J. MEE.

Importance of Raman spectra in the structure [and linking] problems in organic substances. A. PETRIKALN (Z. physikal. Chem., 1929, **B**, **3**, 360—366).—From experimental work on 24 organic compounds of various types it is shown that the linking of hydrogen to carbon can be determined from the Raman spectrum of the compound. The presence of a triple nitrogen linking can be found in the same way. It is easy to separate the compounds into two types according as the carbon is linked to the hydrogen by a single or a double linking. In the case of a $-\overset{\|}{\mathrm{C}}-\mathrm{H}$ linking the wave-length of the Raman lines is 3·25—3·27 μ; for a $-\overset{|}{\underset{|}{\mathrm{C}}}-\mathrm{H}$ linking there are two types: (*a*) giving a wave-length of 3·32—3·43 μ, and (*b*) giving a wave-length of 3·48—3·49 μ for the Raman lines. Compounds with triply-linked nitrogen ($-\mathrm{C}\equiv\mathrm{N}$) give a wave-length of 4·41—4·48 μ. In the case of a compound with a double linking, the binding force of the hydrogen atoms must be greater than one with single linkings. It is supposed that for a triple linking the hydrogen atom would be still more strongly bound. By means of the theory of linear oscillators the binding force and maximum amplitude for single quantum excitation of hydrogen and nitrogen (triply-linked) atoms are calculated. A. J. MEE.

Comparative study of the Raman spectra of some hydrogen compounds. P. DAURE (Compt. rend., 1929, **188**, 1492—1494).—Comparison of the Raman spectra of 40 liquids shows that compounds of the type M–H (where M is a metalloid) are characterised only by lines of λ 278—340 mm.$^{-1}$ (*h*-lines). Compounds containing M–M or C–C linkings may produce lines of 20—196 mm.$^{-1}$, of which the lines 143—146 and 158—162 mm.$^{-1}$ (*l*-lines) are characteristic of single and double linkings, respectively. Lines of λ 166—174 mm.$^{-1}$ obtained in addition to the former type of *l*-lines indicate a C:O group. J. GRANT.

Raman effect in gases. E. L. HILL and E. C. KEMBLE (Proc. Nat. Acad. Sci., 1929, **15**, 387—392).—The results of a study of the Raman effect for diatomic molecules in the case of gaseous hydrogen chloride by Wood, and liquid hydrogen by McLennan and McLeod (cf. this vol., 378) are analysed theoretically, and it is shown that they can be interpreted by assuming new selection rules for the rotational quantum number j, from $\Delta j=\pm1$ to $\Delta j=0,\pm2$, giving rise to a Q, a double R-form, and a double P-form branch, respectively. It is shown that this rule can be derived from quantum mechanics. N. M. Bligh.

Raman effect in acetone. J. W. Williams and A. Hollaender (Proc. Nat. Acad. Sci., 1929, **15**, 421—423).—The Raman effect indicates a means of detecting compound formation in solution. Photographs for acetone were taken and the wave-lengths of the lines determined, the results tabulated, and their theoretical significance was discussed. The positions of a number of infra-red absorption bands were calculated and shown to correspond, as demanded by theory, with absorption bands observed in investigations of infra-red spectra. N. M. Bligh.

Intensity of the secondary scattered radiation (Raman lines). C. Manneback (Naturwiss., 1929, **17**, 364—365).—Theoretical. J. W. Smith.

Raman effect with isomeric organic substances. A. Dadieu and K. W. F. Kohlrausch (Naturwiss., 1929, **17**, 366—367).—The Raman effect has been investigated with series of isomerides and with series of compounds of the same homologous series. Analogy in the spectra is more noticeable in the cases of homologues than with isomerides with different chemical characters. In the case of the xylenes, however, the differences in the relative positions of the methyl groups produce very considerable differences in the spectra. The spectrum of *o*-xylene is very similar to that of toluene. The observations in general agree with the results of infra-red spectroscopy, but the lines which would be anticipated in the region 1800—2800 cm.$^{-1}$ do not appear. J. W. Smith.

Photometric study of the Raman effect. P. Daure (Compt. rend., 1929, **188**, 1605—1606).—The Raman formula for the ratio of the intensities of the positive and corresponding negative Raman lines produced by the same excitation (the mercury line 4358 Å.) has been confirmed within experimental error for the chlorides of arsenic, phosphorus, and carbon, although the results indicate that the value $N = 6{\cdot}6 \times 10^{23}$ gives better agreement. Revision of previous results (A., 1928, 813) has led to the conclusion that the intensity of a Raman line of given characteristic frequency is proportional to the fourth power of the exciting frequency, the energy emitted by the Raman effect attaining in certain cases one tenth of that emitted by molecular diffusion. The majority of the characteristic frequencies of *cyclo*hexane coincide with infra-red absorption frequencies (this vol., 865) although the relative intensities differ for the two phenomena. J. Grant.

Perturbations in band spectra. I. (Miss) J. E. Rosenthal and F. A. Jenkins (Proc. Nat. Acad. Sci., 1929, **15**, 381—387).—Curves are given showing the deviations of lines from the regular formula for the P branches of the (11, 11) and (12, 12) violet CN bands (cf. A., 1928, 566). The perturbations in the a^2S state occur in the normal, instead of as usual in the excited state of the molecule. The observed and calculated frequencies of the Q_1 branch are tabulated in order to detect perturbations. Results are shown to be in accordance with the predictions of Kronig (cf. A., 1928, 1067). N. M. Bligh.

Fluorescence spectrum of oxygen. F. Rasetti (Proc. Nat. Acad. Sci., 1929, **15**, 411—414).—The spectrum of the light from a mercury arc scattered by oxygen at atmospheric pressure and photographed with a quartz spectrograph was found to show, on long exposure, a series of doublets extending from the ultra-violet to the visible region. This appears as a fluorescence spectrum, observed for the first time, excited by the resonance line 1849 Å. of mercury. The relationship of the fluorescence spectrum with the known oxygen bands is determined, and reasons are given for regarding it as a transition case between Raman effect and fluorescence. N. M. Bligh.

Ultra-violet bands of sulphur. J. Gilles (Compt. rend., 1929, **188**, 1607—1608).—A number of unrecorded bands in the ultra-violet spectrum of sulphur vapour (32715—45651), attributed to S_2 molecules, are tabulated (cf. Rosen, A., 1928, 687). J. Grant.

Flame fluorescence and the extinction of fluorescence in gas mixtures at high pressure. R. M. Badger (Z. Physik, 1929, 55, 56—64).—With the exception of the alkali metals the fluorescence of metal vapours in the Bunsen flame appears to be a general phenomenon. Attempts to produce sensitised fluorescence in the flame were unsuccessful. The extinguishing action of mixtures of nitrogen and hydrogen on the mercury fluorescence at high pressures and low temperatures was found to be qualitatively equal to the sum of the effects of the separate gases. J. W. Smith.

Electric moments of some substitution products of benzene and diphenyl. A. Weissberger and J. W. Williams (Z. physikal. Chem., 1929, B, 3, 367—376).—The electric moments of a number of *p*-disubstitution products of benzene were found on the basis of Debye's theory, and analogous compounds of diphenyl were tested to see if similar moments were found for these. Two derivatives of benzene and diphenyl were used in addition, in which the substituents were adjacent. The methods employed were those formerly used by Williams and Krchma (A., 1927, 819) and Williams and Weissberger (A., 1928, 1180). Diphenyl, 4 : 4′-dinitrophenyl, and 4 : 4′-dichlorodiphenyl have no electric moment. The usual formulæ for these compounds will explain this result as well as the arrangements with co-axial, twisted rings. In contrast with these, other *p*-disubstitution products have considerable electric moments. These compounds contain oxygen linkings in which the valency linkings are mutually inclined. Formulæ which would explain this are discussed, and some light is thrown on the structure of diphenyl compounds by this method of investigation. A. J. Mee.

Relation between the electric moment and the *P.D.* at an interface. A. Frumkin and J. W. Williams (Proc. Nat. Acad. Sci., 1929, **15**, 400—405).—Electric moments of molecules calculated from *P.D.* data at interfaces are shown to be approximate only, and a number of reasons for this fact are suggested and discussed. The Gans theory being unsound leads to inaccurate values of the electric moments, which can, however, now be determined by a method depending on the Debye modification of the Clausius–

Mosotti relation. It is concluded that in spite of a striking similarity between inferences drawn from electric moment data and interfacial *P.D.* data, any comparisons between the two can be qualitative only.
N. M. Bligh.

Electric moment of ethylene chloride and ethylidene chloride. P. N. Ghosh, P. C. Mahanti, and D. N. S. Gupta (Z. Physik, 1929, **54**, 711—714).—The permanent dipole moments of ethylene chloride and ethylidene chloride were determined by a null method. The values for the dipole moment obtained were $1\cdot567\times10^{-18}$ e.s.u. for ethylene chloride and $2\cdot045\times10^{-18}$ e.s.u. for ethylidene chloride. The results are discussed with reference to the structure of organic compounds examined previously (cf. Mahanti and Gupta, this vol., 243) and compared with results for methyl iodide, ethyl bromide, ethyl iodide, dichloromethane, and dibromomethane.
J. J. Fox.

Generalisation of stereochemistry. P. Goldfinger (Naturwiss., 1929, **17**, 388).—It is claimed that the conception of chemical stability as the structures in which the packing is densest (cf. this vol., 870) can be applied to general problems of stereochemistry and explains why only a few of the theoretically possible spacial configurations are experimentally realised. This view also explains such phenomena as steric hindrance and the enantiomorphy of *o*-substituted diphenyl derivatives. J. W. Smith.

Chemical combination as an electrostatic phenomenon. VII. A. E. van Arkel and J. H. de Boer (Chem. Weekblad, 1929, **26**, 282—286).—The decrease of ionisation potential with increasing atomic volume in the same sub-group, and the relations of these quantities in the main groups of the periodic table, are discussed, and the theoretical work of Born and Grimm is further examined. S. I. Levy.

Chemical combination as an electrostatic phenomenon. VIII. A. E. van Arkel and J. H. de Boer (Chem. Weekblad, 1929, **26**, 326—330).—A discussion of molecular stability in terms of the electrical properties of atoms. S. I. Levy.

Naphthalene ring and Sugden's parachors. III. S. S. Bhatnagar and B. Singh (J. Indian Chem. Soc., 1929, **6**, 263—266).—The surface tensions of 1-bromonaphthalene, α- and β-naphthols, and α- and β-naphthylamines have been determined by the maximum bubble pressure method. The parachor of the naphthalene ring, calculated from these and previously recorded data, is in better agreement with the value 12·2 (twice the value of the benzene ring) than the previously obtained value 9·2 (A., 1928, 355). H. Burton.

Effects of pressure on the properties of matter. P. W. Bridgman (Proc. Physical Soc., 1929, **41**, 341—360).—The effects of hydrostatic pressures of the same order of intensity as the atomic or molecular forces themselves is considered in the case of gases, liquids, and solids and illustrated graphically for compressibility, thermal expansion, electrical resistance, thermal conductivity, and thermal *E.M.F.*, and by phase diagrams for change of state. The anomaly of compressibility increasing with increasing pressure is shown by certain quartz glasses and by the element cerium. N. M. Bligh.

X-Ray examination of the system anhydrous sodium sulphate–aluminium sulphate. F. A. Steele (Science, 1928, **68**, 156—157).—*X*-Ray examination of the solid obtained by evaporating equimolecular quantities of sodium and aluminium sulphates to dryness near the b. p. and heating at 400° showed a new diffraction pattern which contained no lines characteristic of the individual constituents. Samples richer in aluminium sulphate showed lines due to this substance superimposed on those of the new compound, *sodium aluminium sulphate*; those richer in sodium sulphate also showed these lines together with some new ones due not to sodium sulphate, but to another new compound containing more sodium sulphate than is represented by the formula $Na_3Al(SO_4)_3$. The position of the pattern due to sodium aluminium sulphate remained unchanged in both cases, eliminating the possibility of the formation of a solid solution.
L. S. Theobald.

Soft X-ray emission from various elements after oxidation. L. P. Davies (Proc. Roy. Soc., 1929, **A**, **124**, 268—277).—By means of the apparatus previously described (*ibid.*, 1927, **A**, **115**, 280), a study has been made of the effect of oxidation on the total soft *X*-ray emission from silicon, manganese, iron, cobalt, nickel, copper, molybdenum, palladium, and tungsten. In each case the emission from the oxidised targets was measured before and after bombardment to red heat, and the results are expressed by a series of curves plotting the ratio i_p/i_t against the atomic number of the element at 600, 500, 400, and 300 volts. The effect of oxidation is to level up the efficiencies of the elements, and on the assumption that the oxygen atom simply introduces a common factor into the emitting targets the mean values of i_p/i_t for oxygen are calculated to be 3·61, 3·15, 2·82, and $2\cdot06\times10^{-6}$ at 600, 500, 400, and 300 volts, respectively. L. L. Bircumshaw.

Analysis by X-ray spectroscopy. C. E. Eddy, T. H. Laby, and A. H. Turner (Proc. Roy. Soc., 1929, **A**, **124**, 249—268).—*X*-Ray spectral analysis has the great advantage that it uses a very simple spectrum, the interpretation of which is greatly facilitated by the Moseley relationship. It has the disadvantages that elements of low at. wt. require a vacuum spectrometer, that the excitation of the *K* spectra of elements of high atomic number requires high potentials and highly evacuated *X*-ray tubes, that the technique is difficult, and the apparatus complicated and expensive. It is believed that these difficulties can be considerably diminished. The possibilities of the method have been investigated, and the results obtained in a systematic analysis of the impurities occurring in several samples of zinc and one of manganese are described. The method is found to be sensitive to amounts as small as 0·0001%—*i.e.*, much more sensitive than was indicated by Noddack, Tacke, and Berg (A., 1925, ii, 939), who showed that impurities amounting to about 0·1% could be detected. It is sufficient for the identification of an element to record the α_2, α_1, and β_1 lines of its *K* spectrum, or about five lines of its *L* spectrum, and the known relative intensities of the lines are an additional aid to identification. The optical method (raies ultimes), on the other hand, is capable of detecting impurities down to 0·001%. In this method the number of observable lines from an element tends to diminish as the proportion of the element diminishes, so that the identification of an element may depend on observations of a couple of lines or even only one line in a crowded spectrum. In comparison with analysis by optical spectroscopy, therefore, the *X*-ray method has the advantages that it is more sensitive, that the sensitivity is independent of the elements sought and of the impurities present, and that there is greater certainty in identifying the lines observed. The technique of the construction of an *X*-ray tube and spectrometer to eliminate lines of elements not in the sample under examination is described. L. L. Bircumshaw.

X-Ray investigation of copper–magnesium alloys. G. Grime and W. Morris-Jones (Phil. Mag., 1929, [vii], 7, 1113—1134).—The structure of eight copper–magnesium alloys has been determined by the powder method. Sahmen's equilibrium diagram (A., 1908, ii, 187) was confirmed generally. Two new regions of solid solution were detected, viz., the α-phase, a solution of magnesium in the copper lattice up to approximately 3% of magnesium, and the β-phase, a range of solution extending not more than 2—3% on either side of the composition represented by Cu_2Mg. The α-phase has a face-centred structure with a base varying from 3·610 Å. in copper to 3·634 Å. at the limit of solution. The β-phase has the face-centred spinel structure with eight molecules in the unit cell and a base increasing with the magnesium content from 7·003 to 7·059 Å. The phase Mg_2Cu possesses a hexagonal lattice of invariable dimensions. The unit cell, with $a = 5·281$ Å., has an axial ratio of 3·464 and contains eight molecules. Sahmen's diagram was verified in all other details. Solid solution was not found at the maximum end of the diagram. The lattice constants of copper and magnesium were found to be respectively, $a = 3·610$ and 3·206 Å., with an axial ratio of 1·624.

The results of this investigation agree with those of Westgren and others (A., 1928, 1175) except in the structure assigned to the phase Mg_2Cu.

F. G. Tryhorn.

Determination of the density and shape of sub-microscopic [standard] substances. G. Placzek (Z. Physik, 1929, 55, 81—118).—The behaviour of uncharged metallic particles in heterogeneous electric fields can be used to determine the shape and compact structure of the particles

W. E. Downey.

Multiple absorption and secondary *K*-absorption limits in the Röntgen region. B. B. Ray (Z. Physik, 1929, 55, 119—126).—The secondary absorption edges observed by Nuttall, Lindsay, and Van Dyke can be quantitatively explained on the assumption that a single quantum of radiation can be simultaneously absorbed by two or more electrons. It is further shown that on the hypothesis of free electrons in metals the fine structure absorption edges observed by Kossel should not appear, at least in pure metals. W. E. Downey.

Röntgenographic detection of lattice disturbances in metals. J. Hengstenberg and H. Mark (Naturwiss., 1929, 17, 443).—Deformation can be detected by the measurement of the decrease in intensity of Debye–Scherrer lines with increasing angle of deflexion. The intensity ratio of two lines with different angles of deflexion differs for normal and deformed lattices. Taking the ratio J_{200}/J_{400}, the values for rolled tantalum, tungsten, and molybdenum are all definitely greater than for the unworked metals. Strongly hammered molybdenum shows further increase. R. A. Morton.

Production of the continuous *X*-ray spectrum. A. Sommerfeld (Proc. Nat. Acad. Sci., 1929, 15, 393—400).—The original classical treatment of the angular intensity distribution of the general *X*-radiation of an anticathode was given when observations with solid anticathodes only were available. Following work on mercury vapour and thin foils, data are now available on the stopping process in the single atom. The conditions under which the classical formulæ hold are examined and a method is considered for treating the production of general *X*-radiation by wave mechanics. It is shown that the shift of the intensity maximum will be larger for the longer wavelengths of the continuous spectrum than for the short wave-length limit and that this is confirmed by the experiments of Kulenkampff (cf. this vol., 14).

N. M. Bligh.

Polarisation of the tungsten *L* radiations. P. Kirkpatrick and I. Miyake (Proc. Nat. Acad. Sci., 1929, 15, 418—431).—The $L\alpha_1$, $L\beta_1$, and $L\gamma_1$ radiations of tungsten were examined with an accuracy of 1% by a method using integrated reflected energy measurements, and no polarisation was found for any line. N. M. Bligh.

Absolute intensity measurements with *X*-rays. O. Gaertner (Ann. Physik, 1929, [v], 2, 94—122).—The intensity of filtered radiation (mean wave-length 1·38 Å.) from a tube with a copper anode has been measured by means of an electrically calibrated thermo-element, and compared with the ionisation of gases by the rays. The pressure of gas in the ionisation chamber was so high (for all gases except hydrogen) that the unabsorbing fraction (also measured) was merely a correction factor. The results are expressed in volts per ion-pair: nitrogen, 40·8; air, 36·4; oxygen, 34·4; argon, 29·6. Molybdenum radiation (0·714 Å.) was also used for argon, 29·3 volts per ion-pair being required. Oxygen has a higher saturation potential than nitrogen. R. A. Morton.

X-Ray method for determining the size and shape of crystalline ultramicroscopic particles. M. von Laue (Sitzungsber. preuss. Akad. Wiss., 1929, 227—228).—The breadth of the rings in Debye–Scherrer photographs can be used to determine the size and shape of ultra-microscopic crystalline particles (cf. Brill, this vol., 746; Hengstenberg and Mark, Z. Krist., 1929, 69, 271). R. A. Morton.

Methods for obtaining *X*-ray spectra of gases. A. Björkeson (Z. Physik, 1929, 55, 327—377).—

Different methods for the production of the *X*-ray spectra of gases were investigated. The principle of the methods consists of the collision in a vacuum of cathode rays and a ray from the gas concerned. The first experiments were with sodium. A stream of electrons in an ionisation tube was directed against the opening of a space containing sodium, the whole having been thoroughly outgassed. It was shown that it was possible to obtain *X*-rays from a gas. In later experiments potassium vapour was used, a tube with a hot cathode being employed. It was possible to photograph the *X*-ray spectrum of potassium, but there was only one line of measurable intensity, viz., the $K\alpha$ line. Further experiments were carried out with sulphur in an improved apparatus. The photograph of the *X*-ray spectrum of sulphur had five measurable lines. This was compared with the photograph obtained for copper sulphide. In this case only three lines were obtained, which corresponded with the stronger lines of the sulphur vapour spectrum. A. J. Mee.

Demonstration of polarisation of *X*-rays in a Lilienfeld *X*-ray tube. H. Seemann (Z. Physik, 1929, **55**, 371—374).—Although the blue light of the Lilienfeld tube which gives a continuous spectrum is practically completely polarised, the major part of the decelerated spectrum is not polarised.

A. J. Mee.

Magnetic and crystallographic investigations. Ferric oxide hydrates. W. H. Albrecht (Ber., 1929, **62**, [*B*], 1475—1482; cf. Wedekind and Albrecht, A., 1926, 1196; 1928, 9).—The α-hydrate, identical with goethite, is prepared by oxidation of ferrous hydrogen carbonate solution by (1) hydrogen peroxide, (2) a current of air or oxygen, and (3) prolonged exposure of the solution to air at 37°; substances obtained by method 3 contain ferrous iron. The γ-hydrate, identical with lepidocrocite, is obtained by the oxidation of very dilute ferrous solutions by the equivalent amount of sodium iodate in presence of sodium thiosulphate. Both hydrates are crystalline. The temperature of decomposition of the synthetic hydrates is markedly lower than that of the natural substances. The ratio $H_2O : Fe_2O_3$ is not constant, the water content being usually higher than the theoretical. The magnetic properties show a distinct change with the age of the specimens, whereas determination of water content and Röntgenographic examination indicate stability. Ageing under water causes a diminution of the susceptibility of both hydrates, whereas desiccation at 100° in a current of air diminishes the susceptibility of the α-hydrate but increases greatly that of the γ-hydrate. The natural or synthetic α-hydrate is more stable than the γ-hydrate; dehydration of the α-hydrate affords the α-oxide, whereas the γ-hydrate gives the γ-oxide which passes at a higher temperature into the α-oxide. H. Wren.

Periodic and spiral forms of crystallisation. E. S. Hedges (Nature, 1929, **123**, 837—838).—Spiral crystal growth has been observed with potassium dichromate solution and camphorsulphonic acid (cf. Hughes, this vol., 495).

A. A. Eldridge.

Crystal structure of nickel films. G. P. Thomson (Nature, 1929, **123**, 912).—Films of nickel deposited by sputtering on rock salt in residual gas or argon exhibit a hexagonal structure, *c* 4·06, *a* 2·474 Å., *d* 8·86, differing from that obtained by Bredig and Allolio (A., 1927, 502) by sputtering in hydrogen. A. A. Eldridge.

Crystal structure of barium. A. J. King and G. L. Clark (J. Amer. Chem. Soc., 1929, **51**, 1709—1711).—The structure is a body-centred lattice, each unit cell containing 2 atoms and having an edge of 5·015±0·003 Å. The calculated atomic radius of barium is 2·171 Å. S. K. Tweedy.

Connexion between the zig-zag structure of the hydrocarbon chain and the alternations in the properties of odd- and even-numbered chain compounds. A. Müller (Proc. Roy. Soc., 1929, **A**, **124**, 317—321).—*X*-Ray investigation of a number of carbon chain compounds has shown that the CH_2 groups of the chain molecule lie equally spaced on two parallel rows, the lines between successive centres thus forming a zig-zag (A., 1928, 1176). Whereas in an even-numbered member of a series the lines connecting the two end groups are parallel, this does not hold for the odd members. A number of diagrams are given to show the structural difference between odd and even chain compounds, and the alternations in physical properties (*e.g.*, m. p., molecular volume, and heat of crystallisation of fatty acids, etc.) are readily explained on this basis. Considering molecules in which the two end groups are chemically identical, it is shown that in the actual crystal two molecules should lie along the *c* axis when the crystal is built up of odd-numbered chains, and only one molecule in a crystal composed of even-numbered chains. L. L. Bircumshaw.

Constitution and density of particles in precipitated smokes. H. P. Walmsley (Phil. Mag., 1929, [vii], **7**, 1097—1112).—*X*-Ray analyses have been made by the powder method of the particles electrically precipitated from smokes produced from arcs burning in air between electrodes of various common metals. With the exception of silica particles dispersed from carborundum, the precipitated smokes were found to be crystalline. Readily oxidisable metals gave oxides, whilst gold, silver, and platinum gave metallic smokes. Particles from magnesium, cobalt, nickel, and cadmium arcs were of the simple face-centred cubic monoxides. The dispersion of calcium in the crater of a carbon arc gave calcium monoxide and hydroxide; thallium and chromium gave sesquioxides. Zinc gave the hexagonal monoxide. Other substances may be divided into two classes, those giving more than one substance in the disperse phase (silver, iron, and copper) and those giving polymorphous crystalline modifications (aluminium, arsenic, antimony, lead, and carborundum). Smokes consisting of oxides which are polymorphous usually give the form which is stable at high temperatures. The formation of mixed oxides by copper and iron arcs is attributed to dissociation in the former case, and to low-temperature oxidation in the latter. These results indicate that the formation of the smoke particles is completed at a high temperature and in the immediate neighbourhood of the hot electrodes.

The results for iron are shown to complete the explanation offered by Elihu Thomson of a magneto-optical effect observed with the fume from an iron arc. The densities of the precipitated smoke particles were calculated from the lattice measurements, and shown to be normal. Abnormally low values found by other workers using different methods are attributed to varying modes of aggregation of the particles.

F. G. Tryhorn.

Mesophases (intermediate states of aggregation). I. Nature of mesophases. H. Zocher and V. Birstein (Z. physikal. Chem., 1929, **141**, 413—423).—Theoretical. A general discussion of the nature of states of aggregation. Mesophases occupy an intermediate position between crystals and purely amorphous substances and are characterised by their molecular movements having complete statistical equivalence in certain directions and a definite periodicity in others. The elastic behaviour of nematic and smectic phases (cf. Friedel, A., 1923, ii, 223) is discussed, as well as the *X*-ray interference patterns to be expected in substances in which there is incomplete symmetry of molecular movement. F. L. Usher.

Space lattice of the trigonal modification of acetamide. O. Hassel and N. Luzanski (Z. physikal. Chem., 1929, **B**, **3**, 282—288).—The crystal structure of the trigonal form of acetamide is investigated. The form was obtained by cooling a saturated solution of acetamide in ethyl acetate at 50° to the ordinary temperature over a period of a fortnight. The elementary rhombohedron has an angle of 91° 17′. The length of the edge, *r*, is 8·05 Å. The number of ($CH_3{\cdot}CO{\cdot}NH_2$) groupings in the crystal is six, and the " calculated molecular weight " of the substance will be three times the value indicated by the formula. The substance is thus polymerised in the sense of the term as used by Weissenberg (cf. this vol., 247). In many organic solvents (but not in water) and in the vapour state, acetamide is known to be associated.

A. J. Mee.

Crystal structure of covellite. H. S. Roberts and C. J. Ksanda (Amer. J. Sci., 1929, [v], **17**, 489—503).—*X*-Ray analyses have been made of covellite from Summitville, Colorado, and of synthetic covellite prepared by prolonged heating of copper and sulphur at 500°. A hexagonal unit cell was deduced; a=3·802 Å., c=16·43 Å., and c/a=4·321. It contains six copper and six sulphur atoms in Wyckoff's special position (*d*) and (*f*), and (*a*) and (*e*), respectively, of space-group D_{6h}^{4}, where U_{Cu}=0·093 and U_S=0·126. The structure assigned offers a satisfactory explanation for the perfect basal cleavage, and for the possibility of gliding parallel to the base. F. G. Tryhorn.

Possible reflecting planes in cubic crystals. L. W. McKeehan (Amer. J. Sci., 1929, [v], **17**, 548—556).—A table has been constructed giving the indices, $h\,k\,l$, of possible reflecting planes in cubic crystals, for values of $Q^2=h^2+k^2+l^2$ between 1 and 360. Besides values of Q^2, log $(1/Q)$ to five places of decimals, and $(h\,k\,l)$, a value is given for z, the relative number of planes of each form in holohedral crystals, and those values of Q^2 are also indicated which remain of account in body-centred, face-centred, and diamond-like arrangements. F. G. Tryhorn.

***X*-Ray analysis of cathode-deposited platinum in presence of helium.** R. Salvia (Anal. Fís. Quím., 1929, 27, 285—289).—The *X*-ray diagram of platinum, deposited in presence of helium, shows the existence of a face-centred cubic lattice. Calculations show that there is insufficient space for the entry of the helium atom into the lattice. H. F. Gillbe.

Spinels of bivalent cobalt. Cobaltous aluminate, chromite, ferrite, and cobaltite. G. Natta and L. Passerini (Gazzetta, 1929, **59**, 280—288).—An *X*-ray investigation has been made of the compounds of cobaltous oxide with the oxides of tervalent aluminium, chromium, and iron, obtained by calcining one molecule of cobaltous nitrate with two molecules of the nitrate of the corresponding tervalent metal. These compounds are isomorphous with cobaltous cobaltite previously described (Natta and Strada, A., 1928, 1079) and crystallise in the cubic system with a lattice of the spinel type. The following data have been obtained for the four compounds $CoAl_2O_4$, $CoCo_2O_4$, $CoCr_2O_4$, and $CoFe_2O_4$, respectively: length of unit cell, *a*, 8·06, 8·06, 8·31, and 8·36 Å.; volume of unit cell, 524, 524, 574, and 584×10^{-24} c.c.; $d_{calc.}$ 4·50, 6·11, 5·26, and 5·34; $d_{obs.}$ 4·57, 6·07, 5·14, and 5·19. O. J. Walker.

Stability of atomic space configurations. P. Goldfinger (Naturwiss., 1929, **17**, 387).—It is claimed that the relative stabilities of compounds with different spacial configurations can be predicted from a knowledge of the ionic radii involved, those involving the closest packing being supposed to be the most stable. The theory is supported by several examples of analogous compounds. J. W. Smith.

Examination of the micro-crystals of calcium carbonate in molluscan shells by means of *X*-rays. III. J. Tsutsumi (Mem. Coll. Sci. Kyoto, 1929, **12**, 199—202).—Shells of a number of Japanese molluscs have been examined by means of *X*-rays. In the porcelanous and nacreous layers the calcium carbonate is in the form of aragonite, and in the prismatic layers generally in the form of calcite. The axis of the fibrous arrangement of the micro-crystals is always nearly perpendicular to the surface of the shell, and coincides with the principal axis of calcite or the orthorhombic *c* axis of aragonite.

C. W. Gibby.

Crystal faces developed by etching metallic crystals of aluminium and zinc. B. Fujita (Mem. Coll. Sci. Kyoto, 1929, **12**, 159—163).—The crystallographic indices of the crystal faces produced by etching strained samples of aluminium and of zinc have been measured. The facets of the aluminium crystals are (100) and (110), and of the zinc crystals (0001) and (1010). C. W. Gibby.

Determination of the edge of the lattice of the compound $K_2[PtBr_6]$. M. Mathieu (Compt. rend., 1929, **188**, 1611—1612).—The compounds $K_2[PtBr_6]$ and $K_2[PtCl_6]$ were shown by *X*-ray methods to have the same crystalline structure, and *a* for the former (10·35±0·05) was therefore obtainable from that of the latter and from the mean of the differences in sin θ for the various planes. There are 4 molecules per unit cell. J. Grant.

Crystal properties and conditions of crystallisation. A. Smekal (Z. Physik, 1929, **55**, 289—303).—Crystal properties can be divided into two classes according to whether alteration of the crystal structure through impurities or any other cause leaves the property unchanged or greatly alters it. The former may be called "structure-insensitive" properties, and the latter "structure-sensitive" properties. The "structure-insensitive" properties are governed by the lattice theory of ideal crystals, whereas the others cannot be described by this theory. The "structure-sensitive" properties are wholly or partly "loose-space" properties. "Structure-sensitive" properties are markedly influenced by the conditions of crystallisation, whereas the insensitive are not. The properties of rock salt crystals are taken as examples. Crystals formed from solution, and those formed by the solidification of molten salt at a much higher temperature, show different properties in some respects. Especially is this so with the ionic conductivity of the crystals. The conductivity of crystals from molten salt is almost a thousand times as great as that of crystals deposited from solution. The effect of the crystallisation temperature on the "loose-space" formation is discussed. A. J. Mee.

Distribution of recrystallisation centres in stretched tin strips. P. Beck (Z. Physik, 1929, **55**, 374—377).—The distribution of the first recrystallisation centres in stretched quasi-isotropic polycrystalline tin strips was followed. The number of centres agrees with the Lüders–Hartmann curve. The consequences of this dependence of the number of centres on the deformation are considered.

A. J. Mee.

Property of superconducting metals. J. H. Bartlett, jun. (Nature, 1929, **123**, 869—870).—Polemical against Kapitza (Proc. Roy. Soc., 1929, **A**, **122**, 342). A view which gives a qualitative picture of most of the facts is advanced. A. A. Eldridge.

[**Property of superconducting metals.**] P. Kapitza (Nature, 1929, **123**, 870—871).—A reply to Bartlett (preceding abstract). A. A. Eldridge.

Diamagnetism and crystal structure. C. V. Raman (Nature, 1929, **123**, 945).—The abnormal susceptibility of graphite is intelligible in terms of the peculiar structure of the substance and its electrical conductivity if it is assumed (Ehrenfest) that there are electron orbits circulating round the plane hexagonal rings of carbon in the crystal lattice. Sugar charcoal and lamp-black are not crystalline, and, as anticipated, the susceptibility of amorphous carbon is normal. A. A. Eldridge.

Magnetic properties of isolated atoms of cobalt. L. W. Constant (Nature, 1929, **123**, 943—944).—Platinum containing 5% or 10% of cobalt is ferromagnetic. Determinations of the magnetisation give values corresponding with a magnetic moment per cobalt atom 60% and 25%, respectively, greater than that calculated from the saturation magnetisation of pure cobalt, on the assumption that the platinum atoms do not contribute to the magnetisation. The relation between I and H varies with the heat treatment. A. A. Eldridge.

Magnetic susceptibilities of some inorganic and organic electronic isomerides. S. S. Bhatnagar and S. L. Luther (J. Indian Chem. Soc., 1929, **6**, 303—307).—The value of k in the equation $\chi_m = -2{\cdot}85\times10^{10}kr_1^2$, where χ_m is the molecular susceptibility and r_1 the mean radius of the molecule, increases with the number of atoms in the molecule; thus with 5 atoms $k=4$, with 13 atoms $k=7{\cdot}54$, and with 24 atoms $k=11{\cdot}26$. In the case of groups of isomerides having the same number of atoms in the molecule the values of k increase with the atomic numbers of the groups. A. R. Powell.

Superconductivity of thorium. W. Meissner (Naturwiss., 1929, **17**, 390—391).—Superconductivity has been established in the case of metallic thorium, commencing at about 1·4° Abs. Even slightly above this temperature the resistance is only about 0·017 of that at 0° C., but it drops sharply within 0·2° until at 1·3° Abs. it is less than 0·0001 of that at 0°. It is considered possible that some of the other elements with which superconductivity has not yet been observed (this vol., 250) may show similar effects at temperatures lower than those so far attained.

J. W. Smith.

Triboelectricity of quartz and mercury. L. H. Dawson (J. Opt. Soc. Amer., 1929, **18**, 344—348).—Experiments are described on the electrification produced when the contact between a plane quartz surface and mercury is severed in an atmosphere of air. The electrification is variable unless precautions are taken to exclude water vapour; under these conditions a *P.D.* of about 350 volts is set up corresponding with a charge of about 1 e.s.u. per cm.^{2} of quartz surface. R. W. Lunt.

Quantum theory of dispersion in metallic conductors. R. de L. Kronig (Proc. Roy. Soc., 1929, **A**, **124**, 409—422).—Mathematical.

Photodichroism and photoanisotropy. I. Fundamental phenomena and definitions. II. Fundamental effects of induced photodichroism and experimental method. F. Weigert (Z. physikal. Chem., 1929, **B**, **3**, 377—388, 389—404).—I. When layers of light-sensitive material are illuminated with linearly polarised light they become anisotropic and exhibit the phenomenon of dichroism. The old and new experimental data on these phenomena are discussed. They can be classed together as "photodichroism" and "photoanisotropy"; the effects are very complex. Three different effects appear to be present—primary, secondary, and induced photodichroism (photoanisotropy). Induced photodichroism is a new phenomenon which consists of the presence in a primary photoanisotropic system of new coloured particles which exhibit photodichroism.

II. The phenomenon of induced photodichroism is discussed, and it is stated that it can be obtained pure, and without distortion, in a photographic layer exposed to polarised light with the simultaneous occurrence of primary and secondary photodichroism, if, after exposure, it is fixed and the coloured silver particles are produced by physical development. The experimental method for this new phenomenon is, with few modifications, that previously used for the investigation of primary photodichroism. The application of the new effect to photographic and other problems is given. A. J. Mee.

Kerr effect and molecular structure. H. A. Stuart (Z. Physik, 1929, **55**, 358—370).—The importance of the Kerr effect in the question of molecular structure is shown. An accurate formula for the gaseous state is considered together with a formula for molecular diffraction due to Debye, and discussed from the point of view of its analysis into terms corresponding with certain physical quantities. One term in the Kerr constant is due to the asymmetry of optical and electrostatic polarisation, and the other is due to the dipole moment of the substance concerned. They can be separated by a knowledge of the effect of temperature on the value of the Kerr effect. The possibility of obtaining the amount and direction of the maximum polarisation by means of the Kerr effect is discussed. For dipole-less molecules the agreement between the Kerr constant calculated from the degree of depolarisation and that observed is good. For hydrogen chloride, sulphur dioxide, and ammonia the degree of polarisation is calculated for all three axes. In the case of ammonia there is apparently no axis of symmetry as regards polarisation.
A. J. Mee.

Molecular lengths measured by an optical lever. W. N. Bond (Phil. Mag., 1929, 7, [vii], 1163—1182).—The construction and technique of optical levers are described. The use of such an optical lever enables changes in the thickness of a sheet of mica to be measured with an accuracy of about $1{\cdot}5\times10^{-8}$ cm. On tilting the lever and letting it return gently on to the mica surface apparent changes in the thickness are observed. These changes have been analysed for periodicity. The periodicity, $(10\pm0{\cdot}3)\times10^{-8}$ cm., found for muscovite mica is concluded to correspond with the length of the unit cell of muscovite, which by X-ray measurements is found to be $9{\cdot}95\times10^{-8}$ cm. For steel a periodicity of $(6{\cdot}8\pm0{\cdot}2)\times10^{-8}$ cm. was obtained, agreeing with the X-ray value of $6{\cdot}737\times10^{-8}$ cm. for the cementite cell. It is shown that in each of four experiments described the probability of so marked a periodicity so close to a possible X-ray value is about 1 in 100. The results seem best explained by assuming that the needle tip of the lever ruptures a certain number of the surface layers of the crystal, which flow radially outward until the needle reposes on the first intact layer. If flow did not occur it is estimated that pressures of from 3000 to 180,000 atm. would have occurred at the contact. It is found necessary to conclude that a more or less ordered return flow of a small number of the surface layers occurs when the needle tip is withdrawn. The return flow is attributed to surface tension or cohesion forces. No periodicity was found with selenite, possibly owing to the plastic nature of this substance. F. G. Tryhorn.

Intensive drying of liquids. S. Lenher (Nature, 1929, **123**, 907—908).—The rise of b. p. observed by Baker (J.C.S., 1922, **121**, 568; 1923, **123**, 1223) and Smits (J.C.S., 1924, **125**, 1068) with intensively dried liquids can be observed in a similar apparatus with undried benzene, carbon tetrachloride, and water; hence the effect is attributed to superheating. Conditions favourable to the apparent rise in b. p. have been determined. The b. p. of benzene subjected to a direct-current potential of 450 volts was unchanged (cf. Baker, J.C.S., 1928, 1054). A. A. Eldridge.

***cyclo*Hexanol and the third law of thermodynamics.** K. K. Kelley (J. Amer. Chem. Soc., 1929, **51**, 1400—1406).—The true specific heats of both crystalline forms of *cyclo*hexanol have been determined down to about 15° Abs. The transition of the two crystalline forms occurs at 263·5° Abs.; the heat of transition was determined. The following thermal data are recorded for *cyclo*hexanol: m. p. 297° Abs.; molar heat of fusion at m. p., 406 g.-cal.; molal entropy, 47·5—47·8 g.-cal./1°; molal free energy, —37,500 g.-cal. Both crystalline forms have the same entropy at 0° Abs. S. K. Tweedy.

B. p. of hydrocarbons. B. Nekrassov (Z. physikal. Chem., 1929, **141**, 378—387).—Theoretical. The b. p. of a number of hydrocarbons of various types can be calculated by means of an empirical equation $T=\text{const.}\,(M-\Sigma)/\sqrt{\Sigma}$ (where T=b. p. Abs., M=mol. wt., Σ=sum of various atomic and structural constants) based solely on the structural formula of the compound. Direct comparison of the b. p. is unsatisfactory in discussing the important question of the connexion between b. p. and molecular constitution, since the latter exerts a progressively weaker influence as the mol. wt. increases. For this reason the regularities hitherto found are qualitative. To overcome the difficulty of taking account of the combined effects due to several structural units, the influence of mol. wt. on the b. p. is eliminated by adapting a formula previously deduced (cf. this vol., 497). The influence exerted by different types of structure is represented by numbers, the value for each structure being chosen so as to give the best average result for all compounds in which it occurs. F. L. Usher.

Relation between the b. p. and molecular structure of *cis-trans* ethylenic, saturated, and acetylenic acids. Bourguel (Compt. rend., 1929, **188**, 1494—1496).—The author's values for the b. p./15 mm. of five pairs of these acids are related to the number of carbon atoms they contain (C_4 to C_9) by two straight lines. The ethylenic acids are classified accordingly into those produced by catalytic reduction (*e.g.*, *iso*crotonic acid), and those which undergo isomeric transformation in the presence of iodine (*e.g.*, crotonic acid). The lines for the saturated and acetylenic acids coincide with those for the *cis*- and *trans*-ethylenic acids, respectively. The b. p. and other physical constants depend on the structure as well as on the mol. wt. J. Grant.

Calorimetric absolute measurement of electrolytic conductivity for high-frequency alternating current. E. Justi (Ann. Physik, 1929, [v], **2**, 65—93).—The theory of inductive heating advanced by Fischer and Wever (Mitt. K. W. Inst. Eisenforschung, 69) is confirmed. Encasing the metal in an insulator appears to enhance the skin effect in proportion to an increase in dielectric constant or wall-strength. This implies that the increase in resistance of an insulated wire when carrying high-

frequency current must be ascribed to the high dielectric constant rather than to dielectric loss. When the heating of a body in a high-frequency furnace varies as its conductivity, the rôle of coil length can be treated as a constant factor. In the range of frequencies used in wireless telegraphy no change of electrolytic conduction occurs on a sufficient scale to have any decisive influence on the mode of operation of underground and underwater antennæ.
R. A. Morton.

Derivation of the chemical equilibrium constant. H. Ludloff (Naturwiss., 1929, **17**, 367—368).—Mathematical. J. W. Smith.

Heat balance in crystals in the light of quantum mechanics. T. von Kármán (Naturwiss., 1929, **17**, 385—387).—Mathematical. J. W. Smith.

Experiments in the critical region. III. Energy determinations by means of the Joule effect. K. Bennewitz and N. Andreewa (Z. physikal. Chem., 1929, **142**, 37—66; cf. A., 1926, 1210; 1927, 315).—Two methods of measuring the Joule effect were used, one for medium, the other for low temperatures. The critical isothermals for the gases argon, nitrogen, oxygen, carbon dioxide, and methane were obtained and energy–density diagrams constructed. The use of the Joule effect leads to single values. The application of the Joule–Thomson effect cannot be made, because the values of the specific heat at constant pressure required by it are not definite at the critical point. The critical isotherm for carbon dioxide is higher than that furnished by the *pv* diagram of Amagat. The reduced Joule curves for the critical temperature for argon, oxygen, nitrogen, and methane as a function of the reduced density coincide. The theorem of corresponding states holds. Conclusions are reached respecting the rotation energy, which appears to be practically unchanged for expansion. This point is of importance for a theory of liquids. The Joule curve for carbon dioxide deviates from the normal curve. On the basis of the theorem of corresponding states this indicates a certain association of the carbon dioxide.
A. J. Mee.

Revision of the density of carbon monoxide. L. R. Píre and E. Moles (Anal. Fís. Quím., 1929, **27**, 267—272).—The density of carbon monoxide has been redetermined, the mean value being 1·25011± 0·00005 g. per litre. Taking for the deviation from Avogadro's law $1+\lambda=1{\cdot}00050$, the most probable value of the at. wt. of carbon is 12·006, in accordance with Aston's value of 12·004 derived from the mass spectrograph. H. F. Gillbe.

Densities of the alkaline-earth carbonates. T. Batuecas, A. Rancaño, and J. Ibarz (Anal. Fís. Quím., 1929, **27**, 290—304).—The following densities have been determined by the pyknometer: calcium carbonate, precipitated, 2·690; calcium carbonate, obtained by thermal decomposition of the oxalate, 2·705; calcite, 2·713; aragonite, 2·929; strontium carbonate, precipitated, 3·586; strontianite, 3·712; barium carbonate, precipitated, 4·290; witherite, 4·284. The molecular contraction on formation of the alkaline-earth carbonates increases with increase of the at. wt. H. F. Gillbe.

Density, compressibility, and at. wt. of argon. II. G. P. Baxter and H. W. Starkweather (Proc. Nat. Acad. Sci., 1929, **15**, 441—444).—A continuation of recent work (cf. A., 1928, 343) leads to a corrected value of 1·78394 for the normal density of argon, the previous error being due to a trace of hydrogen. The limiting density is not appreciably affected, and the at. wt. is 39·944. The value found for $(PV)_0/(PV)_1$ is 1·00107. Final purification was accomplished by repeated fractionations from chabazite used as an adsorbent and cooled with liquid air. N. M. Bligh.

Density and cold working. M. Masima and G. Sachs (Z. Physik, 1929, **54**, 666—673).—Measurements have been made of the decrease in density of brass crystals on stretching and of the change of density on annealing such deformed crystals. The interdependence of internal tension, relaxation, and recrystallisation are discussed. J. W. Smith.

Heat equilibrium and temperature. E. Wertheimer (Z. Physik, 1929, **55**, 395—408; cf. *ibid.*, 1925, **32**, 596; A., 1926, 1088; 1927, 1132).—Theoretical. Further evidence is put forward to support the statement made in a previous paper that the temperature of a gas is not kinetic, but can be defined only electromagnetically. In the first place there is thermodynamic equilibrium between a mercury thermometer and the atmosphere only if the air is in radiative equilibrium with a black body. Secondly, the second law of thermodynamics requires radiative equilibrium of the gas with a black body.
A. J. Mee.

Measurement of the relative viscosities of gases and vapours. A. Weissweiler (Physikal. Z., 1929, **30**, 364—367).—A quartz fibre is suspended vertically in a tube and the lower end is turned into a spiral and immersed in oil. A stream of gas or vapour passes through a horizontal tube joined to the vertical tube. The deflexion of the thread is measured on the scale of an ocular micrometer. The magnitude of the deflexion depends on the elastic properties of the fibre and on the streaming velocity, density, and viscosity of the gas. Relative values for the viscosity can readily be calculated; *e.g.*, using air as standard, the viscosity of carbon dioxide at 23° is 0·0001494, in good agreement with results of other observers.
R. A. Morton.

Vapour pressure of mixtures. G. Bredig and R. Bayer (Z. physikal. Chem., 1929, **142**, 92; cf. A., 1927, 1140, 1142).—The empirical equation used in the former work is only a special case of the more general equation put forward much earlier by van Laar. A. J. Mee.

Electrical conductivity, thermal expansion, and hardness of magnesium–zinc alloys. G. Grube and A. Burkhardt (Z. Elektrochem., 1929, **35**, 315—332).—The conductivity of alloys of magnesium and zinc has been measured at 100°, 150°, 200°, 250°, and 300°. On plotting the values against the composition sharp breaks occur at points corresponding with the formation of the compounds $MgZn_2$ and $MgZn_5$, thus confirming the thermal observations of Chadwick (B., 1928, 268). Dilatometric and Brinell hardness curves also show breaks corresponding with these compounds. The conductivity and dilatometric measurements also afford evidence of physical changes in the eutectic mixtures at lower temperatures; these changes have been confirmed by *X*-ray observations.

H. T. S. Britton.

Distribution of austenite in quenched carbon steels. K. Honda and A. Osawa (Sci. Rep. Tôhoku Imp. Univ., 1929, **18**, 47—58).—*X*-Ray examination of quenched steels shows that the proportion of austenite retained in the outer layers of the specimens is greater than that in the inner by an amount which increases with rise of quenching temperature and with increasing carbon content. These results have been confirmed by hardness tests and micrographical examination. A. R. Powell.

Relation between the lattice constant and the density of solid solutions. S. Sekito (Sci. Rep. Tôhoku Imp. Univ., 1929, **18**, 59—68).—The lattice constants for solid solution alloys of copper with aluminium, tin, zinc, and manganese have been determined. From the results obtained the density of the alloys has been calculated using the expression $\rho=\rho_0(100M')/(1+\alpha p)^3[(100-p)M'+pM]$, where M is the at. wt. of copper, M' that of the added element, p the percentage of the latter present, α the rate of change of lattice constant for 1% of added element, and ρ_0 the density of pure copper. The values of ρ for the alloys agree closely with the observed *d*.

A. R. Powell.

Influence of a third metal on the constitution of brasses. I. Lead. O. Bauer and M. Hansen (Z. Metallk., 1929, **21**, 145—151, 190—196).—The effect of adding up to 2·5% Pb on the equilibria in the copper–zinc system has been investigated with alloys containing more than 52% Cu. The solidification of the ternary alloys takes place in a manner analogous to that occurring in the binary lead–copper system. Molten alloys containing more than 67% Cu separate into two phases at 954—850° according to the scheme: $\text{Liquid}_{\text{Cu+Pb}}\longrightarrow\alpha+\text{liquid}_{\text{Pb}}$. With alloys in which β is the primary crystal phase to form, separation of the lead occurs a few degrees below the beginning of the solidification and takes place over a very narrow temperature range according to the scheme: $\text{Liquid}_{\text{Cu+Pb}}\longrightarrow\beta+\text{liquid}_{\text{Pb}}$. In the region of the peritectic reaction $\alpha+\text{liquid}\rightleftharpoons\beta$ the two three-phase equilibria $\alpha+\text{liquid}\rightleftharpoons\beta$ (at 905° in the copper–zinc system) and $\text{liquid}_{\text{Cu+Pb}}\longrightarrow\alpha+\text{liquid}_{\text{Pb}}$ (at 954° in the copper–lead system) unite to form a four-phase equilibrium $\alpha+\text{liquid}_{\text{Cu+Pb}}\rightleftharpoons\beta+\text{liquid}_{\text{Pb}}$ at 886°. In all cases the end of the solidification is at 326°. The solid solubility of lead in both α- and β-brass is less than 0·1%. The ratio Cu : Zn at the boundaries of the various fields in the copper–zinc diagram is unaffected by the addition of lead. A. R. Powell.

Solubility of ammonium hydrogen carbonate in water. E. Jänecke (Z. Elektrochem., 1929, **35**, 332—334).—The following solubilities, expressed in weight percentages, are recorded: 13·8°, 15·2; 24·3°, 19·65; 42·25°, 27·6; 48·4°, 30·8; 54·5°, 33·9; 63·6°, 43·2; 74·8°, 53·2; 81·2°, 56·7; 89·8°, 63·1; 105—111°, 90·0; 108—111°, 95·0; 108°, 100. These numbers are considerably larger than those given by Terres and Behrens (this vol., 141) for temperatures above 20°. H. T. S. Britton.

Solubility of gold in mercury. A. A. Sunier and B. E. Gramkee (J. Amer. Chem. Soc., 1929, **51**, 1703—1708).—The solubilities were determined between 80° and 200° (cf. A., 1928, 470); the results are lower than those previously recorded (cf. Britton and McBain, A., 1926, 474), and, up to 160°, are given by $\log N=-1167{\cdot}4/T+0{\cdot}966$, where N=atomic-% of gold. An accurate method of analysing gold amalgams is described. S. K. Tweedy.

Salting-out of ethyl acetate. N. Schlesinger and W. Kubasowa (Z. physikal. Chem., 1929, **142**, 25—36).—The solubility of ethyl acetate in water, and in 0·1*N*- and *N*-sodium chloride, -potassium bromide, and -potassium iodide solutions was determined at various temperatures. The solubility curves show minima in the neighbourhood of 50—60°. The data obtained were used to test Tammann's theory of salting out. The molecular lowering of solubility, $\lambda=(\log l_0-\log l)/n$, was calculated, and proves to be dependent on temperature, this being in contradiction with Tammann's theory. The dependence on temperature shows that the heat of dissolution of ethyl acetate in water is altered by the addition of salts. The ratio $\Delta l/\Delta c$, where l is the solubility, and c the concentration of water molecules, was also calculated and found to depend both on temperature and concentration. The mean value of $(\lambda n/\Delta\kappa)\times10^4$, where $\Delta\kappa$ is the internal pressure increase, and n is the number of g.-mol. of salt in 1000 g. of water, was evaluated for the three salts, and the values were found to be different. This result is not in agreement with Tammann's theory. The complicated phenomena associated with the lowering of the solubility of non-electrolytes by the addition of salts cannot be explained in the simple way suggested by Tammann. The basic assumptions of his theory appear to be questionable. If two salts are added to the non-electrolyte the effect on the solubility is additive.

A. J. Mee.

Sorption of gas by porous matter. J. Sameshima (Bull. Chem. Soc. Japan, 1929, **4**, 125—128).—A discussion of the mechanism of the sorption of gases by charcoal, silica gel, and chabazite. The author considers that the gas molecules enter into the molecular cavities left by the driving off of water or, in the case of charcoal, by the decomposition of organic matter, forming a homogeneous solid solution.

C. W. Gibby.

Adsorption of electrolytes by crystalline surfaces. II. (Mlle.) L. de Brouckère (J. Chim. phys., 1929, **26**, 250—275).—See this vol., 757.

Catalysis by the action of subdivided metals. IV. Adsorption isotherms of hydrogen, ethylene, and ethane. B. Foresti (Gazzetta, 1929, **59**, 243—258; cf. A., 1925, ii, 692).—The isotherms for the adsorption by catalytic nickel of hydrogen, ethylene, and ethane have been determined at 21° and at low pressures. Contrary to the results obtained by Schmidt (A., 1926, 134), the relation $L=K\sqrt{p}$ (L=c.c. of gas adsorbed, p=pressure) does not hold, except in the case of ethylene, for nickel which has been evacuated at 21°; with a temperature of evacuation

of 255° the agreement is only approximate and restricted to narrower limits. For such pressures as are commonly employed in determining adsorption isotherms it is possible to obtain curves which conform to the above relation, but it is not necessary to assume that the adsorbed gas is in the atomic state. In fact, consideration of Langmuir's theory shows that the relation may be satisfied quite independently of the dissociation of the adsorbed gas, and the results for ethylene show that it holds in the case of molecular adsorption. The shape of the adsorption isotherm obtained with hydrogen indicates that the active surface of the nickel is heterogeneous and consists of at least two types of adsorbing centres, the more active ones being less numerous than the weaker ones.
O. J. WALKER.

Adsorption of Schäffer's sodium naphtholsulphonate and the azo-dye orange-ENL by technically important decolorising charcoals. H. I. WATERMAN, J. GROOT, and M. J. VAN TUSSENBROEK (Kolloid-Z., 1929, **48**, 146—154).—Measurements of the adsorption of orange-ENL by four different kinds of charcoal showed that the adsorptive power decreases in the following order: carboraffin, blood charcoal, purit A, norit T. Similar measurements on the adsorption of Schäffer's β-salt gave the same order.
E. S. HEDGES.

Adsorption as a consequence of polarisation. Adsorption isotherms. J. H. DE BOER and C. ZWIKKER (Z. physikal. Chem., 1929, **B**, **3**, 407—418).—Theoretical. Adsorption of neutral atoms at the surface of an inorganic heteropolar crystal is considered to be due to polarisation of the atoms by the electrostatic field of the lattice ions. The first layer of polarised atoms can then induce similar polarisation in adjacent atoms and thus a multimolecular adsorption film can be formed. The relation between the number of adsorbed layers (n) and the partial pressure of vapour can be expressed by the formula $\log_e p/K_3p_0=K_2K_1{}^n$, where p_0 denotes the saturation pressure, and all three constants have a physical meaning. The formula agrees well with the values obtained by Hüttig and Juza (this vol., 387) for the adsorption of argon by stannic acid.
F. L. USHER.

Electrical condition of hot surfaces during the adsorption of gases. III. Platinum surface at temperatures up to 850°. G. I. FINCH and J. C. STIMSON (Proc. Roy. Soc., 1929, **A**, **124**, 356—365; cf. A., 1927, 1135; 1928, 1087).—Measurements have been made of the surface charge acquired by a platinum sheet when heated to 850° in a vacuum ($p<10^{-5}$ mm.), or in contact with oxygen, hydrogen, argon, nitrogen, carbon dioxide, carbon monoxide, and mixtures of various non-reacting gases. The results show that the surface of a freshly-rolled sheet is in an unstable or "un-normalised" condition until it has been heated alternately in contact with hydrogen and oxygen. A similar effect has been observed with nickel, but not with gold or silver (*loc. cit.*). After "normalisation" at 500° the platinum surface exhibits a positive charge of 0·19 volt either in contact with hydrogen or in a vacuum at the ordinary temperature; "normalisation" at 660° leaves the surface uncharged at the ordinary temperature in a vacuum but still exhibiting a positive charge in contact with hydrogen, but after a similar process at 850° the surface no longer gives a charge at the ordinary temperature. The charge on the "normalised" platinum sheet due to a gas is characteristic of the latter and dependent on the temperature, but is independent of the gas pressure between 1 and 760 mm. It is readily removed by evacuation at 850°. Evidence is cited in support of the view that the vacuum charge is probably a result of structural changes of a permanent nature in the arrangement of the surface atoms of the metal sheet. The experimental results obtained with non-reacting gaseous mixtures enable the gases examined to be placed as follows in order of increasing activity in charging up a hot metal surface: vacuum, argon or nitrogen, carbon monoxide, hydrogen, oxygen. It is suggested that the "normalising" process involves a rearrangement of the surface atoms by a process similar to sintering. The type of adsorption shown by platinum is discussed.
L. L. BIRCUMSHAW.

Stability of unimolecular films. I. Conditions of equilibrium. II. Mechanism of film expansion. III. Dissolution in alkaline solutions. C. G. LYONS and E. K. RIDEAL (Proc. Roy. Soc., 1929, **A**, **124**, 322—333, 333—343, 344—355).—I. A study has been made of the force/area curves of unimolecular films of palmitic acid on the surface of solutions of varying p_H. The results of Gorter and Grendel (A., 1927, 306) could not be reproduced, but Adam's data (A., 1921, ii, 488) are confirmed. The high-pressure region of the curves is practically independent of the nature of the underlying solution, but it increases very slightly in steepness as the solution becomes more alkaline, although the area at zero compression remains unchanged. The more easily compressible form of the film is obtained only at low pressures and on solutions of which the surface layers are definitely acid. The equilibrium spreading pressures of palmitic acid have also been measured on a number of buffer solutions. On acid solutions spreading proceeds slowly, but the rate increases rapidly with increase of alkalinity, and on very alkaline solutions equilibrium is reached practically instantaneously. It is suggested that the attraction of the molecule for surfaces of an acidic nature is very low. This view is confirmed by a study of the latent heat of spreading from a crystal to a unimolecular film on surfaces of varying p_H; the decrease in free energy on spreading over an alkaline surface is greater than for an acid surface. The conversion of a condensed to an expanded film by alteration of the p_H alone has been achieved in the case of pentadecoic acid.

II. Since contraction and expansion of a film coincide respectively with an increase and a decrease in the adhesional forces holding the polar heads to the surface of the solution, it is inferred that expansion is effected by a gradual tilting of the molecules from the close-packed formation existing in the solid condensed state. The solid condensed film is pictured as composed of molecules possessing asymmetrically attached head-groups, which are all tilted to such an angle that the zigzag chains interlock. The two limiting areas of 20·6 and 26·1 Å. observed for long-chain compounds in this state (cf. Adam, A., 1922, ii, 687) are determined by the interlocking of the chains after relative displacements between adjacent molecules of two and four carbon atoms, respectively. The view is advanced that in liquid condensed films the molecules are all freely tilted, but are in general oriented parallel to one another. Such a structure is the two-dimensional analogue of the smectic state of liquid crystals (*e.g.*, ammonium oleate). An approximate measure of the asymmetry of various head-groups is made from the limiting areas observed. The expanded state is regarded as a two-dimensional liquid, and the gradual transition from the solid condensed film through the liquid condensed and expanded films to the vapour film is considered to be due to the gradual increase in the angle of tilt of the film molecules as their mutual interactions become weakened compared with the attractive forces between the chain and the surface. These views are supported by the results of measurements of the force–area curves of heptadecylamine.

III. Measurements have been made of the rates of dissolution of unimolecular films of palmitic acid on buffer solutions of varying alkalinity. The film area is slowly reduced at constant pressure, and curves are drawn showing the rate of decrease in area per unit area of film. The rate of decrease is appreciably enhanced by increasing the alkalinity and raising the temperature, and slightly increased by raising the pressure. If the film pressure is kept constant on solutions of p_H 8·5—13·0, complete dissolution does not occur, but some form of relatively insoluble film is left. It is also found that on a fresh buffer solution the dissolution process is initially autocatalytic in nature, but on repetition of the experiments the curves become constant and reproducible. The new form of film is regarded as a bimolecular leaflet, analogous to the elementary leaflet in a soap bubble, and containing both palmitic acid and sodium palmitate. The lower layer of the bimolecular film is less closely packed than the upper on weakly alkaline solutions, but the closeness of packing increases with increasing alkalinity. Dissolution of a unimolecular film begins at nuclei formed by the adsorption of soap molecules beneath the surface, so that when there is initially no soap in the bulk of the solution the process is autocatalytic; with increasing quantities of soap in solution the process loses its autocatalytic nature, until finally the rate of dissolution is proportional to the area of unimolecular film left on the surface. L. L. Bircumshaw.

Wetting power. E. L. Green (J. Physical Chem., 1929, **33**, 921—935).—A discussion of the subject mainly with reference to spraying with insecticides. L. S. Theobald.

Surface "varnishes" and surface solutions of myristic acid. F. Emir (Compt. rend., 1929, **188**, 1667—1670).—Artificial films (varnishes) of myristic acid produced when a drop of a solution in benzene was placed on a water surface (Devaux) were compressed and the surface tension was shown to fall to a final value (14 dynes/cm.) independent of the initial temperature (between 15° and 20°) and tension (30—50 dynes/cm.), at a rate which increased with rise in temperature. This tension corresponds with the saturation point of the acid and equals that of a film of acid ("surface solution") produced spontaneously, without the use of a solvent, above 15°. After a time there is a further slower and independent fall in the surface tension due to the solubility of the acid, which is greater in water than in 0·05*N*-hydrochloric acid and occurs above 19° and 21°, for the respective liquids. Each mol. occupies 26 Å.^{2} and since the thickness of the film under saturation conditions (16 Å.) is half that of the elementary bimolecular layer of the solid acid determined by *X*-ray methods, Marcelin's hypothesis (A., 1925, ii, 772) is confirmed. J. Grant.

Precipitation and surface tension. J. Wulff (Naturwiss., 1929, **17**, 389).—An iodine precipitate prepared by molecular rays (Dunoyer, Compt. rend., 1911, **152**, 592) is homogeneous only when the collecting plates are free from adsorbed gases and other matter which would cause surface-tension irregularities. When the plate is superficially etched it forms nuclei for the growth of crystals. By weighing the precipitate at various curved glass and silver surfaces a relationship has been established between radius of curvature and thickness of precipitate. This is closely connected with adsorption and diffusion phenomena, and it has been shown that if the radius of curvature is less than 0·4 mm. a multimolecular adsorbed layer is formed. J. W. Smith.

Form of the electrocapillary curves of soap solutions. D. Talmud (Kolloid-Z., 1929, **48**, 164—165).—The interfacial tension between mercury and solutions of potassium oleate at various concentrations has been measured by Gouy's capillary electrometer method and it is shown that the maxima of the electrocapillary curves do not correspond for different concentrations, but undergo a regular drift. The experiments are considered to explain the observation of Frumkin and Donde (A., 1926, 1092) that air-boundaries of similar solutions have a negative charge when the solution is dilute, but a positive charge when concentrated. E. S. Hedges.

Mesophases. (Intermediate states of aggregation.) II. Relative orientation of volume elements of a mesophase. III. Aqueous mesophase of salvarsan. H. Zocher and V. Birstein (Z. physikal. Chem., 1929, **142**, 113—125, 126—138; cf. this vol., 870).—II. In the nematic and smectic state, differences in surface tension are responsible for the orientation of the volume elements parallel, or perpendicular, as the case may be, to the bounding surface. In some instances slight changes in the surface alter the orientation; *e.g.*, if a glass surface is treated with acid, *p*-azoxyanisole usually sets itself perpendicular to the surface, whereas treatment with alkali induces the parallel orientation. Under certain conditions, mesophases may be subjected to much greater elastic deformation than ordinary crystals. The lines representing the direction of the axes from point to point in the distorted condition are convergent or divergent curves in the nematic state, and convergent or divergent straight lines in the smectic state; true points of discontinuity are present in both states.

III. The aqueous mesophase of salvarsan is nematic, the smallest suspended drops being constituted of optically negative volume elements. Addition of sucrose or dextrose gives rise to the same twisted structure and consequent optical activity as has been observed with various other nematic phases. Even when such optically active substances are not added, the twisted structure may often be observed, the direction of twist being in either direction indifferently. R. Cuthill.

Membrane equilibria and selective absorption. N. C. Wright (Biochem. J., 1929, **23**, 352—357).—The results obtained in experiments with unequal distribution of salts on either side of an artificial membrane in systems containing caseinogen and sodium and calcium chlorides could be quantitatively explained if the degree of dissociation of the protein salts and the Donnan equilibrium were taken into account. The presence of one ion influences the distribution ratio of other ions. S. S. Zilva.

Osmotic vapour pressure. II. F. A. H. Schreinemakers (Proc. K. Akad. Wetensch. Amsterdam, 1929, **32**, 392—400).—Mathematical. A substance passes congruently through a membrane when it diffuses from a greater to a smaller osmotic pressure and incongruently when it diffuses in the reverse direction. (See this vol., 759.)

H. F. Gillbe.

Asymmetric induction. I. Asymmetric synthesis and induction. II. Influence of solvent on the optical activity of the menthyl and bornyl esters of α-keto-acids. A. McKenzie and A. G. Mitchell (Biochem. Z., 1929, **208**, 456—470, 471—481).—I. The optical activity of *l*-menthyl phenylglyoxylate is investigated in 15 media in light of three different wave-lengths. Mutarotation was observed in solutions in ethyl, *n*-propyl, *n*-butyl, *iso*butyl, and *l*-amyl alcohols. Both the mutarotation and the asymmetric synthesis of *l*-atrolactic acid from the ester are explained in terms of asymmetric racemisation and induction.

II. With *l*-bornyl and *d*-bornyl phenylglyoxylate no mutarotation was observed in acetone, benzene, or chloroform and the mutarotation when observed was much less than with the corresponding *l*-menthyl compound. In methyl alcohol mutarotation was shown by the *l*-compound, but not by the *d*-compound. By the action of magnesium ethyl iodide on *d*-bornyl phenylglyoxylate, asymmetric synthesis of *d*-phenylethylglycollic acid occurs. With *l*-menthyl pyruvate mutarotation was not observed in methyl alcohol, but occurred in ethyl and *iso*propyl alcohols. With *l*- and *d*-bornyl pyruvate mutarotation was not observed in benzene or methyl alcohol, but occurred in ethyl alcohol, although the rates for the two isomerides were different. P. W. Clutterbuck.

Dispersity and particle size. R. Fürth (Kolloidchem. Beih., 1929, **28**, 293—295).—Existing methods of determining the size of particles in sols are discussed. E. S. Hedges.

Suspensions of kaolin in various media. R. Dubrisay, J. Trillat, and Astier (Compt. rend., 1929, **189**, 41—43).—Suspensions of 10 g. of kaolin in 80 c.c. of lithium, sodium, or potassium hydroxide solution settle at a rate which decreases with increase in the concentration of alkali, passes through a minimum, and then increases (cf. this vol., 26). In concentrated solutions the rate is much greater for potassium than for sodium hydroxide. Calcium and barium hydroxides show analogous results, but the supernatant liquid is turbid for solutions more dilute than $0{\cdot}01N$. Sulphuric, phosphoric, nitric, and hydrochloric acids show little variation with concentration, except for slight anomalies due to dissolution, and no minimum. X-Ray examination of the particles deposited from water and the alkalis showed the microcrystalline ring structure of dry kaolin, although for weaker alkalis the rings were smaller in size.

J. Grant.

Validity of Stokes' law for non-spherical particles. A. H. M. Andreasen (Kolloid-Z., 1929, **48**, 175—179).—Particles of calcined flint were separated into fractions and the velocity of fall was in each case in accordance with Stokes' law.

E. S. Hedges.

Colloidal sulphur. M. Lora and Tamayo (Anal. Fís. Quím. [Tecn.], 1929, **27**, 110—112).—A hydrosol of sulphur of sufficient stability for use as an injection is prepared by adding drop by drop and with stirring 100 c.c. of a hot alcoholic solution of sulphur to an equal volume of a 1% aqueous gelatin solution and heating the mixture under reduced pressure until about one half of the alcohol has evaporated. The resulting sol shows no precipitation within 7 days and the sediment which forms after this period, at least up to 3 months, may be redispersed by agitation.

H. F. Gillbe.

Gold hydrosols of graded particle sizes without addition of nuclei. P. A. Thiessen (Kolloidchem. Beih., 1929, **29**, 122—146).—Experiments have been carried out on the formation of gold nuclei in solutions of chloroauric acid in the presence of potassium oxalate, hydrogen peroxide, carbon monoxide, sodium citrate, potassium thiocyanate, and under the influence of ultra-violet light. The results show that the spontaneous formation of nuclei in the production of gold hydrosols proceeds with a measurable velocity, and that the number of nuclei formed is proportional to the time and depends on the nature of the reducing substance employed. The velocity of the spontaneous formation of nuclei also depends on the temperature and the previous treatment of the reduction mixture. All processes which bring about the hydrolysis of chloroauric acid reduce the velocity of the spontaneous formation of nuclei. The results have been applied to the provision of a method of preparing gold sols with uniform and graded particle sizes. The method is to add a reducing agent which produces very few nuclei to a solution of chloroauric acid, on which a small amount of reducing agent readily producing nuclei is allowed to act for various graded time intervals. E. S. Hedges.

Tartaric acid method for the synthesis of electronegative sols. VIII. Adsorption of *d*- and *i*-sodium tartrate by aluminium hydroxide. A. Dumanski and A. Jakovlev (Kolloid-Z., 1929, 48, 155—156; cf. this vol., 760).—A definite volume of a suspension of aluminium hydroxide was mixed with a definite volume of an aqueous solution of *d*- or *i*-sodium tartrate (concentrations 0·8—0·1N) and after a time the liquid was filtered off and analysed. The *d*-sodium tartrate was more strongly adsorbed than the *i*-sodium tartrate. The possibility of steric hindrance in adsorption is pointed out and it is suggested that an adsorption method for the separation of stereoisomerides of hydroxy-acids may be practicable. E. S. HEDGES.

Dispersity of dissolved cellulose. K. HESS (Kolloid-Z., 1929, 48, 191—193).—A reply to Zeise (this vol., 505). E. S. HEDGES.

Change of physico-chemical properties in the region between colloid and molecular disperse systems. II. WO. OSTWALD and A. QUAST (Kolloid-Z., 1929, 48, 156—164; cf. this vol., 760).—Measurements have been made of the b. p., viscosity, surface tension, and tendency to froth of aqueous-alcoholic solutions of night-blue and crystal-violet. Measurements of the rise in b. p. of solutions of both dyes indicate a maximum in the particle size of the disperse phase in mixtures containing between 40 and 60% of alcohol, in agreement with the results of former diffusion measurements. With the exception of solutions rich in water, the composition of the dispersion medium has little effect on the surface tension of solutions of the dyes, but the viscosity exhibits a minimum and the tendency to froth a maximum for medium concentrations of alcohol. In general, the employment of solvent mixtures of varying composition is a simple means of obtaining sols with systematically graded degrees of dispersion. E. S. HEDGES.

Chemistry of crystalline forms of aggregation. Basic copper compounds. T. LABANUKROM (Kolloidchem. Beih., 1929, 29, 80—121).—An attempt is made to study the crystallisation forms of substances produced under various conditions with the aim of providing a method of characterisation of both the substances and the conditions of formation. A number of basic copper salts were prepared under different conditions and details are given of their macroscopic and microscopic appearance and of their crystallographic and optical properties. Many photomicrographs are included. A large number of compounds usually obtained only in microcrystalline form have been obtained in morphologically well-defined forms, particularly by the slow hydrolysis of normal salts. The mode of formation of single crystals and their mode of union to form aggregates is quite different in different compounds, even when these are similar crystallographically and in chemical constitution. The topochemical reactions of the crystals were also examined and descriptions are given of the various effects. E. S. HEDGES.

Stability of coarse particles in solutions. IV. Formation and removal of liquid sheaths in suspensions of *Bolus alba*. Reversible sol-gel transformation; thixotropism. H. WERNER (Ber., 1929, 62, [*B*], 1525—1534; cf. A., 1928, 584).—Thixotropic properties are exhibited by the flocks and sediment formed by dispersed coarse particles of *Bolus alba* suspended in water containing electrolytes. The suspended *Bolus* particles are not in immediate contact with one another, but each is completely surrounded by a sheath of liquid. The volume of the liquid in the flocks is very great in comparison with the total volume of *Bolus* particles, the ratio varying according to conditions from 2·6 : 1 to 26·6 : 1. Provided that the dispersing medium does not contain strongly adsorbable substances, the liquid in the *Bolus* flocks is essentially unaltered solution. The individual *Bolus* particles and the liquid surrounding them are fixed in the flocks. The mean thickness of the liquid sheath around the individual *Bolus* particles changes, under otherwise similar conditions, with the type and concentration of the electrolyte; the values found vary between 1·0 and 3·4 μ. Based on Stokes' law, a method is elaborated for determining the mean volume of the sinking flocks and the mean mass of *Bolus* in them. Two processes are operative in the production of *Bolus* flocks: (1) the formation of liquid sheaths round the individual *Bolus* particles, and (2) the union of the particles, more or less completely surrounded by liquid, to flocks. The two processes occur to a great extent independently of one another and according to different laws. H. WREN.

Stability of suspensions. III. The velocities of sedimentation and of cataphoresis of suspensions in a viscous fluid. W. O. KERMACK, A. G. MCKENDRICK, and E. PONDER (Proc. Roy. Soc. Edinburgh, 1929, 49, 170—197).—An expression has been obtained for the rate of fall of a spherical particle through a viscous fluid containing a large number of similar spherical particles sedimenting in the same way. A similar expression has been obtained for the velocity of cataphoresis of a single particle in an electrical field when this particle forms one of a large number of similar particles. The result for sedimenting spheres has been extended to sedimenting discs and confirmed by experiments on the sedimentation of suspensions of red blood-corpuscles of various concentrations. Various consequences of these results are discussed, and in particular a simple explanation is obtained of the observation that during cataphoresis in a U-tube, the boundary of the suspension retreating from the electrode tends to become more sharply defined, whilst the other boundary becomes more diffuse. W. O. KERMACK.

Electrical characteristic of solutions, dyes, and biocolloids. R. FÜRTH (Kolloidchem. Beih., 1929, 28, 285—292).—The author discusses the electrical properties of particles of one substance immersed in a medium of another substance, when the particles are of molecular, colloidal, or macroscopic dimensions. A method for the investigation of cataphoresis is described, in which electrodes of poorly conducting material are used in place of metallic electrodes. E. S. HEDGES.

A case of the reversal of adsorption. H. FREUNDLICH and L. L. BURGESS (Z. Elektrochem., 1929, 35, 362—366).—In order to ascertain the effect of the gradual growth of colloidal particles of lead sulphide, and of the consequent diminution in the specific surface, on the amounts of dye which are adsorbed, suitable quantities of a dye were added to

0·1*M*-lead acetate solution which was then treated with 0·1*M*-sodium sulphide in equimolecular proportion. The dyes used were fast-acid-violet 10B and rhodulin-violet. As the particles grow increasing amounts of adsorbed dye are released and pass into the liquid phase, the rate for the acid dye being greater than that for the basic dye.

H. T. S. Britton.

Coagulation of von Weimarn's Au_P sols. I. E. Iwase (Bull. Chem. Soc. Japan, 1929, **4**, 120—125).—The coagulation by sodium chloride and barium chloride of gold sols prepared by the reduction of gold chloride with formaldehyde in vessels of different materials has been investigated. The coagulation numbers varied only slightly.

C. W. Gibby.

Study of the p_H values at which flocculation is produced in sols of arsenious sulphide and of ferric hydroxide. M. Boutaric and (Mlle.) G. Perreau (Bull. Acad. roy. Belg., 1928, [v], **14**, 666—670; cf. A., 1925, ii, 778).—Sols of arsenic trisulphide were mixed with solutions of different acids of varying concentration, and the times of flocculation were determined spectrophotometrically. The p_H of the intermicellary liquid after flocculation was measured with a quinhydrone electrode, as well as the corresponding acid concentration, and curves were drawn from which by extrapolation the p_H and concentration corresponding with infinitely slow coagulation could be found. The limiting value of p_H for a number of acids differing both in strength and basicity was approximately constant, the mean value being 1·22 for a sol containing 1·55 g. of As_2S_3 per litre. With varying concentration of the colloid, the limiting p_H showed a minimum value for intermediate concentrations, less acid being required for very concentrated and for very dilute sols. Similar experiments with a ferric oxide sol (2·18 g. of Fe_2O_3 per litre), using different bases, gave 5·11 as a mean value of the limiting p_H.

F. L. Usher.

Cataphoretic measurements and the theory of the critical potential. H. R. Kruyt and D. R. Briggs (Proc. K. Akad. Wetensch. Amsterdam, 1929, **32**, 384—391).—Observations with arsenious sulphide, selenium, and gold sols show that those univalent cations which are strongly adsorbed and cause flocculation at low concentrations, *e.g.*, strychnine and new-fuchsin, reduce the cataphoretic migration velocity at the complete precipitation concentration to approximately the value which is characteristic of multivalent ions at the corresponding concentration. Powis' rule is therefore valid for such cations.

H. F. Gillbe.

Formation of secondary systems of Liesegang rings. II. M. S. Dunin and F. M. Schemjakin (Kolloid-Z., 1929, **48**, 167—170).—Further experiments (cf. this vol., 645) indicate that the formation of Liesegang rings is more complex than has been supposed, for not only is the space between the ordinary rings occupied by microscopic rings, but the large rings themselves, provided a sufficient number are obtained, can be grouped into periods forming a large-scale ring structure. The experiments were conducted by carrying out the diffusion in tubes 150 cm. in length and leaving them in the dark for 1½ years, and the complex periodicity was observed with rings of silver chromate, silver phosphate, and lead iodide. It is suggested that the precipitation is controlled by three critical concentrations, each of which gives rise to its own periodicity. An analogy is suggested between the existence of "dead zones" exhibited in Liesegang ring formations and the similar dead zones which have been observed in the reception of radio waves and the sound of gunfire.

E. S. Hedges.

Isoelectric point of coproporphyrin and its physiological significance. H. Fink (Naturwiss., 1929, **17**, 388—389).—The isoelectric point of the coproporphyrin occurring in yeast is about p_H 4. This coincides with the minimum solubility, and maximum flocculability and adsorbability. An isoelectric solution examined in short-wave light shows a minimum of light emission, and the fluorescence spectrum takes a mean position between the spectra observed with acid and alkaline solutions. The absorption spectrum shows a similar effect. These observations are applied to the explanation of other phenomena observed with coproporphyrin.

J. W. Smith.

Action of proteins on ferric hydroxide sol. H. Freundlich and G. Lindau (Biochem. Z., 1929, 208, 91—111).—Different proteins have very different effects on a ferric hydroxide sol with sodium chloride as coagulator. Gelatin and trypsin cause coagulation in the absence of salt; egg-albumin first lowers the coagulation value (sensitising action) and then increases it as the amount of protein is increased, hæmoglobin at a given concentration increases the value (protective action). These differences are ascribed to complex formation between the sol and the protein, the complex having a characteristic coagulation value. This is confirmed by the fact that when ferric chloride solution replaces the sol, similar behaviour is observed. These coagulates can be redissolved by dilution with water.

Mixtures of ferric hydroxide sol and protein show a change in coagulation value in course of time; the protective action increases with time at low concentrations and shows an initial decrease followed by an increase at high concentrations of protein. The influence of p_H is small. An explanation of the deposition and dissolution of proteins in plants is suggested.

J. H. Birkinshaw.

Calcium acetate gels. I. P. C. L. Thorne and C. G. Smith (Kolloid-Z., 1929, **48**, 113—125).—The properties of calcium acetate gels have been examined with the aim of obtaining a gelatinous substance of definite chemical composition. The gels were prepared by pouring a saturated aqueous solution of calcium acetate into alcohol, the properties of the product varying with the water content of the alcohol. With larger amounts of calcium acetate, sols of the salt in water–alcohol mixtures are formed. The viscosity of these sols is greater than that of the aqueous solution and is at a maximum when the dispersion medium contains 50% of alcohol. Most of the gels are not stable for more than 24 hrs.: they are opalescent at first and gradually soften with time, small nodules of calcium acetate eventually settling out. In gels which contain a relatively large amount of water, needle-like crystals form radially from numerous crystallisation nuclei, and it is suggested that gelation is an intermediate stage between true solution and crystal formation. The stability of the gels is increased, in some cases to 6 months, by the addition of acetone or various oleates, and in these gels a thread-like structure is visible to the unaided eye. Gels containing sodium oleate exhibit syneresis. Addition of acids or bases produces a decrease in the rate of gelation and the salts of bivalent cations cause a greater retardation than those of univalent cations. The temperature of preparation has little or no influence on the stability of the gels. When dried, the gels become turbid and alcohol is lost, the calcium acetate dissolving in the remaining water; by the addition of alcohol the gel can be formed again. Viscosity measurements indicate that the change from sol to gel takes place between sharp limits.

E. S. Hedges.

Absorption of water by gelatin. III. The sulphate system. (Miss) W. B. Pleass (Biochem. J., 1929, 23, 358—372).—Maximum swelling of gelatin occurs in a solution of sulphuric acid at p_H 3·0. Sodium sulphate in concentrations up to 0·5M in the presence of sulphuric acid suppresses the osmotic swelling of the gelatin due to the acid. At greater concentrations of this salt there is coagulation of the gelatin. Raising the temperature of solutions in the acid zone causes an increased water absorption by the gelatin. The temperature coefficient of swelling is greater the higher is the temperature, but is decreased by an increase in the concentration of sodium sulphate. The osmotic swelling of gelatin in alkaline solutions is suppressed to a greater degree by solutions of sodium sulphate than by equal molar concentrations of sodium chloride or nitrate. At concentrations of sodium sulphate of 0·7M or greater coagulation is induced. At the isoelectric point of gelatin the water absorption in solutions of sodium sulphate is proportional to the logarithm of the salt concentration up to 0·1M. At greater concentrations lyotropic swelling is reduced and coagulation occurs in solutions of greater than 0·7M concentration. In solutions of sodium sulphate of 0·1—1·0M concentration the magnitude of the water absorption of the gelatin is determined chiefly by the sulphate concentration almost independently of the p_H value of the solution. Gelatin in the coagulated condition tends to resist the solvent action of alkaline solutions. Rise in temperature generally causes greater water absorption, the temperature coefficient becoming larger as the temperature rises.

S. S. Zilva.

Swelling of gelatin. W. von Moraczewski and E. Hamerski (Biochem. Z., 1929, 208, 299—327).—The swelling of gelatin increases directly with the concentration of salts and increases with rise of temperature, the more rapidly the higher is the temperature. Dilute hydrochloric and sulphuric acids (below 0·001N) have a smaller swelling power than distilled water, but from this concentration upwards the swelling power increases rapidly, becoming much greater than with salts until maximal swelling is reached at p_H 1·7—1·8 (0·167N), when further increase of concentration causes a decreased swelling power. These two acids at the same normality have approximately the same swelling power. The effect of acetic acid is more similar to that of salts but stronger, the swelling curve following a uniform course. Alcohol and citrate under some conditions have a smaller swelling power than water. Of the anions investigated, thiocyanate has the greatest swelling power and citrate and tartrate least, whilst of the cations, calcium ions have the greatest power. Salt mixtures show additive swelling power. Addition of acid to salt solutions increases, but of salts to acids decreases the swelling power. Non-electrolytes have a considerably smaller swelling power than electrolytes with the exception of carbamide and thiocarbamide, which equal thiocyanate and calcium ions in their swelling power.

P. W. Clutterbuck.

Alteration of surface tension of gelatin with change of p_H and with small electrolyte concentrations. N. Jermolenko (Kolloid-Z., 1929, 48, 141—146).—Measurements of the surface tension of a 0·1% sol of gelatin by the method of capillary rise have shown that a minimum occurs at the isoelectric point at p_H 4·7 and that two maxima occur at p_H 2·85 and 8·3, respectively. These results are in agreement with the observations of Shukov (J. Russ. Phys. Chem Soc., 1927, 1061), but not with those of Johnston and Peard (A., 1925, ii, 659).

E. S. Hedges.

Solid phase relations in swelling. Wo. Ostwald and P. P. Kestenbaum (Kolloidchem. Beih., 1929, 29, 1—79).—Attention is directed to the fact that in most researches on swelling the effect of the "solid phase rule" has been neglected. In general, the specific swelling increases with the ratio of the amount of swelling liquid to the solid phase. In the present paper this relation is extensively studied, both experimentally and theoretically. The effect was observed with agar and with hide powder, and detailed quantitative experiments were conducted with gelatin, using both gravimetric and volumetric methods, the agreement between the two methods being good. Experiments conducted with a constant amount of solid phase or, alternatively, a constant amount of swelling liquid gave results in accordance with the above rule. The effect was further studied not only in pure water, but also in solutions of electrolytes. A close similarity is pointed out between the curve relating the degree of swelling to the amount of solid phase and Kroeker's curves relating the degree of adsorption to the amount of adsorbent. The influence of the solid phase effect is greater at higher temperatures. A theory of the solid phase relations has been developed from experiments on the electrical conductivity and nitrogen determination of the part of the gelatin going into solution on swelling, experiments on swelling in electrolytes, the swelling of electrolyte-free gelatin, and the osmosis of gelatin sols. These experiments lead to the view that, in general, solid phase relations are due to soluble substances in the gel, which dissolve in the swelling water to give a solution the concentration of which is proportional to the amount of solid phase; the solution thus produced affects the course of the swelling. In the case of gelatin in particular, the swelling in pure water depends on the content of calcium sulphate and of degradation products of gelatin. Calcium sulphate hinders swelling and therefore swelling is greatest for large amounts of the swelling liquid, in which the calcium sulphate forms a dilute solution. The theory is well supported by experiments in which substances known to affect the swelling (sodium, calcium, magnesium, and ammonium sulphates, hydrochloric, picric, and sulphosalicylic acids, and tannin) were added: in these experiments the curve representing the solid phase effect was strongly influenced. The most important change was observed in dilute solutions of sulphosalicylic acid (0·16—0·25N) and hydrochloric acid (0·0005 and 0·0003N), where the ordinary solid phase rule was reversed, the greatest amount of solid phase giving the greatest degree of swelling. Curves obtained with some other addition agents (*e.g.*, picric acid) showed a maximum or a minimum. An analogous effect is shown in the taking up of water by a gelatin sol in a collodion bag, where the amount taken up increases every time the outer water is changed in spite of the fact that electrolytes are being removed. It is noteworthy that sols of electro-osmotic gelatin in the osmometer become more viscous in spite of their increasing dilution, indicating that in a sol of gelatin it is insufficient to consider only the osmotic equilibrium, but that solvation and dispersion must be considered also. E. S. HEDGES.

Flotation and p_H. I. Hydrophobic powders. D. TALMUD (Kolloid-Z., 1929, **48**, 165—166).—The powders studied were electrode-carbon and sulphur. These were mixed with a buffer solution of known p_H and one drop of purified petroleum or benzene and shaken; the froth was then separated and analysed. The curves connecting the percentage of flotation with the hydrogen-ion concentration pass through maxima which are close to the region of neutrality.

E. S. HEDGES.

Plastometric studies on the structure of surface layers. A. DE WAELE and G. L. LEWIS (Kolloid-Z., 1929, **48**, 126—131).—Data are adduced to show that in colloid and plastic systems the disperse particles are enveloped in a pseudo-solid layer. A method for determining the ratio of the pseudo-solid phase to the volume of the total disperse phase is described. The thickness of the pseudo-solid layer depends on the radius of the particles and is constant over a wide range of concentration for a given solid–liquid system. Experiments are described which throw light on the properties of the layer. Some abnormalities of plastic streaming are described, which are caused by the adsorption of a solid peptising agent at the surface of the particles. E. S. HEDGES.

Cystine in gelatin-protected noble metal systems. A. STEIGMANN (Kolloid-Z., 1929, **48**, 194—195).—The addition of cystine inhibits the reduction of silver salts in the presence of gelatin and lowers the degree of dispersion of colloidal silver. In absence of gelatin, however, cystine accelerates the reduction and protects rather than coagulates colloidal silver. Similar experiments have been conducted on the preparation of sols of other metals by reduction: in some cases cystine has an inhibiting effect and in others the reverse is true. The influence of cystine on the Ostwald ripening of silver bromide was also investigated and it was found to prevent this process.

E. S. HEDGES.

Special case of syneresis. F. C. JACOBY (Kolloid-Z., 1929, **48**, 171—175).—In technical processes, many dye baths are known to exhibit a type of syneresis, the dye being precipitated as an elastic substance when the temperature is raised and subsequently lowered. This phenomenon has been investigated for the case of benzopurpurin 4B extra. The substance separating does not consist of a homogeneous gel, but is a mass of particles each of which has a gelatinous envelope and contains a sol of the dye. The liquid contained in the envelope is poorer in the dye than the original solution. The favourable effect of the addition of certain agents to the bath has been investigated and it is considered that these determine the velocity of formation and size of particles of the product of syneresis.

E. S. HEDGES.

Expansion and contraction of india-rubber laminæ, the critical "slipping" temperature (Gleittemperatur) and its displacement by additions. M. KRÖGER and W. N. YAO (Z. Elektrochem., 1929, **35**, 358—362).—The deformation of rubber membranes by blowing has been investigated under varying pressures and at different temperatures. Optical properties, such as double refraction, suggest that the deformation is caused by the slipping of molecules over one another. Data are recorded which show the influence of the time allowed for vulcanisation, and of varying quantities of non-vulcanising agents added to the mix, *e.g.*, magnesium hydroxide, aluminium fluoride, and carbon-black. The pressure to be applied to bring about a particular expansion increases with rising temperature, until a certain temperature (the critical slipping temperature) is attained, above which the pressures necessary to cause the change become less and less. The incorporation of carbon in the rubber tends to raise this critical temperature.

H. T. S. BRITTON.

Kleeman's derivation of the law of mass action. R. F. GOLDSTEIN (Phil. Mag., 1929, [vii], 7, 1193—1197).—A proof is given that the van 't Hoff derivation of the law of mass action is not invalidated by the concept of sepro-unstable molecules, and attention is directed to certain fallacies in Kleeman's derivation (A., 1928, 239). F. G. TRYHORN.

Functional form of the constant of mass action and atomic activation. R. D. KLEEMAN (Science, 1928, 68, 462).—Previous work (A., 1928, 955) shows that in a gaseous reaction the law of mass action, as generally formulated, breaks down when the volume is sufficiently increased. The mass action constant is not only a function of temperature, but also of the volume and masses of the constituents. The fate of molecules in a gas depends not only on the chances of encounter, but also on previous encounters with other molecules, when activation may occur. The changes in spectra of a substance with temperature show that they are associated with molecular collisions and their violence. Further, if the pressure in a gaseous system changes continuously, the average activation of any molecule at a given instant probably differs in nature and magnitude from that which obtains at equilibrium. L. S. Theobald.

[Thermodynamic principles.] C. Raveau (Compt. rend., 1929, **188**, 1662—1665).—A criticism of the fundamental principles of thermodynamic theory with special reference to the conception of entropy, Le Chatelier's principle (*ibid.*, 1543) and the relation between the Clausius and Clapeyron equations (Verschaffelt, this vol., 387, 648). J. Grant.

More general formulation of the phase rule. P. Kubelka (Z. Elektrochem., 1929, **35**, 335—337).—A modified form of the phase rule in which attention is paid to forms of energy other than those which are usually considered.

H. T. S. Britton.

Partition of sodium between sodium hydroxide and sodium ethoxide or sodium methoxide in ethyl- or methyl-alcoholic sodium hydroxide solutions. J. M. F. Caudri (Rec. trav. chim., 1929, **48**, 589—592).—From a study of the rates of hydrolysis of phthalide and ethyl acetate in aqueous-alcoholic sodium hydroxide solutions, and the rates of ether formation in aqueous-alcoholic solutions, it is concluded that sodium ethoxide is largely converted into sodium hydroxide on the addition of water to an alcoholic solution. In aqueous methyl alcohol the conversion takes place to a much smaller extent.

C. W. Gibby.

Sodium [hydrogen] maleate: a buffer for the region p_H 5·2—6·8. J. W. Temple (J. Amer. Chem. Soc., 1929, **51**, 1754—1755).—Sodium hydrogen maleate, the preparation of which is described, in presence of sodium hydroxide has a buffer range of p_H 5·2—6·8, giving maximum buffering power in the region where phthalate and phosphate buffers have the least. The compositions of buffers for p_H intervals of 0·2 are recorded. S. K. Tweedy.

Neutralisation of several mineral polyacids. I. and II. L. Malaprade (Ann. Chim., 1929, [x], 9, 104—157).—The theoretical and practical aspects of the study of neutralisation curves of complex acids by measurements of hydrogen-ion concentration or of oxidation potentials are discussed. A platinum or gilt platinum wire (equilibrium being attained much more rapidly with the latter) in a solution of an oxidising acid such as chromic or iodic acid acts as an oxygen electrode, the oxygen pressure (P_{O_2}) and hence the potential depending on the nature of the acid. Since the value of P_{O_2} is independent of p_H it is possible to construct neutralisation curves with oxidising acids by measurement of the oxidation potential during neutralisation. Since the platinum electrode retains its potential for a long period after removal from the acid solution and immersion in another acid of lower oxidation potential, and even after washing with distilled water, accurate and reproducible results are obtained only if the measurements are made with increasing oxidation potentials, since in this case equilibrium is rapidly established. The method was checked by a determination of the neutralisation curve of chromic acid, the results agreeing with those of Margaillan (A., 1914, ii, 57) and Britton (A., 1924, ii, 704), and was then employed to study the curves of iodic and complex molybdic acids (see below). The neutralisation curve of hydrofluosilicic acid has two points of inflexion, the first corresponding with the formation of the salt Na_2SiF_6, which is stable only below p_H 3, and the second with the known decomposition of the anion. Hydroferrocyanic acid gives only one point of inflexion corresponding with the normal salt, and the acid can be titrated using phenolphthalein but not methyl-orange as an indicator. In agreement with the values of the ionisation constants (Abbott and Bray, A., 1909, ii, 660) pyrophosphoric acid shows only two points of inflexion, corresponding with $Na_2H_2P_2O_7$ and $Na_4P_2O_7$, respectively. No evidence for the existence of $NaH_3P_2O_7$ or $Na_3HP_2O_7$ was obtained. The curve for orthophosphoric acid differs appreciably from that of pyrophosphoric acid, and thus by a determination of p_H values it is possible to differentiate between two salts for which the ratio P_2O_5/Na_2O is the same. The conversion of a solution of pyro- (p_H 1·42) into ortho- (p_H 1·64) phosphoric acid by boiling can be similarly followed. Arsenic acid gives a curve similar to that of orthophosphoric acid, but the second point of inflexion is less definite. Iodic acid, in agreement with cryoscopic measurements, shows only one point of inflexion, corresponding with $NaIO_3$, but periodic acid gives two points, corresponding, respectively, with NaH_4IO_6 (p_H 4) and $Na_2H_3IO_6$ (p_H 9·6), the latter suffering slight hydrolysis in solution. There is no indication of the formation of $Na_3H_2IO_6$, although this may be due to its great degree of hydrolysis. Iodates and periodates may be determined in the presence of each other by first titrating the total iodine liberated on addition of acidified potassium iodide solution ($IO_3' \longrightarrow 6I$, $IO_4' \longrightarrow 8I$), and then repeating the titration with the previous addition of mannitol to reduce the periodate to iodate. J. W. Baker.

Neutralisation of several mineral polyacids. III. Neutralisation curves of acid complexes of tungstic and molybdic oxides. L. Malaprade (Ann. Chim., 1929, [x], 9, 159—222; cf. preceding abstract).—A study of the formation of complex acids by the interaction of molybdic and tungstic oxides with phosphoric and silicic acids by measurements of the oxidation potential and by plotting the neutralisation curves by electrometric titration using a hydrogen or quinhydrone electrode, a part of which has been published previously (Malaprade and Travers, A., 1926, 925, 1114). A point of inflexion on the neutralisation curve may correspond with the transition from one acid to another, or the decomposition of the anion. The cases studied in this paper are examples of the latter, the following being a brief summary of the main conclusions. In some cases isolation of the salt corresponding with the point of inflexion was effected. With phosphomolybdic acid, $P_2O_5,24MoO_3,3H_2O$, the first point of inflexion does not correspond with the formation of the normal salt (which is not indicated by an inflexion), but with the salt $P_2O_5,22MoO_3,7M_2O$ (*barium* salt isolated); the second point corresponds with decomposition into the phosphate and molybdate, which is not complete until the end of the neutralisation. The curve for phosphotungstic acid is similar, but the decomposition of the normal salt begins prior to the occurrence of the inflexion. With silicomolybdic acid, $SiO_2,12MoO_3,2H_2O$, the first point of inflexion corresponds with normal salt formation and the second with the beginning of the decomposition (at a higher p_H than that for the phosphomolybdates). A similar curve is obtained with silicotungstic acid, but the second point of inflexion indicates the end of the decomposition of the anion, which is less readily decomposed than the phosphotungstate. Oxidation potential measurements show that in dilute solution periodic acid reacts quantitatively with molybdic acid to yield hexamolybdoperiodic acid, $I_2O_7,12MoO_3,5H_2O$, the first point of inflexion in the neutralisation curve of this acid corresponding with the formation of the normal salt, the second with its decomposition into molybdate and periodate. Monomolybdoperiodates are similarly decomposed, the *potassium* salt, $MoO_3,1\cdot5I_2O_7,1\cdot6K_2O,5H_2O$, being obtained by crystallisation from a solution of 6 g. of periodic acid and 50 g. of potassium molybdate which has been just neutralised (phenolphthalein) with potassium hydroxide. Since in dilute solution metatungstic acid, $(WO_3)_4,H_2O$, does not react with phosphoric or silicic acid either in the cold or at 100°, and only partly in concentrated solutions, it is inferred that phospho- and silico-tungstic acids are formed by interaction of phosphoric and silicic acids with the nascent anhydride WO_3, since metatungstic acid reacts readily under conditions in which it is decomposed into the latter. By analogy this conclusion is extended to the formation of the corresponding complex molybdic acids. The relative stability of phospho- and silico-molybdic acids at various p_H values is discussed, the tendency of the former complex to decomposition being the greater, and a theoretical interpretation of the course of the neutralisation curves is given. Various applications of the results (1) to the detection of complex formation of molybdic acid with mineral and organic acids, polyhydric alcohols, and phenols, (2) to the detection of silica (as silicomolybdic acid) even in the presence of phosphoric acid by addition of a solution of an alkali molybdate to the solution and then acidification (with tartaric acid if phosphates are present, the order of addition being important), and (3) the determination of iodates and periodates in the presence of each other, are described, for details of which the original must be consulted.

J. W. BAKER.

Hydrolysis in solutions of beryllium salts. M. PRYTZ (Z. anorg. Chem., 1929, **180**, 355—369).—The hydrolysis of a series of solutions of beryllium sulphate and chloride at various concentrations has been studied by electrometric titration with *N*-sodium hydroxide. Curves obtained by plotting p_H against equivalents of sodium hydroxide added show three definite divisions: first a continuous rise of p_H with addition of alkali until 1 equivalent of sodium hydroxide has been added; secondly, a flat portion where addition of alkali causes no appreciable change in p_H; and finally a point of inflexion occurring when exactly 2 equivalents of sodium hydroxide have been added in the case of the chloride, or slightly less in the case of the sulphate. Assuming that either $Be^{\cdot\cdot}+H_2O=BeOH^{\cdot}+H^{\cdot}$ or $2Be^{\cdot\cdot}+H_2O=Be_2O^{\cdot\cdot}+2H^{\cdot}$ represents the course of the hydrolysis, the respective hydrolytic constants $K=A_H\cdot C_{BeOH^{\cdot}}/C_{Be^{\cdot\cdot}}$ and $K_0=A_H^2\cdot C_{Be_2O^{\cdot\cdot}}/C_{Be^{\cdot\cdot}}^2$ (where A_H denotes the hydrogen-ion activity) have been obtained from the first part of the curve. When worked out for the addition of 0·5 equivalent of sodium hydroxide, K shows a continuous decrease with dilution of the beryllium salt, whilst K_0 remains sensibly constant. K_0 is therefore accepted as the real constant and the second of the above equations as representing the mechanism. The mean values of K_0 are: for beryllium chloride $1\cdot7\times10^{-7}$, for the sulphate $1\cdot4\times10^{-7}$. The formula of the precipitated beryllium hydroxide is considered to be $Be_2O_3H_2$ (cf. A., 1913, ii, 708) and its solubility product (L) to be $[C_{Be_2O^{\cdot\cdot}}]\times[C_{OH'}^2]$. The mean value of L, calculated for the addition of 1·5 equivalents of sodium hydroxide and using the second part of the titration curve, is $2\cdot9\times10^{-19}$ from measurements in solutions of the chloride, and $1\cdot1\times10^{-19}$ from the sulphate.

F. L. USHER.

Hydration of ions. J. BABOROVSKÝ (Coll. Czech. Chem. Comm., 1929, **1**, 315—318).—Kohlrausch's law of independent ionic migration is not exact for fairly concentrated (N) solutions. Transport, at this concentration, is purely electrolytic and not electro-osmotic, but in more dilute solutions the latter effect increases with increase in dilution. H. BURTON.

Calculation of heat of dilution by Debye and Hückel's theory. G. B. BONINO and V. VAGLIO (Nuovo Cim., 1928, **5**, 115—126; Chem. Zentr., 1929, i, 204).—A more exact interpretation of Debye and Hückel's theory shows that the heat of dilution is the sum of two terms: $U=Ac+B\sqrt{c}$; B is always positive, whilst A may be positive or negative.

A. A. ELDRIDGE.

Internal pressure of strong electrolytes. H. M. EVJEN and F. ZWICKY (Physical Rev., 1929, [ii], **33**, 860—868; cf. A., 1926, 668).—The difference between the thermal properties of dilute solutions and the pure solvent is due to a superposition of a physical effect of the ion on the solvent, or an internal pressure, and a chemical action of the ion on the solvent. The first effect can be calculated by taking account of the ionic atmosphere; the second effect increases linearly with the molar concentration. Satisfactory agreement with experimental results for the thermal expansion and for the compressibility of dilute solutions is obtained. N. M. BLIGH.

Adiabatics of a mixture of liquid and vapour. G. BRUHAT (J. Phys. Radium, 1929, [vi], **10**, 107—114).—Mathematical. F. L. USHER.

Tautomerism of α-diketones. Heat of transformation of tautomerides. H. MOUREU (Compt. rend., 1929, **188**, 1557—1558; cf. this vol., 929).—Calculation of the heats of transformation of the "B" forms of methylbenzyl- and phenylbenzyl-glyoxal into the "A" forms from the heats of combustion and from the relation $Q=\log K_2/K_1\times1\cdot985T_1T_2/(T_1-T_2)$ gives concordant figures of the order of 2·5 kg.-cal./mol. R. K. CALLOW.

Aluminium–copper–nickel system with aluminium as the chief constituent. H. NISHI-

MURA (Suiyokaishi, 1928, 5, 616—626).—The reactions $\text{liq.}\rightarrow\alpha+\text{CuAl}_2+T$, $\text{liq.}\rightarrow\text{NiAl}_3+T$, $\text{liq.}+\text{NiAl}_2\rightarrow\text{NiAl}_3+T$, are said to occur where α is a solid solution containing aluminium as the chief constituent, and T is a ternary compound, considered by Haughton and Bingham (A., 1921, ii, 335) to be Cu_2NiAl_5, but more probably $3CuAl_2,NiAl_3$. The equilibrium diagram is constructed. CHEMICAL ABSTRACTS.

Equilibrium diagram of the iron–molybdenum system. T. TAKEI and T. MURAKAMI (Sci. Rep. Tôhoku Imp. Univ., 1929, 18, 135—153).—The equilibria in the iron–molybdenum system have been reinvestigated by microscopical examination, by the electrical resistance and dilatometric methods, and by magnetic analysis. The γ-field extends to 3% Mo at 1150° and is bounded by a smooth curve joining this point with the A3 and A4 points on the temperature axis. The α-field of solid solution extends to 38% Mo at the eutectic temperature, 1440°, but only to 6% Mo at 20°. The ε-phase consists of the compound Fe_3Mo_2 formed at 1450—1500° by the peritectic reaction, $\eta+\text{melt}\rightleftharpoons\varepsilon$; it forms a eutectic with 38% Mo with the α-phase. The η-phase is the compound FeMo formed by the peritectic reaction, $\text{melt}+\delta'\rightleftharpoons\eta$, at 1540°; it is decomposed at 1500° according to the eutectoid reaction, $\delta'\rightleftharpoons\delta+\eta$. With increasing molybdenum content up to 50% the intensity of magnetisation decreases; the ε and η phases are both non-magnetic. Quenching from a high temperature increases the intensity of magnetisation of alloys containing the α and ε phases at the ordinary temperature; annealing at 700° causes a reversion to the normal magnetic properties. A. R. POWELL.

Use of internal pressure in metallic systems. System lead–antimony–copper. R. A. MORGEN (Science, 1928, 68, 490—491).—The use of internal pressure, m. p. and b. p. data in the prediction of the nature and extent of miscibility gaps in a ternary system and also the effect of compound formation are discussed in relation to the system lead–antimony–copper. L. S. THEOBALD.

System cupric oxide–sulphur trioxide–water. E. POSNJAK and G. TUNELL (Amer. J. Sci., 1929, [v], 18, 1—34).—The equilibrium in the above system at 50°, 100°, and 200° has been investigated by phase-rule methods. The only solid phases encountered were cupric oxide, anhydrous cupric sulphate, and its penta-, tri-, and mono-hydrates, and the basic salts $3CuO,SO_3,2H_2O$, $4CuO,SO_3,3H_2O$, and $3CuO,2SO_3,5H_2O$; no solid solutions were observed. Crystallographic data for these compounds are recorded. R. CUTHILL.

Ternary system $CaO–CO_2–SiO_2$ relative to the setting of mortar. G. F. HÜTTIG and E. ROSENKRANZ (Z. Elektrochem., 1929, 35, 308—314).—The thermodynamics of the reaction $CaSiO_3+CO_2\rightleftharpoons CaCO_3+SiO_2$ at 500—800° are discussed. Experiments show that silica, even when in a specially active form, begins to react with calcium carbonate only when subjected to a temperature of 620°. No reaction occurs at the ordinary temperature between freshly precipitated calcium carbonate and hydrated silica during a period of 6 months, nor when kept for 5 days at either 50°, 100°, or 200°. Analyses of mortars varying in age from 970 to 430 years suggest that they contain chiefly calcium carbonate and silica, and this was confirmed by X-ray observations, which indicate the presence of calcite and quartz but not of wollastonite. H. T. S. BRITTON.

Equilibrium diagrams of the aluminium–antimony–silicon and the aluminium–antimony–copper systems with aluminium as their chief constituent. T. MATSUKAWA (Suiyokaishi, 1928, 5, 596—603).—Only one compound, AlSb, is recognised. The ternary eutectic of aluminium, antimony, and silicon almost coincides with the binary eutectic of aluminium and silicon. The univariant reaction occurring on the liquidus surface is $\text{liq.}\rightarrow\text{AlSb}+\text{Si}$. In the aluminium–copper–antimony (2%, 4%, 6%) system the univariant reactions on the liquidus surfaces are: $\text{liq.}\rightarrow\text{CuAl}_2+\text{AlSb}$, $\text{liq.}\rightarrow\text{CuAl}+\text{AlSb}$, and $\text{liq.}+\text{CuAl}\rightarrow\text{CuAl}_2$. At 585° a new reaction of a non-variant system, $\text{liq.}+\text{CuAl}\rightarrow\text{CuAl}_2+\text{AlSb}$ was found at Sb 2·5, Cu 47, Al 50·5%. The ternary eutectic point almost coincides with the binary eutectic point of the aluminium–copper system. CHEMICAL ABSTRACTS.

Equilibrium between the carbonates and hydrogen carbonates of sodium and potassium in aqueous solution at 25°. A. E. HILL and S. B. SMITH (J. Amer. Chem. Soc., 1929, 51, 1626—1636).—By combining previous data with new observations on the system sodium hydrogen carbonate–potassium hydrogen carbonate–water, the 25° isotherm for the above quaternary system has been determined. A new salt, $K_2CO_3,NaHCO_3,2H_2O$, has been found in the system, but there are no stable salt pairs. S. K. TWEEDY.

The sulphide–sulphate reaction. M. TRAUTZ and S. PAKSCHWER (J. pr. Chem., 1929, [ii], 122, 147—181).—The pressure–temperature curves for the univariant system $ZnS+3ZnSO_4=4ZnO+4SO_2$ have been measured by a static-manometric method. The partial pressure of the sulphur dioxide is 1 atm. at 488°. The roasting of zinc sulphide is discussed from the point of view of the phase rule in the light of the results obtained. The reaction of zinc sulphide with calcium, strontium, or barium sulphates begins at 800—850°. For a pressure of 760 mm. equilibrium is reached at 1130—1137°, 1178°, and 1205°, respectively. It is shown that the reaction may take place in two stages: $4ZnS+3MSO_4=4ZnO+3MS+4SO_2$ and $3(MS+3MSO_4)=3(4MO+4SO_2)$. The heat of the reaction $CaSO_3,2H_2O+H_2O_2\text{ aq.}=CaSO_4,2H_2O+H_2O+81{\cdot}3$ kg.-cal. has been determined calorimetrically. From this is calculated the heat of formation $Ca+S_{\text{rh}}+1{\cdot}5O_2+2H_2O=CaSO_3,2H_2O+284{\cdot}3$ kg.-cal. It is shown that the reaction of sulphide with sulphate to yield oxide and sulphur dioxide can proceed through the intermediate stage of sulphite. Moreover, the assumption of equilibria in the fused state is unnecessary. The reaction can take place in solid phases, as may be deduced from the above heat of formation. R. K. CALLOW.

Chemical equilibria involving reactions between two condensed phases. M. MANNHEIMER

(Amer. J. Sci., 1929, [v], **17**, 534—542).—Theoretical. A general method is derived for judging the reliability of experimental results relating to equilibria between fused salts and metals. The criterion is based on the fact that the points of the equilibrium are located on stoicheiometrically computable curves independent of the special law of mass action, and independent of the true molecular coefficients. The general equations of transformation of the co-ordinate system for change of molecular coefficients are derived. F. G. Tryhorn.

Transport number of aqueous acetic acid. J. W. McBain and C. E. Harvey (Amer. Electrochem. Soc., May, 1929. Advance copy. 12 pp.).—Direct measurements by the Hittorf method have been made of the transport numbers of the ions of aqueous solutions of acetic acid at concentrations from $0{\cdot}1N$ to N and at temperatures from 14·5° to 26·8°. The transport number of the acetate ion is found to have the mean value of 0·108, which seems to be independent of concentration and temperature. The average value calculated from the transport numbers of strong electrolytes is about 3% lower, but the uncertainty of these data is of this order. Determinations of the f. p. and migration ratio of solutions containing acetic acid and sodium acetate give no indication of association of the acetate ion with the undissociated acetic acid molecule to form a complex anion.

H. J. T. Ellingham.

Galvanic electricity and cohesion pressure; "space-energy." R. von Dallwitz-Wegner (Z. Elektrochem., 1929, **35**, 344—349).—The theory previously developed (A., 1928, 483) is amplified to include the *E.M.F.* of galvanic cells, for which purpose the concept of "space-energy," E_r, is introduced, being equal to $R/\delta=10KM/\gamma$ kg. per kg.-mol. (R= gas constant, δ=coefficient of cubical expansion, K=cohesion pressure, γ=density, and M=mol. wt.). By considering the change in space-energy consequent on an adiabatic change, an expression has been derived from which the space-energies of the electrodes of a cell can be found. The theory is tested by considering the Daniell cell and the Bunsen and Grove cells. Explanations are advanced to account for the differences between the calculated and actual values.

H. T. S. Britton.

Effect of air on the potential of the mercury–mercurous sulphate electrode. M. Randall and H. A. Stone (J. Amer. Chem. Soc., 1929, **51**, 1752—1754).—Mercury is soluble in dilute sulphuric acid in the presence of oxygen. The potential of the above electrode in moderately concentrated acid ($0{\cdot}2M$) is negligibly affected by the presence of air.

S. K. Tweedy.

Polarographic studies with the dropping mercury cathode. II. Influence of temperature V. Nejedlý (Coll. Czech. Chem. Comm., 1929, **1**, 319—333).—The temperature coefficients of the deposition potentials for dilute solutions (0·00001—$0{\cdot}01N$) of lead, thallous, indium, cadmium, zinc, and manganous chlorides, ferrous and manganous sulphates, have been determined at 17—98°, and that of hydrochloric acid at −1·5° to 92°. With the exception of thallous chloride the values are negative and the maximum (3×10^{-3}) is shown by hydrogen. The diffusion currents generally increase with rise of temperature, but if heating at 100° is prolonged, a gradual decrease is observed. This diminution is most marked in about $0{\cdot}0001N$-solutions. Maxima on the current–voltage curves are observed: these appear at the lower temperatures with 0·001—$0{\cdot}01N$-solutions, and at about 100° with more dilute solutions. It is presumed that increased adsorption of the salt on the glass surface occurs when a dilute solution of a salt is heated, whereby the solutions become more dilute. H. Burton.

Thermodynamic study of lead monoxide. F. Ishikawa and E. Shibata (Sci. Rep. Tôhoku Imp. Univ., 1929, **18**, 109—119).—The *E.M.F.* of the cell Pb amalgam|PbO, NaOH|H_2 has been measured at various temperatures and by combining the results with existing data the following thermodynamical quantities have been calculated: $PbO(solid)+H_2$ (1 atm.) = Pb(solid) + H_2O(liq.) − 17,017 g.-cal., the change in free energy at 25° being −11,639 g.-cal.; Pb(solid) + $0{\cdot}5O_2$ (1 atm.) = PbO(solid)−51,253 g.-cal., the change in free energy being −44,921 g.-cal.; $Pb^{++}+2OH^-=PbO$ (solid)+H_2O(liq.) with a change of free energy of −20,941 g.-cal. The entropy of lead monoxide at 25° is 18·89 units and its dissociation pressure $1{\cdot}52\times10^{-66}$ atm.; the product $(Pb^{++})(OH^-)$ at 25° is $4{\cdot}55\times10^{-16}$. A. R. Powell.

Cells of molten electrolyte. Cell: copper oxide–molten sodium hydroxide–zinc. G. I. Costeanu (Compt. rend., 1929, **189**, 35—37).—Such cells are produced by placing a stick of zinc, and a moulded electrode of copper oxide paste dried at 1000° under oxidising conditions, in molten sodium hydroxide previously heated at 400° for 4 hrs. in a closed nickel crucible to expel water. Their action depends on oxidation of zinc by the alkali, and reduction of the copper oxide by the hydrogen liberated. There is a fall in potential during the first 30 min. owing to the porosity of the copper oxide electrode, followed by a gradual rise to a final constant value of 1·322 volts. In an atmosphere of nitrogen the *E.M.F.* was 1·200 volts, rising to 1·322 after depolarisation by the addition of sodium peroxide.

J. Grant.

Variations of *E.M.F.* developed [by metals] in contact with aqueous solutions of electrolytes of varying p_H values and salinities. F. Vlès and A. Ugo (Compt. rend., 1929, **188**, 1550—1552).—In general, the potential–time curve of a metal or an alloy in contact with aqueous solutions of potassium chloride of various concentrations, and adjusted by acid or alkali to various p_H values, shows maxima or minima according to the previous treatment of the electrode, and attains a final value which is determined by certain critical values of p_H and p_x (isopotential points). From the nature of the observed changes in p_H of the solution in certain cases it is considered that the isopotential point is analogous to the isoelectric point of an ampholyte. J. Grant.

Conceptions of electrical *P.D.* between two phases and the individual activities of ions. E. A. Guggenheim (J. Physical Chem., 1929, **33**, 842—849; cf. Taylor, A., 1927, 1144).—The view is put forward that "the electric *P.D.* between two points in different media cannot be measured and has not yet been defined in terms of physical realities" and hence has no physical significance. The electrochemical potential, defined as $\bar{\mu}_i=\mu_i+\varepsilon_i\psi$, where ψ is the electrostatic potential of an ion of type i and charge ε_i, and μ_i is the chemical potential, has a real physical significance. The phenomena of diffusion, partition between two media, membrane equilibria, cells with and without liquid junctions, and rates of reaction are completely described in these terms or in such linear combinations of μ_i as can be expressed or defined in terms of $\bar{\mu}_i$; in no case can μ_i or ψ occur separately. Only such combinations of $\bar{\mu}_i$ have physical significance. L. S. THEOBALD.

Current density–potential curves in the region of residual currents. E. LIEBREICH and W. WIEDERHOLT (Z. Elektrochem., 1929, **35**, 367—368).—Attention is directed to the fact that the form of the residual current–potential curve depends on the way in which the current is actually measured—whether the ammeter is placed in the chief circuit, as was the case in the previous work of the authors (A., 1928, 483), or whether it is placed in a circuit including the experimental cell (cf. Müller and Konopicky, this vol., 269). Curves are given showing the differences obtained with a silver cathode in 0·02*N*-sulphuric acid against platinum. Oxidising agents have an effect on the residual current similar to that observed by Müller and Konopicky with oxygen. H. T. S. BRITTON.

Electrolytic polarisation due to retarded crystal growth. H. BRANDES (Z. physikal. Chem., 1929, **142**, 97—112).—When a solution of a metallic salt is electrolysed with a bright platinum electrode the ions liberated are not adsorbed, but pass into the Helmholtz double layer, and the electrode behaves as a condenser, the *P.D.* being directly proportional to the quantity of electricity brought up. If, on the other hand, the ions are deposited on a crystalline electrode of the same metal, depolarisation occurs owing to the ions gradually becoming embodied in the lattice. The depolarisation is proportional to the polarising *P.D.*, but the quotient of the two quantities varies considerably with the temperature, corresponding with the heat of activation required for ionic conduction over the electrode surface. R. CUTHILL.

Theory of passivity. V. Influence of coating layer on the potential of a metal. W. J. MÜLLER (Monatsh., 1929, **52**, 53—58).—The magnitude of the local current in the closed system metal–electrolyte–coating layer is $i=e/(w_1+w_2)$, where $e=E.M.F.$ of the system, w_1=resistance in the pores of the layer, and w_2=resistance in the layer. The apparent potential, iw_1, must be deducted from the metal potential in order to give the electrometrically determined potential. This is designated as the correction coefficient and its magnitude is determined by the expression $A=F\kappa^1/\{F\kappa^1+(F_0-F)\kappa\}$, where F is the coated surface, F_0-F the surface of pores, κ^1 the specific conductivity of covering layer, and κ the specific conductivity of the electrolyte in the pores. The calculated values of this coefficient for various thicknesses and conductivities of layer and electrolyte show that increased coating increases the value in all cases; for equal values of coating and electrolyte conductivity the coefficient increases with the conductivity of the layer, whilst for equal values of coating and layer conductivity it increases with decreased conductivity of electrolyte. A comparison of the results with the previously found values for the potential of coated aluminium electrodes (Müller and Konopicky, this vol., 269) gives plausible values for the degree of coating. H. BURTON.

Electrolytic oxidation of various organic substances. C. MARIE and G. LEJEUNE (J. Chim. phys., 1929, **26**, 237—249; cf. A., 1928, 1102).—The effect of adding varying quantities of primary aliphatic alcohols (methyl, ethyl, propyl, butyl, and amyl) on the current–potential curves for the electrolysis of sulphuric acid and sodium hydroxide solutions has been studied using anodes of platinum, gold, and nickel. With a solution of sodium hydroxide containing the primary alcohol electrolysis commences at about 0·6 volt (*P.D.* between electrodes). As the potential is increased the current rises rapidly, drops again to a very low value, and finally increases rapidly at 1·6 volts. In the absence of a depolarising substance electrolysis commences only at 1·8 volts. The preliminary unstable region in the current–*P.D.* curve, when a primary alcohol is present, is ascribed to reduction at the anode of the unstable oxide PtO_3 to the stable form PtO_2 and formation of the aldehyde. Addition of the primary alcohols to a solution of sulphuric acid also produces an unstable region in the current–*P.D.* curve, but the final rapid increase of the current commences at 1·1 volts instead of at 1·6 volts. The formation of aldehyde occurs only if the anode is in the state which corresponds with the unstable region on the curve. With a gold anode in acid and in alkaline solution, and with a nickel anode in alkaline solution, there is no unstable region in the current–*P.D.* curve, when alcohols are added to the solution, and the curves are practically normal. The effect of other organic substances, *e.g.*, *iso*propyl alcohol, aromatic alcohols, and amines, is also described. The nature of the anode is important in oxidations which take place when the electrode is in the unstable state, but since this condition cannot ordinarily be maintained, the only influence of the nature of the anode metal is to determine the value of the anodic overvoltage. O. J. WALKER.

Reaction velocity, concentration, and activity. A. SKRABAL (Z. physikal. Chem., 1929, **B**, **3**, 247—270).—Theoretical. The theory put forward by the author (Monatsh., 1929, 51, 93) is compared with that of Brönsted. The author's theory assumes that in general there are two types of intermediate products: (*a*) "Arrhenius intermediate products," which are in equilibrium with the initial reactants, and (*b*) "van 't Hoff intermediate products," which are in equilibrium with the end-products of the reaction. The latter class of substances is more unstable than the former, and their concentration will be smaller. The "van 't Hoff" intermediate products correspond with Brönsted's "unstable critical complexes," whilst the Arrhenius products correspond with Brönsted's "intermediate stable complexes." In the first place the velocity of the fundamental reaction $A \rightleftharpoons B$ is considered. Then the velocity of the reaction $A \rightleftharpoons Z \rightleftharpoons B$, in which Z is an intermediate product, is calculated, equations being obtained for the cases where Z is stable or unstable. By comparing the final result with Brönsted's equation it is found to be in agreement, showing that the reaction velocity is directly proportional to the activities of the reacting substances and inversely proportional to the activity coefficients of the unstable intermediate products. There is, however, a difference in so far as according to Brönsted the velocity coefficient of the forward reaction is equal to that of the reverse reaction. The author states that they are different. The analysis of velocity coefficients is then attempted. The general equations which are derived for any media and activity coefficients when the medium is made constant, and when the activity coefficients are constant, become identical with the equations of classical chemical kinetics, and the equations for the intermediate reactions then become identical with those of Brönsted. A. J. Mee.

Kinetics of the reaction $2NO+O_2=2NO_2$ at low pressures and under the influence of a strong magnetic field. G. Kornfeld and E. Klingler (Z. physikal. Chem., 1929, B, 4, 37—66).—A special membrane manometer was used for the pressure measurements. The experiments show that at low pressures (down to below 1 mm. total pressure) the reaction $2NO+O_2=2NO_2$ is termolecular. There was good agreement between the results, the mean value of the constant for twenty sets lying between $2{\cdot}8\times10^4$ and $3{\cdot}3\times10^4$. This is in good agreement with the value obtained by Bodenstein for higher pressures. The reaction is termolecular over very wide changes of the concentrations of nitric oxide and oxygen. The effect of a magnetic field was also studied. There are no changes in the course of the reaction. A. J. Mee.

Ignition pressures of phosphine mixtures. M. Trautz and W. Gabler (Z. anorg. Chem., 1929, **180**, 321—354).—A summary of previous work on the ignition of gas mixtures by expansion is given. New experiments have been carried out to ascertain the influence of the wall material, composition of the mixture, and temperature on the ignition pressure of mixtures of phosphine with oxygen. In general, such mixtures show a definite range of pressure over which spontaneous ignition occurs, the range becoming narrower as the partial pressure of water vapour and the proportion of oxygen increase. Ignition occurs on lowering the pressure slowly to a critical value, but it is often possible by rapid diminution of the pressure to overstep the ignition range, and in such cases ignition can be produced by a slow increase of pressure. The ignition pressures of mixtures of different composition were not noticeably affected by varying the nature of the walls of the containing vessel or by introducing nickel, copper, or iron foil. When the gases were separately dried by cooling at −80° spontaneous ignition occurred on mixing at the ordinary pressure. With mixtures in which the partial pressure of water vapour exceeded 6 mm. ignition could not be produced by expansion when the proportion of oxygen was greater than 0·5 vol., and with increasing moisture content a still higher proportion of phosphine was required before the mixture could be caused to ignite. Within the range over which ignition could be produced the ignition pressure was found to rise with decreasing moisture content and with decreasing ratio of oxygen to phosphine. Admixture of nitrogen, nitrous oxide, hydrogen, carbon monoxide, carbon dioxide, or ammonia lowered the ignition pressure slightly. All the above experiments were carried out at the ordinary temperature. The ignition pressure increased with rise of temperature. In all cases ignition was preceded by the formation of a phosphorescent mist which was electrically conducting. Mixtures of oxygen and methylphosphine could not be ignited by expansion at the ordinary temperature, and addition of the last-named substance to the phosphine mixtures greatly lowered the ignition pressure. F. L. Usher.

Decomposition of alkali carbonates in boiling aqueous solution. II. B. L. Vanzetti and A. Oliverio (Gazzetta, 1929, **59**, 288—300; cf. this vol., 661).—From a study of the various electrolytic and hydrolytic equilibria which can occur in dilute aqueous solutions of alkali carbonates it is to be expected that almost complete transformation into the alkali hydroxide will take place by continued boiling of the solution for several days, if the carbon dioxide is removed from the gaseous phase by a current of an inert gas or of the vapour of the solvent. By boiling 0·2*N*- and 0·4*N*-solutions of sodium carbonate, up to 74% of the carbonate was changed into hydroxide in about 6 days; with a 0·2*N*-solution of potassium carbonate 65% decomposition was obtained in 5—7 days. Decomposition occurred both by passing an inert gas (hydrogen or air) through the boiling solution, as well as by reflux distillation with exposure to the atmosphere and by steam distillation. By distilling in a vacuum the decomposition is no longer noticeable owing to the decreased hydrolysis at the lower temperature. The nature of the vessel does not have much effect, as similar results were obtained with glass and with silver vessels. The amount of carbonate transformed into hydroxide is proportional to the square root of the time. O. J. Walker.

Decomposition of lithium carbonate in boiling aqueous solution. III. B. L. Vanzetti and A. Oliverio (Gazzetta, 1929, **59**, 300—304; cf. preceding abstract).—With a 0·27*N*-solution of lithium carbonate 71% decomposition to hydroxide was obtained in about 10 days; the velocity of decomposition is in this case somewhat slower than in the case of sodium and potassium carbonates. The percentage decomposition is again proportional to the square root of the time. O. J. Walker.

Decomposition of mercurous chloride in concentrated solutions of other chlorides. T. W. Richards and M. Françon (J. Physical Chem., 1929, **33**, 936—950).—The decomposition of mercurous chloride in concentrated solutions of lithium, potassium, and cæsium chlorides at 25° has been investigated. The order of increasing effect is lithium<

potassium<cæsium chloride. The whole question of the effect of solutions of various chlorides on mercurous chloride is discussed, together with the irregularities of the calomel cell. L. S. Theobald.

Velocity of autocatalytic decomposition of α-bromopropionic acid in aqueous solutions. J. Zawidzki and J. G. Zawidzki (Rocz. Chem., 1929, 9, 211—245).—See this vol., 34.

Thermal reaction between potassium oxalate and mercuric chloride. W. E. Roseveare and A. R. Olson (J. Amer. Chem. Soc., 1929, **51**, 1716—1724).—The kinetics of the thermal reaction $2HgCl_2+C_2O_4''=Hg_2Cl_2+2Cl'+2CO_2$ was investigated at 100° and 120° in neutral aqueous solution in the dark. The reaction is of the first order with respect to the mercuric chloride concentration under all conditions, the lowering of the rate on addition of chloride ions being due merely to the effect of the ions on the concentration of this salt. The rate is of the second order with respect to the oxalate concentration, but this velocity is lowered by the presence of oxygen. The rate is nearly inversely proportional to the oxygen concentration when the latter is low, but at higher concentrations the effect of the oxygen is very much diminished. Practically no oxygen is used up in the reaction. The effect of oxygen depends on the amount of iron salts present; traces of the latter can alter the order of the reaction. Since ferric oxalate at 100° loses carbon dioxide and forms ferrous oxalate at a moderate rate, repeated oxidation of the latter by the oxygen present will set up a continuous cycle, the repetition of which would account for the observed catalytic effect of the iron.

S. K. Tweedy.

Action of hydrogen chloride on alcohol. Influence of electrolytes on the reaction velocity. S. Kilpi (Z. physikal. Chem., 1929, **141**, 424—450; cf. A., 1914, ii, 189).—The velocity coefficients in the equations previously given have been determined for the action of hydrogen chloride on alcohol in mixtures containing 25 and 50 mol.-% of alcohol at temperatures near to 96·5° and 110°. Mixtures containing sodium chloride and potassium chloride have also been studied. The value of the equilibrium constant C_2/C_1 (where C_1 is the velocity coefficient of the direct and C_2 that of the reverse change) was found to increase with the concentration of electrolyte between the limits 0·05*N* and 0·8*N*, but more slowly as the concentration was increased. Since C_2 has been shown to be independent of the electrolyte concentration, it follows that as the latter becomes greater the velocity of formation of ethyl chloride decreases, and in this respect the behaviour of the alkali chlorides showed no noticeable difference from that of hydrogen chloride within the range of concentration studied. An attempt is made to explain the relation between electrolyte concentration and reaction velocity in terms of the theories of Brönsted and of Debye and Hückel, for which purpose values of the coefficients A' and α' in the expression $A'\sqrt{c}/(1+\alpha'\sqrt{c})$ in the formula of Debye and Hückel were calculated from the experimental data and compared with the theoretical values. The agreement is as good as can be expected in view of the approximate nature of the comparison. The velocity of the direct action of hydrogen chloride on alcohol is proportional to the product of the concentration of hydrogen ion and chlorine ion as determined potentiometrically. The mechanism of the reaction is discussed and the conclusion reached is that it is not possible to distinguish between a direct action of undissociated hydrogen chloride on the alcohol and a reaction $Cl'+EtOH\longrightarrow EtCl+OH'$ catalysed by hydrogen ions. F. L. Usher.

Velocity of esterification of fatty acids with ethylene glycol and hydrochloric acid. A. Kailan and A. Schachner (Monatsh., 1929, 52, 23—52).—The velocities of esterification of *n*- and *iso*-butyric, *n*- and *iso*-valeric, hexoic, and heptoic acids in anhydrous and moist ethylene glycol with hydrogen chloride as a catalyst have been determined at 25°. The unimolecular velocity coefficients (*k*) for *n*-butyric, *n*-valeric, hexoic, and heptoic acids are the same and can all be expressed by the same formula, which is a function of the concentrations of water (*w*) and the catalyst (*c*) (cf. Kailan and Melkus, A., 1927, 749). The values of *k* for *iso*valeric and *iso*butyric acids are 22·4 and 70%, respectively, of those for *n*-butyric acid. In all the cases examined in anhydrous glycol *k* is proportional to *c*, but in moist glycol this relation holds only up to $c=N/6$. With increased *c* the values of *k* increase more rapidly in the moist glycol. The retarding action of water is of the same order as for glycerol and much less than for ethyl alcohol (cf. *loc. cit.*). When $w=0{\cdot}03$—$0{\cdot}06$ mol. per litre, the values of *k* are 30—40% greater in ethyl alcohol than in glycol, and 2·5 times as great in glycol as in glycerol. For $w=0{\cdot}7$ and $c=N/6$ the values of *k* are only half as great in alcohol as in glycol and only a little greater than in glycerol. The values of *k* for *n*-butyric acid are about 12% higher than those originally found (*loc. cit.*). Under the conditions used esterification is practically complete. H. Burton.

Rate of decomposition of solids. V. Rate of decomposition of mercurous carbonate and some metal salt hydrates. B. Bružs (Z. physikal. Chem., 1929, B, 3, 427—439; cf. A., 1926, 692).—Further experiments with the apparatus previously described have been made on the rate of decomposition of mercurous carbonate containing 90% of the theoretical amount of carbon dioxide. In every case the velocity rises to a maximum and then decreases, and is largely dependent on the external pressure. The results of a large number of experiments in which the temperature was varied between 125° and 150° and the external pressure between 500 and 1000 mm., plotted with velocities expressed as percentages of the maximum velocity and times as percentages of the time (*z*) required for the attainment of the maximum velocity, give a single curve with a well-defined maximum. Hence it is concluded that the mechanism of the reaction is unaffected by changes in temperature or pressure over the range studied. Since log *z* is shown to be proportional to the reciprocal of the absolute temperature, and $1/z$ has the dimensions of a first-order reaction constant, an expression analogous to the Arrhenius temperature function can be written, viz., $d\log_e z/d(1/T)=E/R$, where *E* is the critical increment. The value of the latter is found to be 35,000 g.-cal., which is confirmed by two other methods. Experiments on the rate of dehydration of crystals of the hydrated sulphates of manganese, zinc, and sodium showed that although the reaction is apparently confined to the surface, fine grinding of the crystals, while increase the surface area as much as 10^5 times, increased the velocity only 10 times. A theoretical explanation is offered. F. L. USHER.

Oxidation of tungsten. Evidence for the complexity of tungstic oxide, WO_3. J. S. DUNN (J.C.S., 1929, 1149—1150).—The temperature coefficient of the oxidation of tungsten in air has been determined over the range 700—1000°. It is found to be abnormal between 850° and 950°, although over this range the ordinary parabolic oxidation law is obeyed. The abnormal temperature coefficient is therefore not due to a sintering of the oxide film. The results are explained qualitatively if it is assumed that tungstic oxide exists in two forms which are in equilibrium. F. J. WILKINS.

Corrosion of iron. J. F. G. HICKS.—See B., 1929, 521.

Acid and salt effects in catalysed reactions. XX. Ionisation of acids in salt solutions. H. M. DAWSON and W. LOWSON (J.C.S., 1929, 1217—1229).—An account is given of a method for the determination of hydrogen-ion concentration from reaction velocity data and its application to the study of the influence of the concentration of a sodium chloride solution on the ionisation constants of acids. The rate of hydrolysis of ethyl acetate in sodium chloride solutions (0—$4M$) has been measured in the presence of acetic, glycollic, chloroacetic, and dichloroacetic acids as catalysts. Experiments with hydrochloric acid afford a measure of the catalytic activity of the hydrogen ion in the sodium chloride solutions and the observations are not measurably influenced by the interaction of hydrogen and chlorine ions. Hence it is possible to calculate the ionisation constants of other acids from reaction velocity measurements.

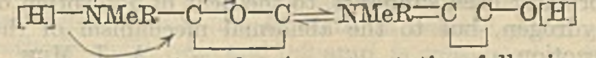
The influence of sodium chloride on the ionisation constants of the acids is given fairly accurately by the equation $\log (K_x/K_0)=a\sqrt{x}-bx$, where K_x and K_0 are the ionisation constants of the acid in an xM-solution of sodium chloride and pure water, respectively, a and b are constants approximately independent of the nature of the acid. Divergences from this equation occur with large ($4M$) concentrations of salt, indicating that in these solutions new specific effects, which vary with the nature of the acid, come into play. It is shown that the above logarithmic formula, whilst of the form predicted by the Debye–Hückel theory, has constants which render it quantitatively incompatible with this theory. The theoretically predicted value of the Debye–Hückel coefficient α is much too large. Also, the experimental value is not independent of the nature of the ionic environment.

Further, the Brönsted equation (A., 1928, 1336) expressing the relationship between the catalytic coefficient k_m and the ionisation constant K accurately fits data obtained from the acetone–iodine reaction. F. J. WILKINS.

Autoreduction of sodium silver sulphite. A. STEIGMANN (Kolloid-Z., 1929, 48, 193—194).—Solutions of sodium silver sulphite, with or without a slight excess of sodium sulphite, when kept for several hours deposit a precipitate, which consists partly of silver sulphite and partly of metallic silver. The longer the solution is kept, the higher is the ratio of silver in the precipitate. This autoreduction is strongly catalysed by very small amounts of copper salts. E. S. HEDGES.

Ultra-violet light, insulin, and amino-acid catalysis. J. M. ORT (J. Physical Chem., 1929, 33, 825—841; cf. A., 1928, 487).—The study of the initial stages of the oxidation of dextrose and lævulose and of the effects of amino-acids, insulin, and ultra-violet light by the oxidation potential method has been continued. Amino-acids of the glycine type catalyse the decomposition of hydrogen peroxide and promote its reaction with the active sugar, the view being developed from this and previous work that the reduction intensity in dextrose and lævulose solution at p_H 10 is due to the presence of a small amount of an active form which is in equilibrium with a comparatively inactive and abundant form. Ultra-violet light has a similar but greater effect. Acids of the type represented by glutamic acid are lacking in this catalytic effect, but appear to develop further reducing intensities when the stronger oxidising conditions no longer obtain. Insulin appears to catalyse negatively the decomposition of hydrogen peroxide. The applicability of the law of mass action to the oxidation of these sugars by air or hydrogen peroxide is discussed. Excess of hydrogen peroxide and irradiation destroyed 80% of the sugar in a short time as compared with 20% under all other conditions investigated. Solutions of dextrose without insulin when irradiated for several hours after the removal of air developed reduction potentials exceeding that of a hydrogen electrode in similar solutions. L. S. THEOBALD.

Mechanism of tautomeric interchange and the effect of structure on mobility and equilibrium. IV. Mechanism of acid catalysis in the mutarotation of nitrogen derivatives of tetra-acetylglucose. J. W. BAKER (J.C.S., 1929, 1205—1210; cf. A., 1928, 967).—A number of derivatives of tetra-acetylglucose of the type $(C_{14}H_{19}O_9)NMeR$ have been prepared and the possibility of mutarotation in the presence of hydrochloric acid consequent on the equilibration of the cationic system



$$[H]-\overset{+}{N}MeR-C-O-C \rightleftharpoons \overset{+}{N}MeR=C\quad C-O[H]$$

has been investigated. A mutarotation following a unimolecular law is observed, but is found to be due not to an isomeric change but to a decomposition into the parent sugar and the hydrochloride of the base.

The following p-substituted benzylmethylamine derivatives were isolated: p-methyl-, b. p. 84°/6 mm. (*hydrobromide*, m. p. 166°); p-chloro-, b. p. 101°/5 mm. (*hydrobromide*, m. p. 196°); p-cyano-, b. p. 143°/6 mm. (*hydrobromide*, m. p. 209—210°). Of the substituted methylamines, the di-(p-methylbenzyl)-, b. p. 180°/6 mm. (approx.), di-(p-chlorobenzyl)-, b. p. 200°/5 mm.

(approx.), and di-(*p*-cyanobenzyl)-, m. p. 65° [*hydrochloride*, m. p. 250° (decomp.)], were isolated.

The tetra-acetylglucosidyl derivatives of the bases were prepared from tetra-acetylglucosidyl bromide and the substituted benzylmethylamine: *benzylmethylamide*, m. p. 125° (*hydrochloride*, m. p. 80°); p-*methylbenzylmethylamide*, m. p. 104—105° [*hydrochloride*, m. p. 175° (decomp.)]; p-*chlorobenzylmethylamide*, m. p. 104—105° [*hydrochloride*, m. p. 137° (decomp.)]; p-*cyanobenzylmethylamide*, m. p. 85—86° [*hydrochloride*, m. p. 146° (decomp.)]. Piperidine gives two different products depending on the experimental conditions: *piperidide* A, m. p. 123° (*hydrochloride*, m. p. 126°); *piperidide* B, m. p. 136° (decomp.); [*hydrochloride*, m. p. 130—131° (decomp.)]. The *hydrochlorides* of the diethyl and dimethylamide derivatives of tetra-acetylglucose have m. p. 152—153° and 159—160° (decomp.), respectively.
F. J. Wilkins.

Theory of heterogeneous catalysed reactions. Multiplet hypothesis. Model of dehydrogenation catalysis. A. A. Balandin (Z. physikal. Chem., 1929, **B**, **3**, 482).—Corrections to a paper recently published (this vol., 519). F. L. Usher.

Catalytic decomposition of ammonia. II. G. M. Schwab and H. Schmidt (Z. physikal. Chem., 1929, **B**, **3**, 337—359; cf. Schwab, A., 1927, 946).—The catalytic decomposition of ammonia at the surface of platinum was investigated over a range of 0·25—4 mm. and 10—300 mm. of ammonia, between temperatures of 1100° and 1485° Abs. A new process of obtaining a constant temperature is described. In the first range the decomposition can be expressed by the equation $-dx/dt=k_1[NH_3]/[H_2]$. The inhibitive action of nitrogen which has been observed at lower pressures vanishes in this range. The heat of activation is found to be 44,000 g.-cal. per mol. In the second range the decomposition cannot be represented by so simple an equation as the first. In this case the velocity may be represented approximately by $-dx/dt=k_2[NH_3]^{1\cdot4}/[H_2]^{2\cdot3}$. The heat of activation in this range is 140,000 g.-cal. per mol. In the lower pressure range the adsorbed ammonia decomposes in part on the active surface. A comparison with previous work on other metals with regard to the heat of activation shows that the decomposition is normal and comparable with other metals only in the lower pressure range. In the higher range the heat of activation is much greater than would be expected. This is not due, as has formerly been supposed, to the heat of desorption of hydrogen, but to the abnormal mechanism of the reaction. A. J. Mee.

Catalysis of the combustion of sulphur in organic substances. L. Bermejo and A. Rancaño (Anal. Fís. Quím. [Tecn.], 1929, **27**, 113—128).—Unsuccessful efforts have been made to find a substitute for the platinum catalyst employed in Pregl's method for the combustion of sulphur in organic substances, and to derive some relationship between the composition of the catalyst and the structure of the organic compound. H. F. Gillbe.

Nickel catalyst. I. Catalyst prepared from nickel chloride. T. Kusama and Y. Uno (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, **8**, 461—466).—Small quantities of chlorine in nickel catalyst prepared from nickel chloride are not fatal to its activity, since the chlorine remaining in the adsorbed state is in the form of nickel chloride and/or sodium chloride, of which the former is reduced to the metal on heating in hydrogen, whilst the latter does not fuse at the temperature used. Basic carbonate was prepared from nickel chloride and sodium carbonate, washed thoroughly, and changed by heating at 480° into an oxide containing 0·023% Cl. The catalyst prepared by reducing this oxide with hydrogen at 350° was as active as a specimen prepared from the nitrate by reducing in naphthalene, benzene, phenol, and aniline. J. W. Smith.

Effect of high-frequency discharges on the dissociation of gases. M. J. Marshall and E. H. Nunn (Amer. Electrochem. Soc., May, 1929. Advance copy. 11 pp.).—When a high-frequency discharge is passed through a gas there is generally a very rapid increase of pressure during the first few seconds, followed by a much slower increase towards a maximum value. The initial sharp rise of the pressure–time curve is attributed to dissociation of the gas, and from the magnitude of this rise the degree of dissociation can be calculated. The subsequent more gradual rise is ascribed to the heating effect of the current. Unpublished work by F. Potter on helium and oxygen shows that the former does not give the initial rapid rise of pressure, and thus supports this view. The present work on hydrogen and air and an unpublished investigation by G. B. Carpenter on chlorine indicate that a considerable proportion of the molecules of a diatomic gas can be dissociated by means of a high-frequency discharge of suitable type. The degree of dissociation attained increases with increase in the initial pressure of the gas, but it is greatly dependent on the shape and dimensions of the discharge chamber: in particular, the smaller are the electrodes the greater is the dissociation. The bearing of these results on the influence of electrical discharges on chemical reactions is discussed.
H. J. T. Ellingham.

Gaseous combustion in electric discharges. III. Cathodic combustion of dry carbon monoxide detonating gas. G. I. Finch and D. L. Hodge (Proc. Roy. Soc., 1929, **A**, **124**, 303—317).—Previous investigations with electrolytic gas (Finch and Cowen, A., 1926, 690; 1927, 1146) have been extended to a case of gaseous combustion in which the water contents of the reacting gases could be rigidly controlled, and the cathodic combustion of dry "detonating gas" (a mixture of carbon monoxide and oxygen in equivalent proportions) has been examined under various conditions. The results show that over a considerable range of gas pressure, gap width, and current, combustion is purely cathodic, although under suitable conditions it also occurs in the inter-electrode zone, such combustion being proportional to the current and superposed on the cathodic combustion. The rate *c* of cathodic combustion is directly proportional to the current, depends slightly on the gas pressure, and is considerably influenced by the nature of the cathode material.

Thus the *c/i* ratio found with a platinum cathode is more than three times that obtained with a copper cathode, and experiments with silver, gold, platinum, palladium, tungsten, tantalum, copper, aluminium, and magnesium cathodes show that combustion is more vigorous at cathodes consisting of freely sputtering metals than at poorly or non-sputtering metals. The cathodic potential falls at the different metals examined vary from 320 to 375 volts. The view is developed that the combustion of dry "detonating gas" in a direct-current discharge is primarily determined by the ionisation of the gases in the cathode zone, both positive and negative ions, but mainly the former, being produced. The electrostatic repulsion between similarly-charged ions greatly reduces the frequency of effective collisions, with the result that the rate of combustion is slow; where combustion occurs at a freely sputtering cathode, the cathode zone contains an abundance of negatively-charged metal atoms, which, by forming electrically neutral metal–gas complexes with positive ions, overcome the electrostatic repulsion and promote combustion. The above conclusions are strongly supported by the fact that three independent methods of calculating the *c/i* ratio all give results of the same order as those obtained experimentally. L. L. Bircumshaw.

Synthesis of ammonia in the glow discharge. A. K. Brewer and J. W. Westhaver (J. Physical Chem., 1929, **33**, 883—895).—The synthesis of ammonia in the glow discharge from a mixture of hydrogen and nitrogen (3 : 1 vols.) at 4—0·1 mm. and under various conditions with different sizes and types of discharge tube has been investigated. Aluminium electrodes were used in discharge tubes of two main types, one U-shaped partly immersed in liquid air and the other bulb-shaped and completely immersed. Electrostatic and magnetic fields were also applied to the discharge. For a given discharge tube and magnetic field, the rate of formation of ammonia is directly proportional to the current passing through the discharge and is constant at a fixed current value. The rate is independent of the pressure and the potential gradient in the discharge. The curves obtained by plotting pressure against time are linear for all the various tubes investigated. The application of a magnetic field of the order of 10^3 gauss affects the character of the discharge, causing sheeting or banding, and with the field at right angles to the electron path, varies the potential necessary to maintain the discharge. A field at right angles to the electric field increases the rate of synthesis of ammonia, whilst a parallel field has no effect. An electrostatic field has little, if any, effect both with alternating and direct current. The current efficiency increases with the length of the discharge column immersed in liquid air, and the power efficiency increases with an increase in diameter of the tube. The data indicate that the reaction is initiated by the positive ions formed in the discharge, and that the rate of synthesis of ammonia is proportional to the rate of formation of positive ions, which, in turn, is proportional to the current. This is suggested as a new electrochemical equivalence law for chemical reactions in discharge tubes. L. S. Theobald.

Anode reactions of fluorine. N. C. Jones (J. Physical Chem., 1929, **33**, 801—824; cf. Fichter and co-workers, A., 1926, 1927, and 1928).—From a consideration of the work of previous investigators, together with some new experiments, the author concludes that the chemical action of fluorine on aqueous solutions is the same as the electrolytic anodic reactions plus any further reactions due to the hydrofluoric acid formed. Further, fluorine instead of reacting with the water of the solution forms persulphate from acid sulphate solutions, and perphosphate, percarbonate, and perborate from phosphates, carbonates, and borates, respectively, hydrogen peroxide from alkali, and ethane from potassium acetate solution. It oxidises also cobaltous, chromic, manganous, and plumbous salts. When passed into pure sulphuric acid fluorine yields fluosulphonic acid because the hydrofluoric acid formed combines with the sulphur trioxide of the compound H_2SO_4,SO_3 which results when pure sulphuric acid is electrolysed. The primary action which occurs when fluorine acts on cold, concentrated solutions of alkali is the discharge of hydroxyl ions which form hydrogen peroxide; ozonate and ozone arise from secondary reactions. Manganous salts when in excess are oxidised to manganese dioxide, but in the presence of hydrofluoric acid manganic fluoride is formed: permanganate results in both cases only after all the manganous ions have been oxidised. The apparent reduction of dichromate to chromic salt is due to a catalytic reduction by small amounts of hydrofluoric or sulphuric acid present in the solution of perchromic acid which is first formed. In strongly acid solution, oxidation of chromic salts to chromate proceeds as in electrolytic oxidation. Lead dioxide is obtained from plumbous salts and fluorine only in alkaline solution or suspension; in acid solution, the lead tetrafluoride formed is stable. The preparation of fluorine by the electrolysis of fused potassium hydrogen fluoride in a modification of Mathers' magnesium cell (A., 1924, ii, 847) is described. The mechanisms of the above reactions are discussed on the view that the reaction which involves the least expenditure of energy is the one which takes place, and the views of Fichter and co-workers are, in many cases, adversely criticised. L. S. Theobald.

Direct electrolytic preparation of ammonium permanganate. G. Rapin (Compt. rend., 1929, **188**, 1547—1548).—The intense but unstable purple colour obtained at the silico-manganese anode (66% Mn, 23% Si) during the electrolysis at 20° of ammonia solution (*d* 1·18) with an isolated platinum cathode at 60 volts and 0·2 amp. is considered to be due to the formation of ammonium permanganate. The conductivity of the solution, but not the intensity of colour, is increased by addition of ammonium chloride. J. Grant.

Preparation of potassium permanganate by electrolysis. J. Roudnick (Bull. Soc. chim. Belg., 1929, **38**, 147—159; cf. A., 1923, ii, 118, 319).—The influence of the nature of the electrolyte and electrodes, temperature, and potential, on the yield of permanganate formed electrolytically has been investigated. The best results are obtained by using as

electrolyte solutions of potassium carbonate of medium concentration (*e.g.*, 6*N*) at a low temperature (3—5°). The cathode should have a smaller surface than the anode, which is best made of ferromanganese containing 80% Mn. The optimum potential is 2·45 volts.
B. W. Anderson.

Precipitation of manganese dioxide by electrolysis with alternating current. A. P. Rollet (Compt. rend., 1929, **189**, 34—35).—Manganese in concentrations of 10^{-3} to 10^{-2} is completely precipitated as a brown deposit of MnO_2,H_2O from solutions of nickel salts in the presence of 0·5—0·005*N*-acid by alternating-current electrolysis (50 periods per sec.) with platinum or nickel electrodes. The presence of nickel is essential, and halogen salts give best results. The current density depends on the temperature, which must not exceed 30°, and is 0·2 and 0·7 amp./cm.² at 0° and 20°, respectively. Higher concentrations of manganese require several hours for complete deposition.
J. Grant.

Electroplating of cadmium from cyanide baths. L. R. Westbrook.—See B., 1929, 560.

Anodic formation of the triacetates of nickel and cobalt and Kolbe's reaction. C. Schall and C. Thieme-Wiedtmarckter (Z. Elektrochem., 1929, **35**, 337—344).—The equivalent conductivities of solutions of the anhydrous diacetates of nickel, cobalt, and lead in perfectly dry glacial acetic acid were measured. They were independent of dilution, but not of temperature (cf. Schall and Markgraf, A., 1924, ii, 342; Schall and Melzer, A., 1923, i, 87). Addition of small amounts of water had appreciable effects. Anodic oxidation of nickelous and cobaltous acetates in water-free acetic acid was carried out in an apparatus similar to that used by Schall and Markgraf, with the exception of a device to keep the anode cool. Under certain experimental conditions cobaltic and nickelic acetates could be formed in the anolytes. Chemical and cryoscopic evidence is advanced to support the view that these acetates are complex and are the normal salts of $[X_3(OAc)_6](OH)_3$, X being either Ni^{III} or Co^{III}.

These salts were also formed by passing ozone, which had been carefully dried over phosphorus pentoxide, through saturated glacial acetic acid solutions of the respective bivalent metallic salts, but as occurred with their anodic formation, there was found to have been formed in the solutions glycollic, glyoxylic, succinic, and oxalic acids. Ethane could be detected in the gases liberated at the anode, and consequently the reactions occurring at the anode in conjunction with the oxidation of the metal ions are considered in connexion with Kolbe's electrosynthesis of hydrocarbons.
H. T. S. Britton.

Designation of quantity of light in photochemistry. M. Bodenstein and C. Wagner (Z. physikal. Chem., 1929, **B**, **3**, 456—458).—It is proposed to denote $6{\cdot}06\times10^{23}$ light-quanta by the name " 1 einstein " and the symbol *E*. It is further suggested that intensity of absorbed light ($I_{abs.}$) should be given in einsteins per sec., that *L* should be used to denote number of einsteins, and $[I_{abs.}]$ the number of einsteins absorbed per litre per second.
F. L. Usher.

Light standard for sensitometry, and the Davis–Gibson light filter with copper–cobalt solutions. J. M. Eder (Z. wiss. Phot., 1929, **26**, 373—374).—The statement has been made that it is difficult to make the Davis–Gibson light filter owing to the difficulty in obtaining pure cobalt ammonium sulphate. It is pointed out that pure cobalt and ammonium sulphates can be used in equivalent amounts to give the required solution. A. J. Mee.

Photochemical temperature coefficients. W. D. Bancroft and R. P. Allen (Proc. Nat. Acad. Sci., 1929, **15**, 445—448).—The view that temperature coefficients of photochemical reactions are relatively small is regarded as incorrect. The Grotthuss theory of chemical depolarisers is applicable to thermal depolarisation, and since exothermic substances can be made unstable by heating, they can be made photosensitive by heating to a suitable temperature. A simple high-temperature ozoniser having porcelain tubes was devised, and used to investigate the decomposition of acetaldehyde. Reaction velocity–temperature curves consist of a rapidly ascending part at low temperatures, followed by a nearly horizontal part, and finally a rapidly ascending part near the region of thermal instability. Conditions at low temperatures are discussed with special reference to the work of Amato (Gazzetta, 1885, **14**, 57) on hydrogen and chlorine at −12°. N. M. Bligh.

Equations for sensitised photolysis. E. Baur (Helv. Chim. Acta, 1929, **12**, 793—806).—Equations for the kinetics of such reactions are derived on the basis of the theory previously advanced (A., 1918, ii, 284) and are examined in the light of the experimental data of various workers. L. S. Theobald.

Behaviour of atomic hydrogen. I. Behaviour towards ethylene. A. Klemenc and F. Patat (Z. physikal. Chem., 1929, **B**, **3**, 289—298).—The atomic hydrogen was produced by the resonance method. With ethylene mixed with hydrogen, no smooth hydrogenation would take place when the total radiation from a mercury-vapour lamp was used, but polymerisation products were formed. The formation and properties of the polymerisation products are discussed. Under the action of ultraviolet light the ethylene is decomposed to give acetylene and hydrogen. The acetylene appears to be formed only as an intermediate product. The polymerised substance cannot be further hydrogenated by atomic hydrogen, contains more hydrogen than is to be expected, and it has the peculiar property of absorbing large quantities of oxygen. The possibility of the occurrence of quinquevalent carbon is mentioned. From ethylene, oxygen, and hydrogen, alcohol is formed on illumination. The experiments show that excited mercury atoms can cause a reaction without the intermediate action of hydrogen.
A. J. Mee.

Influence of the intensity of illumination on the velocity of photochemical union of bromine and hydrogen. M. Bodenstein, W. Jost, and G. Jung (J.C.S., 1929, 1153—1158).—It is suggested that the catalyst for the photochemical union of bromine and hydrogen is the bromine atom. This catalyst may be destroyed by a three-body collision (Born and

Franck, A., 1925, ii, 266) in the gas phase, a reaction proportional to the square of the concentration of bromine atoms, or by recombination at the walls of the reaction vessel, a reaction of the first order. An explanation is therefore obtained of the equation Briers and Chapman (A., 1928, 970) used to express the rate of decomposition of their hypothetical catalyst. Further, the mean life of the catalyst calculated on the basis of this theory is 0·14—0·22 sec., a result in satisfactory agreement with that of Briers and Chapman. The hypothesis also demonstrates that the discrepancies apparent between the work of Lütkemeyer and Bodenstein (A., 1925, ii, 218) and Briers and Chapman are illusory. F. J. WILKINS.

Oxidation of hydrogen iodide in the dark and in the light. III. Constitution of iodine solution. IV. Discussion of the light-sensitiveness. C. WINTHER (Z. physikal. Chem., 1929, B, 3, 299—314, 315—336).—III. The equilibria between different components present in a dilute solution of iodine in potassium iodide and in hydrochloric acid were investigated by studying the distribution of iodine between carbon tetrachloride and water, potassium iodide solution, hydrochloric acid, and a mixed solution of potassium iodide and hydrochloric acid. The equilibrium constants were found. In the course of the work the solubilities of iodine in water and in hydrochloric acid were determined. The true distribution coefficient of iodine between carbon tetrachloride and water is 110, both at 20° and 30°. The extinction coefficients of the components were found for a wave-length of 436 μμ. There is evidence for the formation of an I_5 ion in most iodine solutions.

IV. The oxidation of hydrogen iodide in the dark is considered and a corresponding formula for the light reaction is deduced. Previous determinations have shown that the amount of iodine formed in the dark $\Delta_t = kt + k_1 t C_I$, where t is the time and C_I is the iodine concentration. The oxidation in the dark thus consists of two reactions, one of which is proportional to the iodine concentration, the other being independent of it. The second part of this reaction is investigated and the expression found for the total dark reaction is $\Delta_t = kt + (a_1\sqrt{k m_{I'}^2})/(b_1 + m_{I'}\sqrt{m_{I'} m_I})$, where a_1, b_1, and k are constants and $m_{I'}$ and m_I are the masses of iodine ions and total iodine present. The values of the constants are given for 20° and 30°. A similar equation is obtained for the light reaction. It is possible to calculate by certain simple suppositions the velocity of the light reaction from that of the dark reaction by making use of quantitative absorption measurements. The conclusion reached can be supported by many other experiments. A. J. MEE.

Monatomic iodine and molecular hydrogen. W. D. BANCROFT and D. S. MORTON (Proc. Nat. Acad. Sci., 1929, 15, 438—441).—The conditions under which the halogens, excluding fluorine, react photochemically with hydrogen are discussed generally, and investigated in the case of hydrogen and iodine, different results being obtained with glass and quartz containers. The conclusions reached are that hydrogen is activated by ultra-violet light, but not appreciably by visible light, and that photochemically or catalytically activated hydrogen and halogens are atomic and react at ordinary temperatures under ultra-violet light; visible light causes hydrogen to react with chlorine at the ordinary temperature, with bromine at 196°, but not with iodine at 350°; molecular hydrogen reacts with monatomic chlorine at ordinary temperatures, with bromine at 196°, but with iodine not appreciably at 350°. These considerations apply to equilibrium rather than to overvoltage concentration conditions. N. M. BLIGH.

Photochemical equilibrium in nitrogen peroxide. II. Dependence of quantum efficiency on wave-length. R. G. W. NORRISH (J.C.S., 1929, 1158—1169; cf. A., 1927, 528).—The quantum efficiency (γ) of the photochemical reaction $2NO_2 \underset{\text{dark}}{\overset{\text{light}}{\rightleftharpoons}} 2NO + O_2$ has been measured for six wave-lengths, with the following results: for 5760, 5460, 4360 Å., $\gamma = 0·000$; for 4050 Å., $\gamma = 0·74$; for 3650 Å., $\gamma = 2·10$; and for 3160—2650 Å., $\gamma = 2·07$. The photochemical threshold in the middle of a region over which nitrogen peroxide absorbs strongly, observed by Dickinson and Baxter (A., 1928, 491), has been found to be much sharper than was originally supposed, for, contrary to their result, no photochemical activity was obtained at the wave-length 4360 Å.

F. J. WILKINS.

Kinetics and temperature coefficients of some photochemical reactions in radiations of different wave-lengths. B. K. MUKERJI and N. R. DHAR (J. Physical Chem., 1929, 33, 850—863; cf. this vol., 516).—The temperature coefficients in the light and in the dark have been determined for the following reactions: bleaching of dicyanine, oxidation of iodoform, and reactions between sodium citrate and iodine, sodium malate and iodine, sodium formate and mercuric chloride, potassium oxalate and iodine, sodium potassium tartrate and bromine, quinine sulphate and chromic acid in the presence of sulphuric acid, potassium permanganate and oxalic acid, and chromic and oxalic acids both in the presence of manganese sulphate and sulphuric acid, sodium formate and iodine and sodium nitrite and iodine both in the presence of sodium acetate, ferrous sulphate and iodine, and mercuric chloride and ammonium oxalate in the presence of eosin. The temperature coefficients of the photochemical changes are less than those of the corresponding thermal reactions and depend on the wave-length of the incident radiation, and, in general, the greater is the observed acceleration of the reaction by light, the smaller is the value of the temperature coefficient. All the reactions are accelerated by light of wave-lengths 4725, 5650, and 7304 Å., and in several cases absorption and acceleration are at a maximum at λ 5650 Å. The reactions between sodium malate and iodine and sodium citrate and iodine are both termolecular in the dark. The conception of a photochemical threshold below which radiations of smaller frequencies do not promote a reaction is put forward and values are calculated from the temperature coefficients of the dark reactions. L. S. THEOBALD.

Photography. I. Nature of sensitivity and latent image. F. E. E. GERMANN and D. SHEN

(J. Physical Chem., 1929, **33**, 864—872).—Photographic sensitisers are discussed and a bibliography of the sensitising effect of silver iodide in silver bromide emulsions is given. A formula for the preparation of silver iodide emulsions of a large range of grain size is also detailed. Contact of spent developer with dilute acids was found to be accompanied by luminescence and hence washing with water is preferable to the use of a fixing bath. A study of the grain sensitivity of iodide emulsions showed that in those which are unsensitised only 17% of the grains ever develop. Centrifuging and coating of different fractions on various plates of an emulsion of a wide range of grain size failed to show any difference in development between the fractions and the original emulsion. Large and small grains thus appear equally sensitive and, further, insensitivity is not due to lack of sensitising material, but is attributed to rapid reversal.

L. S. THEOBALD.

Photochemistry of silver halides. V. Silver value and fixing process. H. H. SCHMIDT and F. PRETSCHNER (Z. wiss. Phot., 1929, **26**, 375—380; cf. A., 1928, 1340; B, 1928, 625).—Various emulsions were used, and it was found that the amount of silver present after fixing was not equal to the amount in the control plate. With the normal plate the amount is smaller after fixing, and therefore some must be lost in the fixing bath. Whether there is a change to silver sulphide is uncertain. There is approximately the same amount of silver after fixing in all the plates. The decomposition of the silver complex solution with the formation of silver sulphide is a diffusion process which proceeds with a slower velocity than the diffusion of the solution from the gelatin. In the gelatin itself there is a silver complex solution, and a silver compound soluble in nitric acid, which can be identified as silver sulphide. The amount of silver remaining in the gelatin is directly proportional to the thickness of the layer and therefore for nodules of emulsion is very high. The diffusion of the complex solution from the thick layers is naturally slower than from thin, and therefore the formation of silver sulphide can proceed further. The method of washing also plays a part. The effect of different fixing baths on the amount of silver remaining in the gelatin is small.

A. J. MEE.

Primary process in the formation of the latent photographic image. S. E. SHEPPARD (Nature, 1929, **123**, 979—980).—The results of Toy and Harrison (this vol., 660) support the view that the inner photo-electric effects (photo-voltaic and photoconductance), as also the photographic and photochemical effects, are all derived from the same primary separation of the electron from the bromide ion. The formation of a latent image involves both the segregation of bromine and the aggregation of the silver atoms produced. A. A. ELDRIDGE.

Photodichroism and photoanisotropy. III. Quantitative measurement of induced photodichroism. F. WEIGERT (Z. physikal. Chem., 1929, B, **4**, 83—112; cf. this vol., 871).—The phenomenon of induced photodichroism in developed photographic layers is further discussed. It is a phenomenon of the same general nature as primary photodichroism and can be produced in almost all light-sensitive colouring matters in layers. The degree of reproducibility of determinations of induced photodichroism is discussed. The phenomenon is influenced, *e.g.*, by changes in the composition and preparation of the emulsion, and the method and time of fixing and development. The effects are different if a dry or a moist layer is excited, and also if the duration and colour of the excitation are altered. The effects of these alterations are studied in detail. The importance of micelle deformation in this connexion is pointed out, it being assumed that this is the primary action in each case. A. J. MEE.

Mechanism of photochemical changes occurring in a fluorescing electrolyte. J. C. GHOSH (Z. physikal. Chem., 1929, B, **3**, 419—426).—Theoretical. The *E.M.F.* generated in a cell containing a solution of a fluorescent material, *e.g.*, alkali fluorescein, in which are two platinum electrodes, one of which is illuminated, is attributed to the formation of an unstable intermediate product, the concentration of which at a time t after exposure to light is $C_B=(\sqrt{k_4 I}/\sqrt{k_3}) \tanh t\sqrt{k_4 I}$, where I is the intensity of the incident light. The *E.M.F.* calculated from Nernst's formula, using values of C_B obtained from the above expression, agrees well with the experimental results of Rule (Proc. Nat. Acad. Sci., 1928, **14**, 272). F. L. USHER.

Photochemical formation of carbonyl chloride. IV. Change at low pressures and an improved interpretation of the mechanism of the reaction. M. BODENSTEIN, S. LENHER, and C. WAGNER (Z. physikal. Chem., 1929, B, **3**, 459—478; cf. A., 1928, 254).—The reaction between chlorine and carbon monoxide has been further studied at the ordinary temperature and at low pressures (below 40 mm.) with improved experimental arrangements and with minute precautions against the entry of impurities. The expression for the velocity coefficient obtained previously does not fit the observations at lower pressures and it has been found necessary to make different assumptions regarding the mechanism. It is suggested that, in addition to the changes in the gas phase which result in the removal of chlorine atoms, there is at lower pressures diffusion of COCl and Cl to the walls of the vessel, where they remain adsorbed until recombination occurs. The explanation of the mechanism of the reaction given in an earlier paper (cf. A., 1927, 1154) is regarded as unsatisfactory and it is now considered that the specific influence of carbon monoxide on the recombination of chlorine atoms can be expressed by the equation $COCl+Cl=CO+Cl_2$, and that direct recombination in the gas phase is negligible. This assumption leads to a simple explanation of the photochemical formation of carbonyl chloride at the ordinary temperature, the individual reactions being (1) Cl_2+E (see this vol., 892)$\longrightarrow 2Cl$; (2) $CO+Cl\longrightarrow COCl$; (3) $COCl\longrightarrow CO+Cl$; (4) $CO+Cl_2+Cl\longrightarrow COCl_2+Cl$; (5) $COCl+Cl\longrightarrow CO+Cl_2$. The inhibitory action of oxygen and the mechanism of the reaction at higher temperatures are also discussed. F. L. USHER.

Influence of active carbon and of zinc on the formation of complex aldehydes and of

sugars from solutions of potassium hydrogen carbonate under the action of ultra-violet rays. G. Mezzadroli and T. Babes (Gazzetta, 1929, **59**, 305—308; cf. this vol., 155).—The reducing power of a 5% solution of potassium hydrogen carbonate exposed to the action of ultra-violet rays increases to a constant value in presence of active carbon (norit), instead of rising to a maximum and then decreasing, as previously found in the absence of carbon. When zinc is present with the carbon the reducing power of the solution is still further increased and reaches a higher constant value. The adsorption of carbon dioxide and hydrogen by the carbon brings about a more intimate contact and facilitates reaction between these two gases. O. J. Walker.

Photochemical reaction between ethylene glycol and dichromate. E. H. Riesenfeld and O. Hecht (Z. wiss. Phot., 1929, **26**, 369—372).—The action of light on a solution of sodium dichromate in ethylene glycol is considered. The presence of water affects the amount of dichromate reduced. For equal amounts of light the ratio of reduction occurring in 1 hr. with water present and water-free preparations was 59 : 79. Within the range of concentrations 0·2—0·6% of sodium dichromate in ethylene glycol, the amount of decomposition was proportional to the time. A layer of the 0·2% solution 1 cm. thick was sufficient to absorb completely the active radiation. For the light used, 50 milli-equivalents of dichromate, on the average, were reduced per hr., independently of time, concentration, and thickness of layer, with the condition previously mentioned in the case of the latter. A. J. Mee.

Photochemical transformation of *o*-nitrobenzaldehyde. R. Wegscheider (Monatsh., 1929, **52**, 68—72).—The results of Weigert and Brodmann (A., 1925, ii, 1075) on the photochemical transformation of *o*-nitrobenzaldehyde into *o*-nitrosobenzoic acid in acetone solution are not consistent with the assumption that two quanta are used for 1 mol. of end product. The observations amenable to calculation are explicable on the assumption that a partial inactivation of the light-activated molecules occurs (cf. A., 1923, ii, 49), and agree with the kinetic requirements that the quantum number depends on the region of change. This assumption also explains the different behaviour of solid *o*-nitrobenzaldehyde.
H. Burton.

Photobromination of coumarin. D. M. Williams (J.C.S., 1929, 1383—1384).—The photobromination of coumarin in carbon tetrachloride or chloroform leads to an equilibrium. Whereas in the thermal reaction the velocity of bromination is greater in chloroform solution (A., 1928, 412), the reverse is true of the photobromination. F. J. Wilkins.

Photographic effect produced by sterols after exposure to ultra-violet rays. J. Cluzet and Kofman (Compt. rend., 1929, **189**, 45—47).—Sterols exposed to ultra-violet light, *X*-rays, or radium blacken a photographic plate. Since this property is destroyed by heat (80°) or by infra-red radiation, there is evidence that it is due to gaseous substances produced by irradiation rather than to radiations emitted by the activated sterols (cf. following abstract). J. Grant.

Photochemical activity of various sterols and the nature of their action. L. Hugounenq and E. Couture (Compt. rend., 1929, **189**, 47—49; cf. preceding abstract).—Indole, skatole, and the sterols of cod-liver oil, *Bombyx,* and beer yeast darken a photographic plate in direct contact after exposure to ordinary diffused daylight, whilst cholesteryl acetate (*Bombyx*) and sterols of the oils of egg, fresh or red herring, ergot of rye, snail, cow's blood and brain, and biliary calculus are inactive. In some cases the activity is lost after a period in darkness, and in others it is manifested even if the substance and plate are not in direct contact. It is intensified by heat (40°) and oxidising agents (manganese borate), but is absorbed by quartz. These and chemical tests indicating the presence of an aldehyde and active oxygen imply the formation of ozonides at the double linkings of the sterol molecules. J. Grant.

New photo-reaction with ergosterol. A. Steigmann (Z. wiss. Phot., 1929, **26**, 363—368).—Alcoholic anthraquinone dissolved in pyridine bleaches alcoholic methylene-blue (1 in 10^4) reversibly on exposure to light. Shaking with oxygen brings back the colour. Quinone acts in a similar way, but not quinol. To explain this reaction it is stated that the methylene-blue, in itself very photoactive, has no chemical contact with the alcohol, but the anthraquinone has. On exposure, the methylene-blue and anthraquinone take up light energy. This is transferred to the alcohol from the anthraquinone. The activated hydrogen of the $-CH_2{\cdot}OH$ group does not act as an acceptor itself, but passes it on to the better methylene-blue hydrogen acceptor, the methylene-blue thereby becoming bleached. When ergosterol (a secondary alcohol) was used instead of ethyl alcohol in this reaction, being dissolved in a non-alcoholic solvent (pyridine), the methylene-blue was rapidly and reversibly bleached at first, but later an irreversible change set in. Control solutions, one containing cholesterol and the other being free from sterol, were used; both were slower than the ergosterol, and the change was irreversible. To explain this reaction experiments were made with ergosterol and methylene-blue alone, and with pyridine and anthraquinone alone, in atmospheres of oxygen. The anthraquinone does not react with the pyridine, but only with the ergosterol, of which it makes the hydrogen atom reactive, so that it bleaches methylene-blue. The explanation is, therefore, similar to that of the reaction with ethyl alcohol. A. J. Mee.

Displacement of iodine from an iodide by a solution in oil of cholesterol or ergosterol irradiated by solar light. E. Rousseau (Compt. rend., 1929, **189**, 37—39).—Solutions (0·5%) of ergosterol in olive oil have a greater power of oxidation when irradiated by solar light in a limited supply (17 c.c.) of air than those of cholesterol. The photochemical effect of the total solar radiations measured in terms of the active oxygen equivalent of the iodine liberated from a 20% solution of an iodide is approximately 10 times as great as that of the mercury arc rays 3650, 3341, and 3132 Å., or of the monochromatic radiation 3650 Å. isolated from the same source.
J. Grant.

Modifications of collagenic substances by radiation from radioactive bodies. J. Loiseleur (Compt. rend., 1929, **188**, 1570—1572, and Bull. Soc. Chim. biol., 1929, **11**, 635—636).—The action of β-rays from radium or radon on solutions of gelatin or collagen causes a rise in the gold number in the former case and flocculation in both cases. Lead and gold salts have a sensitising action. The effect produced is independent of the temperature between 0° and 37° and is proportional to the intensity of the radiation. R. K. Callow.

General principles underlying oxidation–reduction reactions and chemical combination. I. B. Jirgensons (Z. Elektrochem., 1929, **35**, 352—358).—A theoretical discussion based on the electronic theory. H. T. S. Britton.

Potassium hexathionate. J. R. Partington and A. F. Tipler (J.C.S., 1929, 1382—1383).—Confirmatory evidence has been obtained of the work of Weitz and Achterberg (A., 1928, 381) on the preparation of potassium hexathionate. F. J. Wilkins.

Complex salts. II. Preparation, properties, and stability of some bisdicarboxylato-copper salts. H. L. Riley (J.C.S., 1929, 1307—1314).—Copper forms with certain dicarboxylic acids complex salts of the type $Na_2[CuX_2(H_2O)_2]$, displaying a co-ordination number of six. The *dioxalato-*, *dimalonato-*, and *diphthalato-*complex salts of this type have been isolated. It is shown that the stabilities of these complexes decrease in the order : oxalato-, malonato-, phthalato-, carbonato-, and succinato-compound. F. J. Wilkins.

Tetrathionates. II. Strontium tetrathionate. R. Portillo (Anal. Fís. Quím., 1929, **27**, 351—357).—Strontium tetrathionate hexahydrate (from a mixture of alcohol and ether) is stable in the air but in a vacuum over sulphuric acid readily loses $4H_2O$, especially at 40—50°; dehydration of the resulting dihydrate sets in at about 70°, but is accompanied by decomposition. The densities (d_4^{25}) of the hexa- and di-hydrates are 2·148 and 2·480, respectively, the mol. vol. of the water of crystallisation being 13·8, in agreement with that found by Moles for the water in hydrated crystals. The solubility of strontium tetrathionate in water is less than that of the barium salt at temperatures below 27°, and greater at higher temperatures, the solubility at 0°, 18°, and 30° being 20, 26·3, and 39% by weight, respectively. The molecular heat of dissolution at 17° in 1000 mols. of water is −11·6 kg.-cal. H. F. Gillbe.

Decomposition of barium sulphate. (Mlle.) G. Marchal (Bull. Soc. chim., 1929, [iv], **45**, 339—343).—Decomposition of barium sulphate by heat alone is very slight at 1300° and is attributed to the presence of impurities. In presence of silica, alumina, or kaolin, decomposition is accelerated, being initially rapid, but the loss in weight of the sulphate does not exceed 20—25% in 5 hrs. at 1300° (cf. A., 1926, 359, 487; B., 1926, 51). R. Brightman.

Purification of mercury. D. Roller (J. Opt. Soc. Amer., 1929, **18**, 357—359).—The procedure appropriate to the purification of mercury preparatory to use in photo-electric cells, and a simple centrifugal mixing device for the preliminary purification by washing with potash, dilute nitric acid, etc., are described. R. W. Lunt.

Action of gaseous ammonia on mercuric bromide and on mercuric chloride. M. François (Compt. rend., 1929, **188**, 1500—1501).—Dry powdered mercuric chloride or bromide slowly adsorbs ammonia in the cold with the formation of the additive compound $HgCl_2,2NH_3$ or $HgBr_2,2NH_3$. The rate of adsorption depends on the nature of the solid surface. J. Grant.

Behaviour of amorphous carbon and sulphur compared with that of diamond and graphite; the carbon sulphide of Ciusa. J. P. Wibaut and E. J. van der Kam (Proc. K. Akad. Wetensch. Amsterdam, 1929, **32**, 501—511).—Only the amorphous forms of carbon are able to fix sulphur when the two elements are heated in a closed tube at 500—600°. Part at least of the sulphur appears to be held to the carbon by valency forces, and the difference between the behaviour of the amorphous and crystalline forms of carbon is ascribed to the relatively high degree of unsaturation of the surface atoms of the amorphous material. There is considerable variation of the force with which the individual sulphur atoms are held, as evidenced by the gradual loss when the material is heated at rising temperatures in a vacuum or in a current of hydrogen; this observation is in accord with the views of Garner and McKie on the differing energy contents of the surface atoms of an amorphous material. H. F. Gillbe.

Action of air–carbon tetrachloride vapour mixtures on several natural sulphides, thioarsenites, and thioantimonites. K. Braddock-Rogers (Chem. News, 1929, **138**, 385—387).—Galena is decomposed readily at 300—325°, and chalcocite, after first being heated at 300—325° for 15 min., at 500—525°. Covellite is heated first at 275—300°, on account of the rapidity of the initial stages of the reaction, then at 500—525°. Arsenopyrite decomposes very smoothly at 450—460°, but enargite is heated first at 200—225°, then at 300—325°. Cobaltite requires an initial heating at 325—340°, and further heating at 540—560°. Tetrahedrite and jamesonite do not require to be heated during the initial stage of the decomposition, but after 30 min. should be heated at 250—300°; bournonite requires to be heated at 225—250° throughout the decomposition. H. F. Gillbe.

Action of cyanogen bromide and hydrogen cyanide on titanium tetrabromide. F. Oberhauser and J. Schormüller (Ber., 1929, **62**, [*B*], 1436—1441; cf. A., 1927, 756).—The action of cyanogen bromide on titanium tetrabromide in carbon disulphide affords the *compound* $TiBr_4,2CNBr$, m. p. 151—152° (corr.) in a sealed capillary, immediately decomposed by moisture. The *substance* $TiCl_4,2CNBr$ is obtained similarly. The bromide is transformed by gaseous ammonia into the ammonate, $TiBr_4,2CNBr,NH_3$. With ether, titanium tetrabromide yields the *compound* $TiBr_4,2Et_2O$. With anhydrous hydrogen cyanide, titanium tetrabromide affords the *substance* $TiBr_4,2HCN$, m. p. 132—133° (corr. decomp.) after darkening at 100°; tensimetric degradation yields the *adducts* $2TiBr_4,3HCN$ (172 mm., 70°) and $TiBr_4,HCN$ (72 mm., 70°).

Cyanogen bromide is determined by treatment with about 100 c.c. of dilute ammonia at the ordinary temperature in a closed flask for 10—20 min. The mixture is warmed on the water-bath, diluted with 300 c.c. of water, boiled to expel the bulk of the ammonia, acidified with nitric acid, and titrated with 0·1*N*-silver nitrate solution. Decomposition may be effected with potassium or sodium hydroxide.

H. WREN.

Existence of higher oxides of nitrogen. H. J. SCHUMACHER and G. SPRENGER (Z. angew. Chem., 1929, **42**, 697—700).—A discussion of the evidence for the existence of the compound NO_3.

C. W. GIBBY.

Preparation of ammonium dichromate. Y. T. GERASIMOV (Trans. Inst. Pure Chem. Reagents, Moscow, 1927, No. 6, 22—26).—Chromium trioxide is neutralised in unsaturated solution with ammonia, and the mixture evaporated at 50°. Double decomposition of sodium dichromate and ammonium chloride does not give a pure product. Ammonium dichromate is slightly decomposed on boiling in aqueous solution.

CHEMICAL ABSTRACTS.

Monobromoamine. W. MOLDENHAUER [with M. BURGER] (Ber., 1929, **62**, [*B*], 1615—1618).—Bromine reacts with ammonia in anhydrous ether according to the equation $2NH_3+Br_2=NH_2Br+NH_4Br$. The bromoamine is too unstable to permit its isolation. It liberates iodine from hydriodic acid and oxidises aqueous sulphite to sulphate. In dilute aqueous solution, bromine and ammonia evolve nitrogen violently, but with increasing concentration of ammonia the initial nitrogen evolution becomes less complete and monobromoamine can be removed from the solution by ether. Decomposition of the bromoamine in aqueous solution is a unimolecular change, probably proceeding according to the scheme: $NH_2Br+H_2O=NH_4BrO$ and $3BrO^-+2NH_3=3Br^-+N_2+3H_2O$; the first change only is measured. Sodium hypobromite and ammonia appear to yield nitrogen almost exclusively, small amounts of bromoamine being formed in the presence of concentrated ammonia. Unlike chloroamine, bromoamine is not transformed by an excess of warm ammonia into hydrazine.

H. WREN.

Phosphorous oxide. II. Reciprocal action between phosphorus trichloride and phosphorous acid. L. WOLF, E. KALAEHNE, and H. SCHMAGER (Ber., 1929, **62**, [*B*], 1441—1449; cf. this vol., 662).—The action of phosphorus trichloride on phosphorous acid under widely varied conditions invariably yields yellow to orange, syrupy products from which a trace of phosphorous oxide cannot be isolated by distillation or extraction. A similar product is derived from hydrogen chloride and phosphorous oxide at the atmospheric temperature; if reaction is effected at −30°/760 mm., the colourless product consists of phosphorus trichloride and phosphorous acid. The yellow compound is formed by the action of phosphorous oxide on phosphorous acid. The preparation of the oxide from phosphorus trichloride and phosphorous acid is therefore impossible. When heated above 110°, the yellow product is gradually transformed into red phosphorus. The formation of phosphorous oxide from the trichloride and acetic anhydride or glacial acetic acid could not be confirmed.

H. WREN.

Thermal formation of hydrogen chloride. J. A. CHRISTIANSEN (Z. physikal. Chem., 1929, **B**, **3**, 481).—A correction (cf. this vol., 654).

F. L. USHER.

Hydrogen–chlorine flame. E. B. LUDLAM, H. G. REID, and G. S. SOUTAR (Proc. Roy. Soc. Edin., 1929, **49**, 156—159).—The flame of chlorine burning at a jet in hydrogen consists of a livid white portion surrounded by a pale blue cone. When hydrogen burns in chlorine, however, this pale blue cone almost disappears owing to the extensive absorption of chlorine in the violet. The maximum intensity of the continuous spectrum from the white inner portion occurs in the green. It is suggested that the reaction between hydrogen and chlorine proceeds through two stages, (*a*) $H_2+Cl\longrightarrow HCl+H$; (*b*) $H+Cl_2\longrightarrow HCl+Cl$. The existence of the white flame is ascribed to the combination of free chlorine atoms. In support of this hypothesis it is shown that the white flame is considerably diminished in size when an excess of hydrogen is present.

F. J. WILKINS.

Nitridation of manganese. L. DUPARC, P. WENGER, and C. CIMERMAN (Helv. Chim. Acta, 1929, **12**, 806—817).—The influence of the following factors on the nitridation of manganese has been investigated: chemical composition of the manganese, duration of the reaction, temperature, pressure, and catalysis by lithium nitride. Pyrophoric manganese oxidises immediately in air and can be converted into the nitride only by removing the mercury from amalgam in a current of nitrogen. In agreement with previous workers, the temperature at which nitrogen commences to be absorbed by commercial manganese varies with the specimen used (500° and 740°). The temperature of maximum fixation of nitrogen also varies with the sample, and both variations are attributed to difference in the silicon and aluminium contents of the manganese. The curves showing the amounts of nitrogen absorbed at various temperatures rise to a maximum and then fall with dissociation of the nitride. At the temperature of maximum absorption the duration of heating has little, if any, effect on the quantity of nitrogen fixed; at low temperatures, equilibrium is reached in 2 hrs. Fixation increases with an increase in pressure over the range studied, viz., up to 60 atm.; the addition of lithium nitride lowers the temperature at which absorption of nitrogen commences, increases the amount absorbed, and accelerates the subsequent dissociation at higher temperatures.

L. S. THEOBALD.

Processes of oxidation. Behaviour of cyanogen bromide and hydrogen cyanide towards iron salts. F. OBERHAUSER and J. SCHORMÜLLER (Ber., 1929, 62, [*B*], 1482—1488).—Antimony pentachloride, cuprous or cupric bromide, phosphorus tribromide, and phosphorus trichloride do not appear to give additive compounds with cyanogen bromide. Ferrous bromide is converted by cyanogen bromide at 60° into the *compound* $2FeBr_2,CNBr$, which decomposes at 160° with partial formation of ferric iron and free cyanogen. With an excess of cyanogen bromide at 100°, ferrous bromide gives the *substance*, $Fe_3Br_8,3CNBr,C_2N_2$, tensimetric degradation of which gives the compound Fe_3Br_8, described in the literature as ferric bromide. This compound reacts readily with cyanogen bromide at the ordinary temperature or when gently heated, giving the *substance*, $Fe_3Br_8,4CNBr$, m. p. 143—145° (corr., decomp.), which loses its cyanogen bromide completely under the action of ammonia. Treatment of the additive compound with the requisite quantity of bromine at 80—90° gives the *substance*, $3FeBr_3,4CNBr$, m. p. 96—98° (corr., decomp.) in a closed capillary, which readily loses bromine. The very hygroscopic *compound*, $Fe_3Br_8,4HCN$, m. p. 163—165° after softening at 125°, is obtained from its components; it immediately evolves hydrogen cyanide when exposed to air.

H. WREN.

Alkoxonium hexacyanocobaltiates. F. HÖLZL, T. MEIER-MOHAR, and F. VIDITZ (Monatsh., 1929, 52, 73—82).—When hexacyanocobaltic acid is dissolved in alcohol and then evaporated to dryness in absence of moisture a crystalline ethoxonium derivative is obtained. Treatment of this, dissolved in alcohol and sulphuric acid, with hydrogen chloride affords the *compound* (I) $[Co(CN)_6](H{\cdot}EtOH)_3$. When I is treated with hydrogen chloride in presence of methyl and propyl alcohols the *substances* $[Co(CN)_6]H(H{\cdot}MeOH)_2$ and $[Co(CN)_6](H{\cdot}PrOH)_3$ are produced. These alkoxonium salts are crystalline, not very hygroscopic, easily soluble in water, and titrate as free acids. Treatment of I with pyridine yields *tripyridine hexacyanocobaltiate*, $[Co(CN)_6]H_3(C_5H_5N)_3$. The formation of these alkoxonium salts is presumably due to reaction between hexacyanocobaltiate ions and alkoxonium ions (produced during the treatment of the alcohol with hydrogen chloride, viz., $R{\cdot}OH+H^+\longrightarrow R{\cdot}OH{\cdot}H^+$).

H. BURTON.

New polynuclear co-ordination compounds of cobalt. E. G. V. PERCIVAL and W. WARDLAW (J.C.S., 1929, 1317—1322).—The reaction products obtained when dry air is drawn through an alcoholic solution of cobaltous chloride in the presence of various amines have been investigated. The earlier work of Bucknall and Wardlaw (A., 1928, 1345) has been confirmed and extended to the *propylamine* derivative. From benzylamine a complex *salt* of the probable composition $[3R{\cdot}Co(OH)_2Co{\cdot}3R]Cl_3$ ($R{=}CH_2Ph{\cdot}NH_2$) has been isolated. No definite results have been obtained when the oxidation is carried out in the presence of ethylamine, ethylenediamine, diethylamine, piperidine, or methylamine. All the reactive amines contain the group $CH_2{\cdot}NH_2$.

F. J. WILKINS.

Nitrites. II. Ammines of nickel nitrite. L. LE BOUCHER (Anal. Fís. Quím., 1929, 27, 358—367).—Nickel nitrite tetra-ammoniate has been prepared by passing ammonia over the tetra- or hexa-pyridinate until all the pyridine has been substituted by ammonia; on keeping in a vacuum desiccator over sulphuric acid the free pyridine, together with part of the ammonia, is removed, leaving the tetra-ammoniate, which has d_4^{25} 1·826. Treatment of the tetra-ammoniate with ammonia leads to the formation of the violet hexa-ammoniate. The equilibrium pressure of ammonia above this compound has been determined from 15° to 115°, and the correspondence of the curve obtained with that found by Ephraim for the supposed penta-ammoniate shows the latter to be merely a mixture of the hexa- and tetra-ammoniates. The tetra-ammoniate possesses an appreciable vapour pressure at temperatures above 100° (19 mm. at 105°), and by heating in a current of dry air at 115—120° the deep green diammoniate is produced. It is of importance that 120° be not exceeded during the process, as decomposition of the nitrite then sets in; it is thus impossible to obtain anhydrous nickel nitrite by complete deammination.

H. F. GILLBE.

Pneumatic apparatus for volumetric micro-analysis. E. SCHILOV (Mikrochem., 1929, 7, 163—184).—Micro-titrations can be carried out with considerable accuracy provided that apparatus is calibrated using mercury and that the pneumatic methods for the manipulation of burettes previously described by the author are used. J. S. CARTER.

Micro-crystalloscopy in gels. A. MARTINI (Mikrochem., 1929, 7, 236—241).—When carrying out micro-reactions it is often advantageous to use a gel, preferably a collodion gel, as medium. Reactions, especially those involving crystal formation, are often more sensitive than in aqueous media.

J. S. CARTER.

Rapid qualitative analysis. I. Specific and special reactions of the commoner cations and anions. G. GUTZEIT (Helv. Chim. Acta, 1929, 12, 713—740).—Specific and special reactions, generally colour reactions with an organic reagent, are enumerated for the following ions: silver, lead, mercury, bismuth, copper, cadmium, arsenic, antimony, tin, iron, chromium, manganese, nickel, cobalt, zinc, aluminium, barium, strontium, calcium, magnesium, potassium, sodium, ammonium, fluoride, chloride, bromide, iodide, sulphide, thiosulphate, sulphite, sulphate, nitrite, nitrate, phosphate, borate, silicate, carbonate, cyanide, ferro- and ferri-cyanide, thiocyanate, and oxalate. The reactions are suitable for the spot method of analysis. Special conditions are detailed when necessary, and colour reactions common to more than one cation are tabulated.

L. S. THEOBALD.

Perchloric acid as an agent for the clean destruction of organic matter. R. J. C. FABRY (Chemist-Analyst, 1929, 18, No. 2, 8—9).—For the removal of tartaric acid used to prevent precipitation of iron or titanium, the solution (600 c.c.) is kept overnight mixed with nitric acid (15 c.c.) and 20% perchloric acid (10 c.c.). CHEMICAL ABSTRACTS.

Destruction of organic matter in the determination of ash constituents. E. CHERBULIEZ (Helv. Chim. Acta, 1929, 12, 818—819).—The addition of fuming nitric acid (1 c.c.), or nitrous acid as sodium nitrite, to concentrated sulphuric acid (20 c.c.) and 20% perchloric acid (10 c.c.) gives a rapid means for the destruction of organic matter without leaving foreign, non-volatile substances in solution. The mixture is warmed for 15 min. and then heated until white fumes appear. If necessary, further quantities of perchloric and fuming nitric acids are added and the treatment is repeated until a colourless sulphuric acid solution is obtained. Chlorine is evolved during the initial warming, but the formation of chlorine dioxide in dangerous concentration is unlikely, since this substance is unstable at the temperature at which the reaction begins. L. S. THEOBALD.

Apparatus for electrometric titrations. A. UHL (Z. anal. Chem., 1929, 77, 280—283).—The apparatus comprises a wide glass tube stoppered at the upper end and having a narrow portion at the lower end which is plugged with a wad of filter paper soaked in potassium chloride solution. The narrow portion is filled with a hot solution of 3 g. of agar and 40 g. of potassium chloride in 100 c.c. of water, which sets to a jelly on cooling. Above this the tube is filled with a comparison solution consisting of a titrated solution of the same type as that under investigation, in which dips a platinised rod electrode terminating in a wire which is joined to one terminal of the galvanometer. The other terminal is connected to a clamping device carrying a pressure contact fixed to the upper part of the tube. One terminal of the contact is connected by means of a platinum or gold strip with a piece of platinum or gold foil fixed round the outside of the lower part of the tube just above the plug, to make contact with the solution being titrated. By means of the clamp the apparatus can readily be attached to the rim of the titrating vessel. A. R. POWELL.

Determination of hydrogen-ion concentration with the antimony electrode. I. I. SHUKOV and G. P. AVSEJEVITSCH (Z. Elektrochem., 1929, 35, 349—352).—The different experience of previous investigators with the antimony electrode is attributed to the variable nature of the electrodes used. A method of preparation is described for an antimony electrode the voltage of which, compared with that of a normal calomel electrode, varies in accordance with the equation : $E=0\cdot009+0\cdot053p_H$ at 14°. This linear relationship was shown to be satisfactory when the electrode was tested in buffer solutions of p_H 2·78—9·19.

The method of preparing the electrode is : first, a thin layer of mercury is deposited electrolytically (thereby forming an amalgam) on a platinum wire, about 1 cm. long, and fused into a glass tube, from a 2% mercuric chloride or mercurous nitrate solution with a current of 0·4—1·0 milliamp. for about 2 min. Too thick a layer leads to the formation of mercury drops and is thus a disadvantage. Secondly, antimony is deposited on the amalgamated platinum, which has been thoroughly dried, from a 25% solution of antimony trichloride in perfectly dry acetone, using an antimony anode and a current of 0·6—2·2 milliamp. for about 30 min. The antimony deposit should be about 2 mm. in thickness. In this way, the antimony amalgam which is first formed becomes covered with a fine crystalline layer of antimony. Thirdly, the electrode is treated with a hot solution of sodium hydroxide.
H. T. S. BRITTON.

Salt error of indicators due to standard alkaline buffers themselves. II. J. W. MCBAIN, M. E. LAING, and O. E. CLARK (J. Gen. Physiol., 1929, 12, 695—710; cf. A., 1926, 590).—A dilute solution of pure sodium hydroxide and a buffer solution which show identical colours when equal quantities of the same indicator are added to each do not necessarily have the same p_H values when the latter are determined electrometrically by means of the hydrogen electrode. The neutralising action of the indicator may be partly responsible for this discrepancy, but the magnitude of this effect is usually small in comparison with the total error, which in certain cases, *e.g.*, with phenol-red and a borate mixture at p_H 7·3, may exceed 2·0 p_H units. No appreciable error occurs with alizarin-yellow G, tropæolin O, and thymol-violet, but the anomaly may be very considerable with phenolphthalein, *o*-cresolphthalein, thymol-blue, and phenol-red.
W. O. KERMACK.

Microchemical colour reaction for sulphur. E. GRÜNSTEIDL (Z. anal. Chem., 1929, 77, 283—284).—For the detection of free sulphur or of an inorganic or organic sulphide the substance is evaporated with a few drops of sodium hydroxide solution just to dryness, a few drops of a 0·1% solution of sodium cyanide are added, and evaporation is repeated, the residue is moistened with dilute sulphuric acid, and dilute ferric chloride solution added; the formation of the characteristic ferric thiocyanate colour proves the presence of sulphur. A. R. POWELL.

Determination of sulphur in galena and lead. H. LEYSAHT.—See B., 1929, 521.

Iodometric determination of thiocyanate. A. SCHWICKER (Z. anal. Chem., 1929, 77, 278—280).—The thiocyanate solution is measured into an excess of 0·1*N*-iodine solution and 5—10 c.c. of *N*-ammonium borate solution, or of sodium borate solution and ammonium chloride, are added. After a few minutes 10 c.c. of 2*N*-sulphuric acid are added and the excess of iodine is titrated with thiosulphate (cf. Thiel, A., 1902, ii, 706). A. R. POWELL.

Determination of nitrogen by Dumas' method. F. HALLA (Mikrochem., 1929, 7, 202—207).—A theoretical consideration of the various equilibria involved suggests that Pregl's method of packing the tube does not of necessity eliminate errors due to the formation of carbon monoxide.
J. S. CARTER.

Colorimetric determination of phosphoric acid. A. Y. LEVITZKI (Nauch. Agron. Zhur., 1927, 4, 783—793).—The solution (80—90 c.c.) containing P_2O_5 (0·02—0·2 g.) is treated with 2·5 c.c. of a solution composed of equal volumes of 10% aqueous ammonium molybdate and concentrated sulphuric acid. After shaking, 0·25 c.c. of a solution obtained by dissolving (heat) 0·25 g. of lead in 5 c.c. of concentrated hydrochloric acid and adding 2—5 c.c. of 10% copper sulphate solution is added, the solution is diluted to 100 c.c., mixed, and compared colorimetrically with standards after 15 min. The method is applied to soils, plants, and fertilisers.
CHEMICAL ABSTRACTS.

Detection of phosphoric acid with ammonium molybdate and benzidine. F. Feigl (Z. anal. Chem., 1929, 77, 299—300).—To prevent the interference of silica, arsenic acid, and boric acid in the test previously described as specific for phosphoric acid (A., 1928, 1107) the molybdate solution must be treated with 15 g. of tartaric acid per 100 c.c. prior to use; 1 drop of the solution to be tested is mixed with 1 drop of the molybdate solution, warmed over a small flame, treated with 1 drop of the benzidine solution, and exposed to the vapour from an ammonia bottle. A blue colour develops in the presence of more than 1·5 μg. of phosphorus pentoxide.

A. R. Powell.

Determination of phosphoric acid in mineral phosphates and fertilisers. G. Jorgensen.—See B., 1929, 515.

Determination of silicon. T. Heczko (Z. anal. Chem., 1929, 77, 327—328).—The usual separation of an ignited silica precipitate from oxides of tervalent metals by addition of sulphuric and hydrofluoric acids and volatilisation is greatly accelerated if after addition of the acids an ashless filter paper is added to the crucible; if the filter paper is then ignited in the usual manner, rapid volatilisation is assured.

H. F. Gillbe.

Gravimetric and colorimetric method for the direct determination of sodium. E. R. Caley [with C. W. Foulk] (J. Amer. Chem. Soc., 1929, 51, 1664—1674).—A method of determining sodium as magnesium sodium uranyl acetate, $NaOAc,Mg(OAc)_2,3UO_2(OAc)_2,6·5H_2O$, is detailed (cf. Barber and Kolthoff, A., 1928, 859). Neglect of certain precautions, such as maintaining the temperature of precipitation at 20°, stirring vigorously during precipitation, etc., as well as an incorrect knowledge concerning the number of molecules of water of crystallisation in the precipitate, serve to explain the non-quantitative nature of the results previously obtained by this method. A modified procedure adapted for the colorimetric determination of sodium is described.

S. K. Tweedy.

Direct volumetric determination of potassium and sodium, applicable to other alkali and alkaline-earth metals. F. Díaz de Rada (Anal. Fís. Quím., 1929, 27, 390—399).—Sodium may be determined volumetrically in neutral or acetic acid solution containing 80—82% of alcohol by precipitation as sodium ferrocyanide with a solution of lithium ferrocyanide; the end-point is recognised either conductometrically or by the production of a bluish-green coloration when a drop of the solution is applied to cobalt nitrate paper. Ammonium, potassium, rubidium, and cæsium may also be completely precipitated, at suitable alcoholic concentration, in the same way, although in these cases double salts of the type $Li_2M_2Fe(CN)_6$ are produced; magnesium, barium, strontium, and calcium yield simple ferrocyanides. Potassium may be determined in a solution containing 50% of alcohol by addition of a calcium salt and titration with lithium ferrocyanide solution, whereby calcium potassium ferrocyanide is precipitated; the presence of four to five times the quantity of sodium does not interfere. Since total sodium and potassium may be determined by the method first described, a complete analysis of a solution containing both sodium and potassium may be effected by direct titration. H. F. Gillbe.

Determination of purity of potassium and sodium ferrocyanides by titration with zinc sulphate solution. Farbsalz-G.m.b.H.—See B., 1929, 555.

Micro-chemical mineral analysis. III. A. Martini (Mikrochem., 1929, 7, 231—234).—The formation in acid media of a complex cæsium zinc gold chloride having a well-defined micro-crystalline structure is a sensitive test for cæsium and zinc. A light brown isomorphous complex is formed when zinc is replaced by copper. Molybdenum may be detected by the formation of an orange pyrogallol–acetic acid–piperazine complex. The micro-crystalline structure is triclinic. Vanadium is detectable by the formation of a black, micro-triclinic pyrogallol–*o*-toluidine *complex*. Silver may be detected in presence of lead and mercury by the formation of silver methylamine acetate. Photomicrographs of all the compounds are given. J. S. Carter.

Systematic spot-analysis. I. K. Heller and P. Krumholz (Mikrochem., 1929, 7, 213—222).—Spot tests to be carried out on a porcelain plate are given for the identification of silver, copper, bismuth, mercury, cadmium, nickel, cobalt, iron, chromium, zinc, aluminium, and manganese. The majority of the reactions involved have been described by previous workers. The *p*-dimethylaminobenzylidenerhodanine test for silver (Feigl, A., 1928, 1108) is also given by mercury, but is specific for silver when carried out in presence of potassium cyanide. The detection of cadmium in presence of copper is based on the fact that cadmium only is precipitated as hydroxide by formaldehyde from solutions of the complex cyanides and that the hydroxide so precipitated is coloured blue in presence of dinitrodiphenylcarbazide. J. S. Carter.

Rapid determination of cadmium. G. Spacu and G. Suciu (Z. anal. Chem., 1929, 77, 340—343).—The neutral solution (100—300 c.c.) is treated with an excess of potassium iodide solution, and heated to boiling; a hot concentrated solution of diethylenediamine copper nitrate is added, and on cooling a coarsely crystalline precipitate of $(CdI_4)(Cu\,en_2)$, containing the whole of the cadmium, separates. After washing with the reagent, 96—100% alcohol, and ether, and drying for 5—10 min. in a vacuum desiccator, the precipitate, containing 13·99% Cd, is weighed. Excess of ammonia, ammonium salts, or of free ethylenediamine leads to low results.

H. F. Gillbe.

Colour reaction of copper. S. G. Clarke and B. Jones (Analyst, 1929, 54, 333—334).—Traces of copper sulphate may be detected and determined by neutralising the solution (which must be free from chloride), rendering slightly acid with sulphuric acid, diluting to 100 c.c., adding ammonium persulphate (1 g.), 1 c.c. of saturated alcoholic dimethylglyoxime, 0·5 c.c. of silver nitrate solution (0·5%), and 2 c.c. of 10% aqueous pyridine, and stirring. The colour is immediately compared with a standard. A slight opalescence due to traces of chlorides may be discharged by a slight excess of pyridine. As little as 0·01 mg. of copper yields a distinct reddish-violet colour, and not more than 0·1 mg. can suitably be determined. D. G. Hewer.

Sensitive reaction of cuprous ion. O. Funakoshi (Mem. Coll. Sci. Kyoto, 1929, **12**, 155—157).—*p*-Dimethylaminobenzylidenerhodanine in alcoholic solution forms a sensitive reagent for cuprous ion. In neutral solution a reddish-violet precipitate is formed, and one part of copper in 4×10^6 c.c. can be detected. A large excess of the reagent must be avoided. C. W. Gibby.

Rapid determination of mercury. G. Spacu and G. Suciu (Z. anal. Chem., 1929, **77**, 334—340).—The neutral or slightly ammoniacal solution is treated with an excess of potassium iodide solution and heated nearly to boiling; a hot concentrated solution of diethylenediamine copper nitrate is added, and the solution allowed to cool, whereupon there separates a dark violet, coarsely crystalline precipitate, $(HgI_4)(Cu\ en_2)$, which is washed first with a little of the dilute reagent, then with 95% alcohol, and finally with ether. After drying for 5—10 min. in a vacuum desiccator the precipitate, containing 22·49% Hg, may be weighed. Separation of mercury and copper may be effected by addition of ethylenediamine to the neutral solution prior to the precipitation. The method is rapid, not more than 1 hr. being required for complete determination. Since a definite precipitate is produced in 1 c.c. of solution containing 0·000007 g. of mercury, the method may be employed for micro-determinations. H. F. Gillbe.

Rare earths. XXXI. Ionic migration and magnetism in the separation of the rare earths. P. W. Selwood and B. S. Hopkins (Amer. Electrochem. Soc., May, 1929. Advance copy. 14 pp.).—Kendall's ionic migration method for the separation of the rare earths (A., 1925, ii, 977; 1926, 1117) is investigated. A partial separation of samarium and gadolinium and of erbium and yttrium was effected, but no separation of neodymium and samarium or of praseodymium and neodymium could be obtained. Where partial separation is possible the method cannot compete with established methods of separating the rare earths. The passage of an alcoholic solution of the chlorides of samarium and erbium through a non-homogeneous magnetic field led to no detectable separation, although the magnetic susceptibilities of the salts are in the ratio of about 1 : 40. It is believed that a very much more powerful magnetic field would be necessary to effect any separation by this method. H. J. T. Ellingham.

Rare earths. XXXII. Fractional hydrolysis of rare earths by electrolysis. H. C. Kremers and L. L. Quill (Amer. Electrochem. Soc., May, 1929. Advance copy. 6 pp.).—Electrolysis of a solution of rare-earth nitrates with a platinum anode, surrounded by a porous cup, and a molybdenum cathode yields a granular precipitate of hydroxides at the cathode with a current efficiency of 25—50%. This method leads to a partial separation of the constituent rare earths owing to differences in their basicity. Varying the current density from 0·01 to 0·5 amp./cm.^{2} caused no apparent variation in the efficiency of fractionation. The separation of yttrium from erbium and holmium is conveniently effected by the method. H. J. T. Ellingham.

Utilisation of the spectrophotometer in the determination of minute amounts of aluminium. E. W. Schwartze and R. M. Hann (Science, 1929, **69**, 167—170).—The reaction between aurintricarboxylic acid and aluminium is used as the basis for a spectrophotometric method for the determination of quantities of aluminium of the order 0·0025 mg./100 c.c. and less. The results are preferable to those obtained with a colorimeter. L. S. Theobald.

Potassium cyanate as a reagent for detection of cobalt. B. J. F. Dorrington and A. M. Ward (Analyst, 1929, **54**, 327—332).—The addition of varying volumes of *M*-cobalt nitrate solution to 2 c.c. of saturated alcoholic potassium cyanate solution gave for 0·3 c.c. of cobalt solution a deep royal blue with reddish tinge, with 0·1 c.c. a deep royal blue, diminishing to a pale blue for 0·01 c.c. A pale but definite colour was obtained with 0·01 c.c. of a 0·01*M*-cobalt nitrate solution, but the test is less delicate when carried out in aqueous solution. As little as 0·3 mg. of cobalt may be detected in presence of nickel and with precautions, using a blank test, 1 part in presence of 1000 parts of nickel. In the ordinary analytical scheme, ammonia is added to the solution after dissolving the mixed cobalt and nickel sulphides until slightly alkaline, and then one drop of the solution to 2 c.c. of alcoholic potassium cyanate solution. Ferric iron gives a brown colour which masks the colour of the cobalt complex, but after keeping the ferric salt is precipitated and the blue colour due to cobalt can be seen in the solution; with precautions 1 part of cobalt in presence of 1600 parts of iron may be demonstrated. Copper salts also give blue precipitates, but although the precipitate settles and the colour due to cobalt may be seen in the liquid, it is better to remove the copper by hydrogen sulphide. Uranium, titanous chloride, gold, and vanadium also give coloured solutions or precipitates. D. G. Hewer.

Rapid determination of various elements after precipitation by the classical methods. I. J. Dick (Z. anal. Chem., 1929, **77**, 352—363).—Accurate and rapid analyses may be carried out by thoroughly washing the precipitate in the usual manner, finally washing it with alcohol and ether, and drying it for 5—10 min. in a vacuum at the ordinary temperature. The following precipitates may be so treated: nickel dimethylglyoxime, mercuric sulphide, silver chloride, bromide, iodide, and thiocyanate, lead sulphate, barium sulphate, and calcium oxalate. H. F. Gillbe.

Potentiometric determinations with ferricyanide in alkaline solution. I. Vanadium and hyposulphite. C. del Fresno and L. Valdés (Anal. Fis. Quim., 1929, **27**, 368—389).—Vanadium may be determined by reduction in acid solution to the quadrivalent state, addition of sodium hydroxide solution, and potentiometric titration with potassium ferricyanide solution in an atmosphere of nitrogen; sodium hyposulphite may be directly titrated by the same method. The reactions involved are $VO^{\cdot\cdot}+Fe(CN)_6'''+4OH'\longrightarrow VO_3'+Fe(CN)_6''''+2H_2O$, and $H_2S_2O_4+2OH'+2Fe(CN)_6'''\longrightarrow 2H_2SO_3+2Fe(CN)_6''''$. With increase of hydroxyl-ion concentration the potential curve, prior to the break, is displaced towards the negative side, and the potential change at the end-point is correspondingly increased.

H. F. Gillbe.

Analytical chemistry of tantalum, niobium, and their mineral associates. XIV. Separation of small quantities of tantalum and niobium from titanium. W. R. Schoeller and C. Jahn (Analyst, 1929, 54, 320—326).—The solution containing the oxalates of titanium and niobium and the oxalo-earth acids is treated with excess of sodium salicylate and the characteristic orange colour of the salicylic–titanium complex produced. The oxalate ion is then removed from solution by addition of calcium chloride, when the bulky oxalate precipitate carries down the earth acids, leaving the titanium compound unaffected. As the precipitation of the earth acids is not quantitative the titanium is recovered from the filtrate and the treatment repeated. The oxalate precipitates are dissolved in hydrochloric acid, the oxalic acid is destroyed with permanganate, and the earth acids are precipitated as tannin complexes. The ignited precipitates are then submitted to tartaric hydrolysis, being fused with potassium hydrogen sulphate in silica, the product dissolved in a concentrated solution of 0·25 g. of tartaric acid, and the liquid treated while boiling with 5 c.c. of nitric acid. After boiling for 5—15 min. the solution is left for a few hours, the precipitate mixed with a little filter pulp, washed with dilute ammonium nitrate solution, ignited wet, and weighed as $(Ta,Nb)_2O_5$. The consistently negative errors of the method are ascribed to incomplete earth acid flocculation at the calcium oxalate precipitation stage, and a correction of 0·0015 g. for quantities of oxides found less than 0·006 g. up to 0·0035 for 0·0260 g. enables serviceable results to be obtained.

D. G. Hewer.

Direct-current amplifier for measuring small currents. J. M. Eglin (J. Opt. Soc. Amer., 1929, 18, 393—402).—Wynn-Williams' method (Phil. Mag., 1928, [vii], 6, 324) has been improved.

N. M. Bligh.

Use of the thermionic valve in measurements of ionisation currents. J. A. C. Teegan (Nature, 1929, 124, 91—92).

Thermoelements for high temperatures in a reducing atmosphere. J. A. M. van Liempt (Rec. trav. chim., 1929, 48, 585—588).—The *E.M.F.* developed by tungsten–molybdenum, tungsten–platinum rhodium, and molybdenum–platinum rhodium thermocouples have been measured between 0° and 1500°. The two last-named are particularly suitable for continuous use in a reducing atmosphere. The *E.M.F.* developed by a tungsten–molybdenum couple is very small, attaining a maximum value of 0·81 millivolt at about 600° and decreasing above that temperature.

C. W. Gibby.

Micro-determination of m. p. using a thermo-element. A. Niethammer (Mikrochem., 1929, 7, 223—226).—The essential feature of the arrangement, which is described in detail, is that a small portion of material at the junction of the thermo-element is observed through a microscope.

J. S. Carter.

Field γ-electroscope and its application to the investigation of radioactive minerals. G. O. Ertschikovski (Trav. Acad. Sci. U.R.S.S., 1928, 3, 127—160).—A description is given of an instrument devised for the purpose of determining the γ-rays at any point of the earth's surface and thus of ascertaining if radioactive substances are present. In the conditions prevailing at Tiuja-Mujun, it was found to be of little value in this respect.

T. H. Pope.

Magnesium light as a normal light source for photographic sensitometry and its connexion with the international sunlight standard. J. M. Eder (Z. wiss. Phot., 1929, 26, 353—362).—The light from burning magnesium filtered through a copper–cobalt solution is recommended as a light source for photographic sensitometry. It has the spectral energy distribution of mid-day sunlight of the colour-temperature 5000° Abs. In the visible spectrum the transmission is 0·5; the transmission in the ultra-violet is somewhat greater, but can be compensated. The magnesium light is very similar to the light from the electric arc. A table is given by means of which the transition from one light source to another of a different colour temperature, which is important in the determination of exposure times for panchromatic plates, and for three-colour photography, can be made. The table is prepared for the blue, green, and red spectral ranges and for different light sources. Various sensitive papers are examined. Silver chloride–gelatin paper sensitised by pinaflavol and sodium nitrite is particularly sensitive to green and yellow; such paper used in a direct copying process has a dominating sensitiveness over this part of the visible spectrum, the sensitiveness here exceeding that for the violet and ultra-violet, and being greater than with any other sensitiser. It is very useful for spectrometric work in the visible spectrum.

A. J. Mee.

Integrating microphotometer for *X*-ray crystal analysis. W. T. Astbury (Trans. Faraday Soc., 1929, 25, 397—401).—See this vol., 745.

Two-circle *X*-ray spectrometer. W. A. Wooster (Trans. Faraday Soc., 1929, 25, 401—402).—The instrument consists, in addition to the usual slits and crystal holder, of a small combined ionisation chamber and electrometer (Schonland) mounted on a vertical circle which is carried on the horizontal circle. It is specially suited to a measurement of reflected beams which fall into "layer" lines, and bears the same relation to the Bragg ionisation spectrometer (the analogue of the one-circle goniometer) as does the two-circle to the one-circle goniometer.

L. L. Bircumshaw.

Photo-electric method of measuring the light of the night sky. Course of variation through the night. (Lord) Rayleigh (Proc. Roy. Soc., 1929, A, 124, 395—408).—The method involves the use of a photo-electric cell and an electrometer with leakage resistance. The intensity of a patch of sky is matched with that of a white screen illuminated by an incandescence lamp, the brightness being controlled by a resistance in the lamp circuit. The voltage across the lamp is a measure of the intensity of the sky illumination. For the blue region near the green auroral line a rubidium cell is used, and the results indicate a regular diurnal variation with a maximum at midnight. Apart from irregular variations, the value at 6 p.m. in winter is 0·7 or 0·8 of the value at midnight. L. L. Bircumshaw.

Modified Pirani gauge. T. de Vries (J. Opt. Soc. Amer., 1929, **18**, 333—335).—In each arm of a Wheatstone bridge a carbon- or metal-filament lamp is connected, and provision is made so that the pressure in two of the bulbs in opposite arms is that under measurement. Balance of the bridge is attained by inserting a resistance box in series with one of the two other bulbs, and this balancing resistance may be used as a measure of the gas pressure. The device may be used in the range 0·001—1 mm. Carbon filaments are more satisfactory than metal filaments, and the voltage on the bridge for maximum sensitivity varies with the gas pressure. R. W. Lunt.

Vacuum recording gauges. K. C. D. Hickman (J. Opt. Soc. Amer., 1929, **18**, 305—331).—The development, construction, and operation of differential mercury manometers adapted as recording gauges in the range 0·01—5 mm. are described. In principle the device consists of a U-tube containing mercury supported by a pivot; one limb is closed and evacuated, and the other is connected by a flexible connexion to the vessel containing the gas the pressure of which is to be measured. If the pressure in the limb attached to the flexible connexion changes, the mercury will move in the U-tube, which will in consequence move about its pivot to a new position of equilibrium. By attaching an arm to the pivoted U-tube continuous records of pressure may be obtained. It is shown that by appropriate construction a deflexion approximately proportional to the pressure may be obtained. R. W. Lunt.

All-glass circulating pump for gases. R. Livingston (J. Physical Chem., 1929, **33**, 955).—A vertical modification of the pump designed by Funnell and Hoover (A., 1927, 850), which has less frictional resistance and a decreased sensitivity to the presence of saturated vapours, is described. L. S. Theobald.

Centrifugal filtration device for purification of small amounts of material by recrystallisation. E. L. Skau (J. Physical Chem., 1929, **33**, 951—954).—A simple device is described whereby filtrations can be effected at low temperatures as easily as at the ordinary temperature, and without contamination by dust. The weights of the crystals and mother-liquor can also be determined. The device is particularly suitable for fractional crystallisations of small amounts of material. The meso-form of αε-dichlorohexane has been isolated by this means. L. S. Theobald.

Leakage of helium through pyrex glass [at 0°]. G. P. Baxter, H. W. Starkweather, and R. B. Ellestad (Science, 1928, **68**, 516—517).—Leakage of helium through pyrex glass at 0° at a rate of 0·04 mm.^{3} per day per cm.^{2} has been observed at 1 atm. pressure. Mechanical leakage was excluded by comparative experiments at 770 and 627 mm. pressure, when the rate of leakage was approximately the same. The apparatus had previously shown no such effect with argon and had held a high vacuum for a long period before being filled with helium. The helium density determinations by Baxter and Starkweather (A., 1926, 233) are not invalidated. L. S. Theobald.

Cadmium lamp. H. Nagaoka and Y. Sugiura (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, **10**, 263—270).—A lamp for precision measurements is described. J. S. Carter.

Potentiometer. F. J. Watson (Chem. Eng. Min. Rev., 1929, **21**, 312—315).—A potentiometer of sufficient accuracy for carrying out potentiometric titrations or rough determinations of p_H is described. Parts of wireless receiving sets are largely used in the construction. J. S. Carter.

Apparatus for fractional distillation under vacuum. A. A. Ashworth (J. Inst. Petroleum Tech., 1929, **15**, 211—213).—An apparatus for collecting and withdrawing any number of fractions during a distillation under reduced pressure without interrupting the continuity of distillation is described. Distillate from the condenser outlet passes into an upper receiver which is furnished at the lower end with a wide (not less than 3 mm. bore) stop-cock, *A*, leading by a short length of wide tube to a graduated receiver. The latter is also provided at the lower end with a wide stop-cock, *B*, to which are connected a length of heavy rubber tubing and a mercury reservoir. Above the graduated receiver a side-arm and wide stop-cock, *C*, are provided. Stop-cocks *B* and *C* being closed and *A* open, a required fraction of distillate is collected in the graduated receiver; the mercury reservoir is then raised, *A* is closed, and *B* and *C* are opened, and the fraction is thus transferred to any convenient receiver, the mercury being allowed to rise to the level of *C*. *C* is then closed and the mercury reservoir lowered, whereby the graduated receiver is evacuated. *B* is then closed and *C* opened; the portion of distillate that has meanwhile collected in the upper receiver passes into the graduated receiver, and the distillation is continued. W. S. Norris.

Determination of width of pore of earthenware filters by means of the systems air–liquid and liquid–liquid. H. Bechhold and R. Schnurmann (Z. physikal. Chem., 1929, **142**, 1—24).—The pore width of various earthenware filters was determined by finding the pressure necessary to filter certain substances. The liquids used were water, methyl alcohol, ethyl ether, ethyl alcohol, *n*-propyl alcohol, *iso*butyl alcohol, acetone, carbon disulphide, benzene, nitrobenzene, and toluene. The pore widths found by the use of different liquids agreed fairly well if the pores were not larger than 4 μ. For pores larger than this the systems water–air and carbon disulphide–air gave values greater than those obtained with the other systems. For certain of the filters the determinations were repeated by finding the pressure required to filter a liquid mixed with another immiscible liquid (water and *iso*butyl alcohol). Values were obtained by this method from 0·5 to 0·1 of those arrived at from the air–liquid systems. This difference may be due to the moistening of the porous walls by the second liquid. It is also thought that the union of invisible drops to form visible drops, which would be conditioned by the differing viscosities of the liquids, may play a part. A. J. Mee.

Weight burette. I. Itabashi (J. Paints, 1928, 2, 107).—The glass apparatus is suitable for weighing viscous liquids. Chemical Abstracts.

Pipette for exact gas analysis. E. Moles and L. R. Píre (Anal. Fís. Quím. [Tecn.], 1929, 27, 107—109).—A modification of Travers' gas pipette is described. H. F. Gillbe.

Graphical method of teaching the thermochemistry of high temperatures. A. Stansfield (Amer. Electrochem. Soc., May, 1929. Advance copy. 7 pp.).—The method represents diagrammatically the influence of temperature on heats of reaction and the heat evolved or absorbed when the temperature of the reactants or the products is altered. H. J. T. Ellingham.

Nomenclature of inorganic compounds. E. Fritzmann (J. Russ. Phys. Chem. Soc., 1929, 61, No. 3, Suppl., 3—44). A. C. Bork (*Ibid.*, 45—52).

Russian chemical nomenclature. A. P. Semencov (J. Russ. Phys. Chem. Soc., 1929, 61, No. 3, Suppl., 53—55). E. V. Alexeevski (*Ibid.*, 56).

Early history of the synthesis of closed carbon chains. W. H. Perkin (J.C.S., 1929, 1347—1363). —A lecture.

Geochemistry.

Relation between the ozone contents of air at the earth's surface and air in the high atmosphere. A. Lepape and G. Colange (Compt. rend., 1929, 189, 53—54; cf. Dobson, this vol., 419).—The ozone contents of both air at the earth's surface (Paris, 1877—1904) and in the high atmosphere (Arosa, 1927, *loc. cit.*) are at a maximum in June, the former being approximately one half the latter in January and two thirds in June. If the layers of air in the high atmosphere mix only slowly with the troposphere, ozone should exist in appreciable proportions in the lower layers of the stratosphere (cf. Cabannes and Dufay, A., 1927, 1164). J. Grant.

Helium content of some Japanese minerals. II. J. Sasaki (Bull. Chem. Soc. Japan, 1929, 4, 111—112; cf. A., 1927, 225).—The helium contents of a number of Japanese minerals have been determined. C. W. Gibby.

Trinidad well waters. J. S. Parker and C. A. P. Southwell (J. Inst. Petroleum Tech., 1929, 15, 138—173).—The Trinidad well salt waters, which are to be regarded as intermediate waters, since they are overlain and underlain by strata containing oil-saturated sands, are essentially hydrogen carbonate waters of low sulphate content, whereas the water of the Gulf of Paria is a chloride water of high sulphate content. Although this might tend to suggest a meteoric origin, it is thought more probable that the well salt waters were originally chloride waters of connate origin which have acquired a high hydrogen carbonate content by interaction with organic matter. The well salt waters on an average closely approximate in total solids content to the sea-water surrounding the island. The latter does not contain any iodine, whereas a variable iodine content is found in the well salt water. W. S. Norris.

Replaceable bases in shales and clays overlying petroliferous strata. E. McK. Taylor (J. Inst. Petroleum Tech., 1929, 15, 207—210).—Five clays and shales overlying the petroliferous strata of Trinidad, 12 from Mexico, and 6 from Alsace are shown to have undergone base exchange in salt water followed by hydrolysis in fresh water, this being in accord with the results found with Rumanian and Venezuelan shales and with the theory previously advanced suggesting a possible relation between base exchange and the genesis of petroleum (this vol., 168). Thus the shales from Trinidad, Mexico, and Alsace have p_H values 8·8—9·4, 8·6—10·5, and 9·0—9·4, respectively, and contain 0·7—5·1, 1·8—6·5, and 1·2—2·1 mg.-equiv. of replaceable calcium per 100 g. of shale, and 24·5—31·4, 33·5—63·5, and 16·2—29·2 mg.-equiv. of replaceable sodium per 100 g. of shale, respectively, (cf. Taylor, *loc. cit.*; Hissink, Internat. Mitt. Bodenkunde, 1922, 12, 81). W. S. Norris.

Morphology and geochemistry of Tiuja-Mujun. A. Fersman (Trav. Acad. Sci. U.R.S.S., 1928, 3, 1—92).—The general and morphological characters and the mineralogy and geochemistry of the ore deposits at Tiuja-Mujun are described, and a theory is advanced to explain their origin. T. H. Pope.

Barytes of the radiferous mine at Tiuja-Mujun. L. L. Solodovnikova (Trav. Acad. Sci. U.R.S.S., 1928, 3, 93—104).—The minerals of the successive veins in this mine are described. T. H. Pope.

Migration of uranium and radium in the principal veins of the Tiuja-Mujun deposits. V. G. Chlopin and M. A. Pasvik (Trav. Acad. Sci. U.R.S.S., 1928, 3, 105—110).—In spite of the occurrence of the phenomena of the migration of uranium and radium in these veins, for the ore-mass as a whole the relation between radium and uranium corresponds exactly with the condition of radioactive equilibrium. Two forms of secondary accumulation of the radium are observed; in one the radium is crystallised with barium as copper-yellow radioactive barytes, and in the other, conditioned probably by adsorption, it occurs in masses of ore of colloidal character. T. H. Pope.

Hydrothermal alteration of serpentine. F. G. Wells (Amer. J. Sci., 1929, [v], 18, 35—52).—When olivine was treated with aqueous solutions of various inorganic compounds at 100—600° and under presures of 1—310 atm. a certain amount of dissolution occurred, but in no case was serpentine formed.

R. Cuthill.

" Terra rossa " as residue from dissolution of marine limestones. Wilh. Graf zu Leiningen (Chem. Erde, 1929, **4**, 178—187).—A series of comparative analyses of " terra rossa " from a number of localities and of material left after the dissolution of various limestones is adduced as additional evidence in support of the author's view that the first-named substance is to be regarded as a solution-residue of certain marine limestones. H. F. Harwood.

Origin of the strontium in the strata of the lower Muschelkalk and Röt formations near Jena. K. Dinger (Chem. Erde, 1929, **4**, 167—177).—The celestine occurring in certain strata of the lower Muschelkalk and Röt formations is not primary, but is due to secondary enrichment. The strontium has been transported in solution, probably as hydrogen carbonate, and precipitated as sulphate by interaction with gypsum, since the deposits of celestine occur only where this mineral is, or has been, present. Spectroscopic and chemical examination of the various strata of the above two formations showed the presence of traces of strontium in practically all cases, derived initially from sea-water through the agency of certain radiolaria which abstract it to form their shells. H. F. Harwood.

Red marls of the Trias formation. H. E. Krauss (Chem. Erde, 1929, **4**, 188—207).—A number of marls from the red trias formation have been subjected to chemical and rational analysis, and their mineral composition has been calculated. After subtraction of clastic minerals (quartz, felspar, and carbonates) and recalculation of the results to 100% it is found that the ratio of $Al_2O_3 : SiO_2 : H_2O$ in the residual material is practically the same as that in specimens of " terra rossa." It is therefore concluded that both these substances represent similar products of weathering. H. F. Harwood.

Isomorphous series in the tourmaline group and the genetic relationships between tourmaline and the micas. W. Kunitz (Chem. Erde, 1929, **4**, 208—251).—Theoretical.

H. F. Harwood.

Microscopic and spectroscopic investigation of the platinum-bearing rocks of the Bushveld igneous complex (Transvaal). H. Schneiderhöhn (Chem. Erde, 1929, **4**, 252—286).—A description is given of the rocks and associated ore minerals from the Rustenburg, Potgietersrust, and Lydenburg districts, together with an account of the genesis of the deposits. In the pegmatites and contact-metamorphic zone sperrylite and stibiopalladinite occur, whereas in the unaltered intrusive rocks the platinum metals are entirely present in the form of platiniferous sulphides of other metals; free platinum, palladium, and gold are encountered only as secondary occurrences in the weathered rocks. Investigation of the minerals by means of the quartz spectrograph showed that the platinum metals occurred solely in the pyrrhotite, pentlandite, and nickeliferous pyrite, the greatest quantity being present in the oldest minerals. Platinum and palladium are present in practically equal amounts, iridium, rhodium, and ruthenium occur to the extent of 1—10% of the platinum present, whilst osmium is present in traces only.

H. F. Harwood.

Chemical and petrological investigation of bituminous rocks of various ages from N. Germany. F. Hiebenthal (Chem. Erde, 1929, **4**, 343—368).—Bituminous material from four different formations (alluvial, diluvial, tertiary, and cretaceous) has been examined chemically and petrologically. The bitumens from these marine sediments show increasing carbon content with age, but unlike those of terrestrial origin there is no corresponding decrease in the hydrogen content. Elementary sulphur was found in the specimen from the alluvium, and a stable " metabitumen " was detected in the tertiary rock.

H. F. Harwood.

Relations of electrode potentials of some elements to the formation of hypogene mineral deposits. B. S. Butler and W. S. Burbank (Amer. Inst. Min. Met. Eng. Tech. Pub., 1929, No. 166, 3—15).—When arranged in order of their electrode potentials, groups of elements exhibit a periodicity and a relation to their occurrence in primary ore minerals. Chemical Abstracts.

Natrolite of Viagrande (Etna). S. di Franco (Atti R. Accad. Lincei, 1929, [vi], 8, 657—663).—Natrolite occurs as colourless transparent crystals, *d* 2·19—2·21, more than 1 cm. long and 0·1 cm. diameter in cavities of a very old reddish lava on Etna, in the forms (110), (111), (100), and (010). The more frequent combination is of the prism (110) and the pyramid (111). The crystallographic and optical constants have been determined. Analysis gave H_2O 9·58, SiO_2 46·93, Al_2O_3 27·02, Na_2O 16·43; total 99·96%, agreeing with the formula $Na_2Al_2Si_3O_{10},2H_2O$. On dehydration less than 1% of water is lost at 275°, but nearly the whole of the water is lost between 290° and 315°. This loss is reversible.

F. G. Tryhorn.

Organic Chemistry.

Non-explosive oxidation of propane and the butanes. R. N. Pease (J. Amer. Chem. Soc., 1929, **51**, 1839—1856).—Mixtures of propane and oxygen were passed through pyrex glass tubes heated in a constant-temperature bath at 300—625°, without attempting to render the reaction isothermal. The amounts of propane, oxygen, unsaturated hydrocarbons, methane, hydrogen, carbon monoxide and dioxide in the products and the proportions of hydrocarbon reacting according to schemes I, II, and III (p. 906) are tabulated. The liquid products have not been examined. In general, unsaturated hydrocarbons and carbon monoxide are the chief products, the amount of methane formed increasing as the furnace temperature is raised. The results are explained by the occurrence of three types of reaction: (I) dissociation into an unsaturated hydrocarbon and hydrogen or methane; (II) oxidation to an unsaturated hydrocarbon and liquid products, *e.g.*, water, alcohol, or formaldehyde, and (III) the "aldehyde oxidation," *e.g.*, $C_3H_8+O_2 \longrightarrow C_2H_5{\cdot}CHO+H_2O$; $C_2H_5{\cdot}CHO+O_2 \longrightarrow CH_3{\cdot}CHO+CO+H_2O$ (cf. Pope, Dykstra, and Edgar, following). Types I and II are homogeneous gas reactions of the first order with respect to propane. Since they always appear simultaneously, they have probably a common initial stage. When reaction III is prevented they do not occur below 550—600°, but they are subject to excitation by III at lower temperatures. Type III is a faintly luminous chain reaction, promoted by the presence of excess of hydrocarbon, but hindered by dilution with oxygen, methane, nitrogen, carbon dioxide, and hydrogen, which are given in order of increasing effectiveness. The inhibiting action is greater at higher temperatures, so that, under these conditions, the reaction may have a negative temperature coefficient, although it eventually becomes explosive (cf. Bone and others, J.C.S., 1904, 85, 693, 1637). A packing of coarsely powdered glass suppresses the reaction and has also a positively catalytic effect, which is destroyed by coating it with potassium chloride. The reaction is also suppressed by using a tube of small bore or by lowering the pressure to 5—10 mm. The oxidation of *n*- and *iso*-butanes proceeds, under these conditions, similarly to, but more readily than, that of propane. *n*-Butane is the more reactive. The optimum conditions for oxidising a paraffin to (*a*) aldehydes and (*b*) unsaturated hydrocarbons are discussed. H. E. F. Notton.

Vapour-phase oxidation of isomeric octanes. I. *n*-Octane. J. C. Pope, F. J. Dykstra, and G. Edgar (J. Amer. Chem. Soc., 1929, **51**, 1875—1889).—The oxidation of *n*-octane, vaporised in nitrogen and preheated to the reaction temperature, by sufficient oxygen for complete combustion has been examined by the flow method (*a*) at constant temperature and (*b*) with the temperature rising during about 2 hrs. from 200° to 650°. Reaction begins at 200° and, up to 270°, the principal products are aldehyde, acid, traces of peroxide, carbon dioxide, and water. Sharply at 270° a pulsatory reaction begins, accompanied by flashes of white light and by the formation of carbon monoxide. At 300—320° the pulsations disappear and the reaction becomes localised near the entrance of the furnace. Up to 650° the oxygen consumption and formation of carbon monoxide increase, but above this temperature complete combustion occurs with strong pulsations and a bright blue luminescence. The changes observed below 650° are explained by the following reactions:

(I) $C_7H_{15}{\cdot}CH_3+O_2 \longrightarrow C_7H_{15}{\cdot}CHO$;

(II) $C_nH_{2n+1}{\cdot}CH_2{\cdot}CHO+O_2 \longrightarrow C_nH_{2n+1}{\cdot}CHO+CO$;

(III) $C_nH_{2n+1}{\cdot}CH_2{\cdot}CHO+1{\cdot}5O_2 \longrightarrow C_nH_{2n+1}{\cdot}CHO+CO_2$.

The initial reaction, I, is followed at 200—270° by III, which is apparently a homogeneous gas reaction and continues at a slightly increasing rate up to 650°. The chain reaction, II, predominates at 270—650°, the average mol. wt. of the resulting aldehydes decreasing as the temperature rises. When, at 400°, molecules of the size of butaldehyde or smaller have been produced, further oxidation proceeds much more slowly until the temperature reaches 650°. This explanation is supported by analyses of the gaseous products and by parallel experiments with *n*-butaldehyde and *n*-heptaldehyde. Thus, it is shown that, in the oxidation of 1 mol. of octane to aldehydes and oxides of carbon, the formation of a given quantity of the latter requires 1 mol. of oxygen more than that required to produce the same quantity by oxidising either aldehyde. The oxygen consumed in all experiments with the three substances agrees with that calculated by means of the above equations from the amounts of oxides of carbon formed. The oxidation of heptaldehyde begins at about 150°. Carbon monoxide and dioxide are formed in almost equal amounts up to 235°, when the production of the former suddenly increases and the reaction becomes pulsatory. With butaldehyde the reaction begins at 200° and feeble pulsations are observed at 335°. H. E. F. Notton.

Carotinoids. II. Determination of the degree of unsaturation of polyenes by iodine chloride and perbenzoic acid. R. Pummerer, L. Rebmann, and W. Reindel (Ber., 1929, 62, [*B*], 1411—1418; cf. A., 1928, 765).—After prolonged contact with iodine chloride the presence of eleven double linkings in carotin is established, this agreeing with the number found by hydrogenation. The detection of the thirteen double linkings in lycopin by means of iodine chloride depends on the extreme prolongation of the action and the use of an unusually large excess of the reagent; liberation of iodine chloride or iodine from the additive product during titration is not observed. Xanthophyll behaves similarly to carotin. With isoprene, saturation of two double linkings by iodine chloride can be effected only if a large excess of reagent is used. At 0°, the hydrocarbon adds only 1 atom of oxygen from perbenzoic acid and the double linking remaining in the product can be determined by iodine chloride. Bixin adds five mols. of bromine, and not more than six double linkings react with iodine chloride under the most favourable conditions, whereas hydrogenation indicates the presence of nine double linkings; it absorbs only six atoms of oxygen from perbenzoic acid, whereas thiocyanogen at 0° indicates only three double linkings. In ωω′-diphenyloctatetraene four double linkings are detected by bromine, rather less than four by iodine chloride, and 3·2—3·3 by perbenzoic acid. With *r*- and *d*-limonene, iodine chloride indicates 2·2—2·3 double linkings, whereas about 1·6 atoms of oxygen are absorbed by perbenzoic acid at 0°.

Determination of the acid liberated during the titration of the carotin–iodine chloride adduct indicates 6 mols. per mol. of hydrocarbon instead of 3 recorded previously (*loc. cit.*). Considering 2 mols. of halogen acid to correspond with a double linking, the presence of three such "peculiar" linkings is indicated; this agrees with the results of the action of hydrogen and perbenzoic acid.

The absorption curves of xanthophyll, lycopin, and carotin are closely similar. H. Wren.

Preparation of amylene with a theoretical hydrogen value. H. I. Waterman, P. van 't Spijker, and H. A. van Westen (Rec. trav. chim., 1929, 48, 612—615).—An amylene preparation, b. p. below 36°, n_D^{20} 1·3811 (bromine value 208·4), by treatment with the theoretical quantity of bromine (calculated on the bromine value) in carbon tetrachloride at —10° to —15° gave a 50% yield of a mixture of bromides, b. p. 58—62·5°/17 mm., which, when treated with water and a zinc–copper couple at 60°, afforded a very pure amylene, b. p. 36·8—38·4°/760 mm., n_D^{20} 1·3856 [bromine value (McIlhiney) 229·0; thiocyanogen bromine value 228·5]. The hydrogen value determined by the method of Waterman, Perquin, and van Westen (B., 1928, 512) was found to be 100·8% of the theoretical value; the hydrogenation product had b. p. 28·0—28·5°, n_D^{20} 1·3545, in agreement with constants recorded for β-methylbutane (*lit.*). The original amylene preparation therefore consisted largely of the isomeride $CHMe\colon CMe_2$. C. W. Shoppee.

Additive products of diacetylenic hydrocarbons. V. Grignard and Tchéoufaki (Compt. rend., 1929, 188, 1531—1534; cf. this vol., 448).—$\Delta^{\zeta\theta}$-Tetradecadi-inene yields with bromine in carbon disulphide at the ordinary temperature *ζηθι-tetrabromo-$\Delta^{\zeta\theta}$-tetradecadiene*; at the b. p. only resinous products are formed; at —5° an unstable, oily ζι(?)-dibromide is formed, which yields α-bromo-Δ^{α}-heptinene when distilled.

Hydrogenation of diphenyldiacetylene (Straus, A., 1906, i, 77) in presence of platinum oxide–platinum-black yields *cis–cis*-diphenylbutadiene (20%), m. p. 69—70°, dibenzylacetylene (20%), m. p. 80°, and αδ-diphenylbutatriene, b. p. 185—187°/13 mm., which yields an isomeride, m. p. 95°, when exposed to light. The constitution of this last substance is proved by its ozonolysis to benzaldehyde, unaccompanied by oxalic or glyoxylic acids. Diphenyldiacetylene is converted by boiling with hydrobromic acid into *α-bromo-αδ-diphenylbutadiene*, m. p. 92°, which may be reduced by zinc dust in acetone to αδ-diphenylbutatriene. R. K. Callow.

Action of the zinc–copper couple on methylene iodide. G. Emschwiller (Compt. rend., 1929, 188, 1555—1557).—The action of the zinc–copper couple on methylene iodide in boiling ether yields initially *zinc iodomethyl iodide*, $CH_2I{\cdot}ZnI$, which is subsequently decomposed with the production of zinc iodide and ethylene and a small quantity of *zinc methylene iodide*, $CH_2(ZnI)_2$. The solution of zinc iodomethyl iodide reacts with iodine to yield methylene iodide, and slowly with water to yield methyl iodide. With water containing oxygen an oxidation product is first formed, hydrolysed with the formation of formaldehyde and zinc iodide. Zinc methylene iodide, like the analogous magnesium compounds (A., 1926, 1224), is decomposed by water to give methane. R. K. Callow.

Formation and fission of glucosides as a method for chemical and biochemical separation of racemic alcohols into their optically active forms. C. Neuberg, K. P. Jacobsen, and J. Wagner (Fermentforsch., 1929, 10, 491—531).—A new method for the resolution of optically active alcohols is based on glucoside formation with α- or β-acetobromoglucose in the presence of silver carbonate or quinoline. The *dl*-, the *d*-, or the *l*-alcohol *d*-glucoside may be formed, the last two being separated by fractional crystallisation or the *dl*-compound being submitted to asymmetric enzymolysis. In some cases if an excess of alcohol is used the unattacked portion is found to be optically active. Thus by interaction of 8 mols. of *dl*-borneol with 1 mol. of acetobromoglucose and silver carbonate and removal of the excess of borneol by steam distillation, a tetra-acetylglucoside is obtained which, after complete hydrolysis, yields a specimen of borneol having $[\alpha]_D$ +1·60° and containing, therefore, 4·3% excess of the *d*-compound. When only 2 mols. of *dl*-borneol are used, steam distillation yields a lævorotatory borneol, $[\alpha]_D$ —1·05°, whilst complete hydrolysis of the glucoside yields a dextrorotatory borneol, $[\alpha]_D$ +1·5°. Similar treatment of *dl*-menthol and steam distillation of the excess alcohol yields a product which is sometimes lævo- and sometimes dextro-rotatory. When a large excess of *dl*-menthol is heated with β-acetobromoglucose and quinoline at 100° it yields a mixture of α- and β-tetra-acetylglucosides, which when heated with 2*N*-alcoholic potassium hydroxide at 60° and then diluted with water yields *l*-menthol-α-*d*-glucoside, which is hydrolysed by *N*-sulphuric acid to yield *l*-menthol, $[\alpha]_D$ —48·3° (96·6% pure). If, instead, the partly deacetylated mixed α- and β-glucosides are reacetylated with pyridine and acetic anhydride and the product is crystallised from dilute alcohol, *d*-menthol-β-*d*-tetra-acetylglucoside is obtained, which hydrolyses to *d*-menthol, $[\alpha]_D$ +10° to +40°, whilst oily *l*-menthol-α-*d*-tetra-acetylglucoside is obtained from the mother-liquor and hydrolyses to *l*-menthol, $[\alpha]_D$ —24° to —44°. Thus *l*-menthol combines with α-glucose and *d*-menthol with the β-form, a conclusion which is confirmed by the fact that the *l*-mentholglucoside suffers 100% enzymolysis with maltase (α) and is unattacked by emulsin, whilst the *d*-mentholglucoside is hydrolysed to the extent of 93% by emulsin (β), but is unaffected by maltase. By the silver carbonate method methylpropylcarbinol yields, after deacetylation, *dl*-methylpropylcarbinol-*d*-β-glucoside, no resolution taking place. Fractional crystallisation of this glucoside from ethyl acetate yields a glucoside which on hydrolysis gives almost pure *d*-methylpropylcarbinol, $[\alpha]_D$ +12·8°. By enzymolysis of a 0·5% solution of *dl*-menthol-β-*d*-glucoside with emulsin at 37° and ether extraction when 46% hydrolysis has occurred (by determination of the sugar), *d*-menthol (50—70% purity) is obtained, whilst after removal of the ether continued hydrolysis of the residue yields *l*-menthol (57—79% purity). By similar enzymolysis *dl*-borneol-β-*d*-glucoside yields first *l*-borneol (50—54% purity) and then *d*-borneol (36—51% purity). Resolution of *dl*-methylpropylcarbinol-β-*d*-glucoside (obtained by hydrolysis of the tetra-acetylglucoside with methyl-alcoholic ammonia) by hydrolysis with emulsin is much less complete, the first fraction containing 6% of the *l*-alcohol and the second 13% of the *d*-compound. J. W. Baker.

β-Methyl-Δ^{β}-hepten-ζ-ol and natural *d*-citronellol. J. Dœuvre (Bull. Soc. chim., 1929, [iv], 45, 351—364).—Geraniol, b. p. 117—118°/16 mm.,

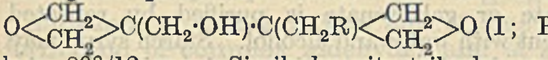
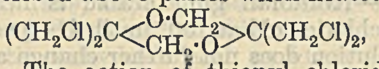
d_4^{17} 0·875, n_D^{17} 1·4722, $[\alpha]_D^{15}$ +1·13°, bromine value, 167%, obtained from Java citronella oil and containing some *d*-citronellol, when ozonised by the quantitative method (this vol., 542), gave 16% of formaldehyde, 35% of formic acid, and 90% of acetone, indicating that the β-form is the principal constituent. Determination of the α-(limonenic) form is not possible on account of the coloration given by the glycollaldehyde formed with the Grosse-Bohle reagent. The large amount of formic acid produced is attributed to formation of the aldehyde peroxide, $OH\cdot CH_2\cdot CHO_2$, yielding, by addition of water, formic acid and formaldehyde. Alcoholic potassium hydroxide converts this geraniol into β-methyl-Δ^{β}-hepten-ζ-ol, b. p. 78—79°/14 mm., 177—178°/760 mm., d_{14}^{14} 0·855, n_D^{14} 1·5411 (*allophanate*, m. p. 99—100°), together with *d*-citronellol and a viscous residue. The β-methyl-Δ^{β}-hepten-ζ-ol when ozonised affords 1% of formaldehyde, 9% of formic acid, and 90% of acetone, indicating that the alcohol is a mixture of 10% of the α- and 90% of the β-form, the proportions being thus unchanged by the action of potassium hydroxide. In accordance with Tiemann (A., 1899, i, 184) agitation with 25% sulphuric acid yields β-methylheptane-βζ-diol, b. p. 124—126°/14 mm., $d_4^{12\cdot4}$ 0·946, $n_D^{12\cdot4}$ 1·4569, converted into β-methylheptene oxide, b. p. 127—128°/750 mm., $d_4^{11\cdot3}$ 0·855, $n_D^{11\cdot3}$ 1·4288. The conversion of geraniol into methylheptenol is attributed to addition of 1 mol. of water at the double linking nearest to the hydroxyl group and scission of the glycol:
$CMe_2{:}CH\cdot CH_2\cdot CH_2\cdot CMe(OH)\cdot CH_2\cdot CH_2\cdot OH \longrightarrow$
$CMe_2{:}CH\cdot CH_2\cdot CH_2\cdot CMe\cdot OH + CH_3\cdot CH_2\cdot OH$, evidence of the reducing action of potassium ethoxide being afforded (*a*) by the formation of methylheptenol in the action of alcoholic potassium hydroxide on natural methylheptenone, b. p. 70—71°/18 mm., and (*b*) by the isolation from the viscous fraction of b. p. above 125°/15 mm., in the action of potassium hydroxide on geraniol, of a liquid condensation product, b. p. 174—180°/16 mm., formed from 2 mols. of methylheptenone by elimination of water (Léser, A., 1898, i, 512). ζ-Chloro-β-methyl-Δ^{β}-heptene, b. p. 59—61°/15 mm., forms no Grignard reagent, but *ζ-bromo-β-methyl-Δ^{β}-heptene*, b. p. 71—72°/14 mm., d_4^{17} 1·146, n_D^{17} 1·4720 (obtained in 60% yield using phosphorus tribromide in carbon tetrachloride), reacts readily with magnesium in ether in presence of iodine. When ozonised it affords 6% of formaldehyde, 16% of formic acid, and 76% of acetone, the proportion of α-form having been thus increased to 22%, probably by the hydrogen bromide produced in the reaction. The action of boiling hydriodic acid on methylheptenol yields, in addition to methylheptene oxide, a liquid, b. p. 95—105°/6 mm., containing mono- and di-iodo-derivatives which reacts readily with magnesium in ether. Repeated treatment of the fraction of b. p. 115—125°/14 mm. with alcoholic potassium hydroxide to destroy the geraniol afforded a *d*-citronellol, b. p. 119—120°/20 mm., d_4^{17} 0·866, n_D^{17} 1·4617, $[\alpha]_D^{16}$ +2·23°, bromine value 109% (cf. A., 1928, 654; this vol., 542), giving when ozonised 6% of formaldehyde, 18% of formic acid, and 80% of acetone, a result which indicates that natural *d*-citronellol is a mixture of approximately 20% of the α- and 80% of the β-form. Purification of *d*-citronellol through the benzoate, b. p. 190—200°, gave a citronellol, b. p. 118—119°/18 mm., d_4^{15} 0·860, n_D^{15} 1·4572, α_D^{15} +2·3°, bromine value 96%, affording when ozonised 15% of formaldehyde, 24% of formic acid, and 59% of acetone (cf. A., 1928, 1113). The isomerisation is attributed to the action of hydrogen chloride formed from the benzoyl chloride, since the original *d*-citronellol when heated at 100—150° for 2 hrs. in presence of hydrogen chloride gives a product, b. p. 118—119°/17 mm., d_4^{15} 0·863, n_D^{17} 1·4577, yielding when ozonised 14% of formaldehyde, 28% of formic acid, and 54% of acetone. The transformation is regarded as an exception to the Seytzev–Markovnikov rule, addition of hydrogen chloride at the double linking giving a chloro-derivative from which the α- and β-forms are regenerated in proportions differing from those originally existing by elimination of hydrogen chloride in both the directions possible.

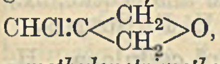
R. BRIGHTMAN.

Mechanism of organic reactions. II. "Non-existence" of a migratory methyl group in the conversion of glyceryl dichlorohydrin into monomethyl glyceryl ether. H. HIBBERT and M. S. WHELEN (J. Amer. Chem. Soc., 1929, **51**, 1943—1947).—Contrary to the results of Gilchrist and Purves (A., 1926, 153), methylation of pure glyceryl αγ-dichlorohydrin, prepared from epichlorohydrin, with silver oxide and methyl iodide proceeds normally to the *β-methyl ether*, b. p. 157—159°, n_D^{17} 1·4550, identified by hydrolysis through the acetate to β-methyl glyceryl ether. Commercial glyceryl αγ-dichlorohydrin always gives a mixture of products. *Glyceryl αβ-dichlorohydrin γ-methyl ether*, b. p. 153—157° (slight decomp.), n_D^{17} 1·4489, is also converted normally through the diacetate into pure α-methyl glyceryl ether. The results emphasise the value of α- and β-methyl glyceryl ethers for identification purposes.

H. E. F. NOTTON.

Elimination of the nitro-group from tertiary nitro-compounds. I. Derivatives of "nitro*iso*butylglycerol." II. Action of sodium amalgam on derivatives of "nitro*iso*butylglycerol." H. KLEINFELLER (Ber., 1929, **62**, [*B*], 1582—1590, 1590—1597).—I. Nitro*iso*butylglycerol (nitrotrihydroxymethylmethane) (cf. Schmidt and Wilkendorf, A., 1919, i, 249) is converted by phosphorus pentachloride mainly into *αγ-dichloro-β-nitro-β-chloromethylpropane*, m. p. 104°, in which the halogen atoms are retained with remarkable firmness. *γ-Chloro-β-nitro-β-chloromethylpropan-α-ol*, m. p. 127°, *γ-nitro-γ-chloromethyltrimethylene oxide*, b. p. 45—46°/9 mm., *αγ-dichloro-β-chloromethyl-Δ^{α}-propene*, b. p. 62—64°/9 mm., and *ααγ-trichloro-β-chloromethylpropane*, b. p. 77—80°/9 mm., are obtained in minor amount together with the *phosphate* of *αγ-dichloro-β-nitro-β-hydroxymethylpropane*. With red phosphorus and bromine, nitrotrihydroxymethylmethane yields the phosphate described above, *αγ-dibromo-β-nitro-β-bromomethylpropane*, m. p. 85°, *αγ-dibromo-β-bromomethyl-Δ^{α}-propene*, b. p. 105—107°/9 mm., and *ααγ-tribromo-β-bromomethylpropane*, b. p. 133—136°/9 mm. Reduction of trichloronitro*iso*butane with aluminium amalgam and alcohol affords *αγ-dichloro-β-hydroxylamino-β-chloromethylpropane*, m. p. 81°, whereas with stannous chloride and alcoholic hydrogen chloride *αγ-dichloro-*

β-*amino*-β-*chloromethylpropane* [*hydrochloride*, m. p. 245—246° (decomp.); *picrate*, m. p. 180°] is produced. β-*Nitro*-αγ-*dibenzoyloxy*-β-*hydroxymethylpropane*, m. p. 122—124°, is obtained as by-product of the preparation of the tribenzoyl compound. The action of alcoholic potassium hydroxide on αγ-dichloro-β-nitro-β-chloromethylpropane consumes 3·5 mols. of alkali and gives potassium nitrite and the *compound*  $O{<}{\overset{CH_2}{\underset{CH_2}{}}}{>}C(CH_2{\cdot}OH){\cdot}C(CH_2R){<}{\overset{CH_2}{\underset{CH_2}{}}}{>}O$ (I; R=Cl), b. p. 80°/12 mm. Similarly, nitrotrihydroxymethylmethane, its tri- and di-benzoyl derivatives react with 1, 4, and 3 mols. of potassium hydroxide, respectively, with production of potassium nitrite; the *substance*, $C_8H_{14}O_4$ (cf. I; R=OH), b. p. 108—112°/9 mm., is prepared from the dibenzoyl compound. The phosphoric ester described above passes when heated into the compound  $(CH_2Cl)_2C{<}{\overset{O{\cdot}CH_2}{\underset{CH_2{\cdot}O}{}}}{>}C(CH_2Cl)_2$, b. p. 60—61°/9 mm. The action of thionyl chloride on nitrotrihydroxymethylmethane affords the corresponding *sulphite*, $C_4H_7O_6NS$, m. p. 104°, and a second *form*, m. p. 180°, of nitrotrihydroxymethylmethane; the last-named compound is also obtained by means of phosphorus pentachloride or sulphuryl chloride; it slowly passes into the modification of lower m. p., and may possibly be present in the original material which does not melt sharply. The benzoyl derivative of either form has m. p. 111°.

II. αγ-Dichloro-β-nitro-β-chloromethylpropane and the corresponding tribromo-compound are indifferent towards silver, copper, or zinc at varied temperatures and yield amorphous products with sodium, potassium, or their alloy in presence of the customary solvents. When cautiously heated with 4·5% sodium amalgam in the absence of solvent, the trichloro-compound affords αγ-dichloro-β-chloromethyl-Δ^{α}-propene (see above) and *γ-chloro-β-chloromethyl-Δ^{α}-propene*, b. p. 30—31°/9 mm., converted by bromine into *αγ-dichloro-αβ-dibromo-β-chloromethylpropane*, b. p. 140°/10 mm., and *γ-chloro-αβ-dibromo-β-chloromethylpropane*, b. p. 115°/10 mm., respectively, and by chlorine into *ααβγ-tetrachloro-β-chloromethylpropane*, b. p. 99—101°/12 mm., and *αβγ-trichloro-β-chloromethylpropane*, b. p. 87°/9 mm., respectively; either compound is hydrogenated in the presence of spongy platinum to *γ-chloro-β-chloromethylpropane*, b. p. 45°/10 mm. γ-Chloro-β-nitro-β-chloromethylpropan-α-ol with sodium amalgam affords *γ-chloromethylenetrimethylene oxide*,  $CHCl{:}C{<}{\overset{CH_2}{\underset{CH_2}{}}}{>}O$, b. p. 63—66°/760 mm., and *γ-methylenetrimethylene oxide*, b. p. 35—40°/760 mm., obtained also from γ-nitro-γ-chloromethyltrimethylene oxide. αγ-Dibromo-β-nitro-β-bromomethylmethane affords *βε-dibromomethyl-$\Delta^{\alpha\epsilon}$-hexadiene*, b. p. 140—143°/9 mm. (slight decomp.), in addition to αγ-dibromo-β-bromomethyl-Δ^{α}-propene (see above) and *γ-bromo-β-bromomethyl-Δ^{α}-propene*, b. p. 70—72°/9 mm. These compounds are converted by bromine in chloroform into *αβεζ-tetrabromo-βε-dibromomethylhexane*, m. p. 115°, *ααβγ-tetrabromo-β-bromomethylpropane*, b. p. 185—190°/9 mm. (slight decomp.), and *αβγ-tribromo-β-bromomethylpropane*, b. p. 143—145°/9 mm. β-*Nitro*-*αβγ-tribenzoyloxymethylmethane* and sodium amalgam give *βε-dibenzoyloxymethyl-$\Delta^{\alpha\epsilon}$-hexadiene*, b. p. 220°/9 mm., and *γ-benzoyloxy-β-methyl-Δ^{α}-propene*, b. p. 120°/50 mm.; *αβεζ-tetrabromo-βε-dibenzoyloxymethylhexane* is described. Nitrobenzene reacts violently with sodium amalgam, giving azobenzene in good yield. With the aliphatic compounds, the alkali metal appears to remove an atom of oxygen from the nitro-group, leaving a nitroso-compound which decomposes into nitric oxide and a radical from which the ultimate products are derived by re-distribution of valencies. H. WREN.

Syntheses of bromomethanedisulphonic acid. H. J. BACKER (Rec. trav. chim., 1929, 48, 616—621).—Potassium formylbromomethanedisulphonate (this vol., 792) when treated with cold concentrated potassium hydroxide furnishes an 86% yield of potassium bromomethanedisulphonate (cf. Rathke, A., 1872, 388; Kohler, *ibid.*, 1899, i, 488), which can be purified by precipitating the aqueous solution with alcohol; crystallisation from water affords the *dihydrate*. Barium hydroxide may be used in the above preparation, which is the best method. Bromomethanedisulphonic acid may also be obtained by the following methods: (1) direct bromination of methanedisulphonic acid at 250° for 5 hrs.; (2) addition of the monohydrate of potassium diazomethanedisulphonate (cf. Pechmann and Manck, A., 1896, i, 14) to concentrated hydrobromic acid at 0°; (3) double decomposition of potassium dibromomethanesulphonate (cf. A., 1927, 39) with aqueous potassium sulphite at 130° (yield 20%). The following salts are described and their solubilities tabulated: *strychnine* (*trihydrate* losing $3H_2O$ at 105°, or by boiling with alcohol); *sodium* (*dihydrate*, crystallographic data); *thallous* (crystallographic data); *barium* (*hydrate* +4 or $4\frac{1}{2}H_2O$, lost at 100° in a vacuum). The free acid may be obtained by decomposing the barium salt with dilute sulphuric acid or by treating the strychnine salt with barium hydroxide; the use of the latter salt for purification is recommended. The acid (dihydrate, m. p. 125—126°) and its salts are considerably more soluble in water than methanesulphonic acid and its derivatives. C. W. SHOPPEE.

Action of acetic anhydride on carboxylic acids. A. W. VAN DER HAAR (Rec. trav. chim., 1929, 48, 607—611).—Consequent on the results of Caudri (this vol., 655), the author withdraws his former views on the constitution of the anhydrides (I) and (II) of sugar-beet sapogenin (A., 1928, 68) and ursolic acid (*ibid.*, 644). The compounds are the mixed anhydrides derived from the above acids and acetic acid; I melts at 215°, with conversion into sugar-beet sapogenin anhydride, m. p. 315°, which is largely converted by 0·1*N*-alcoholic potassium ethoxide into potassium diacetylursolate, and ethyl acetate; II melts at 200—201°, with conversion into diacetylursolic anhydride, m. p. 320—322°, and its mol. wt., determined cryoscopically in benzene, agrees with the revised structure. Caudri's results on the titration of acetylopianic acid with alcoholic sodium ethoxide, leading to the production of ethyl acetate in almost theoretical yield (*loc. cit.*), are confirmed.

The action of acetic anhydride on aldehydo- and keto-acids is considered; the formation with phenylhydrazine of a *compound*, m. p. 173° (containing 10·07, 10·10%N), from opianic acid, but not from acetylopianic acid, in acetic acid solution is reported and discussed. C. W. Shoppee.

Anodic formation of the triacetates of nickel and cobalt and Kolbe's reaction. C. Schall and C. Thieme-Wiedtmarckter.—See this vol., 892.

Velocity of esterification of fatty acids with ethylene glycol and hydrochloric acid. A. Kailan and A. Schachner.—See this vol., 888.

Esters of αα-dimethylbutyric acid. B. B. Corson, J. S. Thomas, and D. D. Waugh (J. Amer. Chem. Soc., 1929, **51**, 1950—1951).—αα-Dimethylbutyric acid, formed together with *tert.*-amyl alcohol and a *by-product*, b. p. 164—167·5°, n_{D}^{2} 1·4335, from magnesium *tert.*-amyl chloride and carbon dioxide, gives the following esters [b. p. °/746 mm. (corr.), d_4^{25}, and n_{D}^{25} being given for each]: *methyl*, 125—125·5°, 0·8943, 1·3991; ethyl, 141·8—142·2°, 0·8601, 1·3989 (cf. Bouveault, A., 1904, i, 642); n-*propyl*, 164—164·4°, 0·8575, 1·4040; n-*butyl*, 184—184·7°, 0·8566, 1·4098; n-*amyl*, 202·5—203·5°, 0·8544, 1·4140; and iso*amyl*, 192·5—196·5°, 0·8533, 1·4128.

H. E. F. Notton.

Action of per-acids on certain unsaturated organic substances and of benzoyl peroxide on a mixture of paraffins. J. Böeseken, W. C. Smit, and Gaster [with M. Slooff] (Proc. K. Akad. Wetensch. Amsterdam, 1929, **32**, 377—383).—By the action of perbenzoic or peracetic acid on methyl linoleate the ester of a dioxidostearic acid, m. p. 31°, is produced; hydrolysis at a low temperature yields the free acid, m. p. 79°. Hydrolysis of the triatomic ethylene oxide ring in this substance with dilute sulphuric acid at 80° or with 80% sulphuric acid at 0° yields two isomeric tetrahydroxystearic acids, m. p. 95° and 148°, respectively. Two other dioxidostearic acids, of m. p. 89° and 75°, have been prepared, in which, owing to steric hindrance, the ethylene oxide rings are not hydrolysable by acid. Treatment of ricinelaidic acid with perbenzoic acid yields two oxidoelaidic acids, m. p. 64° and 59°, $[\alpha]_{\mathrm{D}}^{17}$ −17·2° and 3·4°, respectively; on hydrolysis, two trihydroxystearic acids, m. p. 137° and 112°, are formed. The velocity coefficients of the oxidation by peracetic acid of oleic, elaidic, ricinoleic, and ricinelaidic acids, at 18°, are 0·036, 0·023, 0·026, and 0·016, respectively. Determination of this velocity thus serves to differentiate between the oleic and elaidic types. Acids containing a triple linking, *e.g.*, stearolic, are oxidised very slowly by peracetic acid: the primary product is probably a diketonic acid which then undergoes rupture at the ketonic carbon atoms. The group CMe⋮C· is attacked with about the same velocity as is stearolic acid, but the CH⋮C· group is scarcely affected. Tertiary alcohols may be synthesised directly from certain paraffins by treatment with benzoyl peroxide and hydrolysis of the benzoyl ester which is formed together with a large quantity of secondary products.

H. F. Gillbe.

Preparation of *d*-gluconic and galactonic acids. M. Hönig and W. Ruzicka (Ber., 1929, **62**, [*B*], 1434—1436; cf. Kiliani, this vol., 541).—Dextrose or galactose in 1% aqueous solution is mixed with sufficient 0·1*N*-bleaching powder solution to supply one equivalent of oxygen and rather more than sufficient milk of lime to maintain alkalinity. The liquid is kept well stirred and exposed to the light of a quartz lamp until a test portion does not colour starch iodide paper. The heated mixture is then saturated with carbon dioxide, filtered, and the filtrate concentrated in a vacuum to a syrup, which is poured into alcohol. The precipitated calcium gluconate or galactonate is purified by repeated treatment with water and alcohol. Starch syrup may also be used in the preparation of gluconic acid. An alternative process using barium hypobromite and hydroxide is also described, the acids being isolated as the calcium salts. H. Wren.

Preparation of *d*-glycuronic acid from gum arabic. F. Weinmann (Ber., 1929, **62**, [*B*], 1637—1639).—Kordofan gum arabic is heated with 2% hydrochloric acid at 100° until the specific rotation of the solution does not further change and the filtered solution is treated with alcohol, thereby precipitating the gum acids, which are boiled with *N*-sulphuric acid until the optical activity of the solution becomes constant. The solution is neutralised with barium hydroxide and finally barium carbonate, and filtered; the filtrate is boiled with a further small amount of barium carbonate, after which it is concentrated and the barium *d*-glycuronate is precipitated with alcohol. About 50 g. of acid are obtained from 1 kg. of gum.

H. Wren.

Alginic acid from *Macrocystis pyrifera*. W. L. Nelson and L. H. Cretcher (J. Amer. Chem. Soc., 1929, **51**, 1914—1922).—Mannitol (4—5%) and alginic acid (15%) (sodium salt, $[\alpha]_{\mathrm{D}}^{20}$ −133°) were isolated from the alga. The latter has an equivalent of 179 towards alkali and, when boiled with hydrochloric acid, evolves carbon dioxide (1 mol./equiv.). It is a polyuronic acid, $(C_5H_7O_4{\cdot}CO_2H)_n$, with no free aldehyde groups. It is partly decarboxylated by boiling with water or dilute sulphuric acid or by heating at 100° and is hydrolysed by cold 80% sulphuric acid to a new *polyuronic acid* and a syrupy *aldehydo-acid* (*barium* and *cinchonine*, m. p. 152° with effervescence, $[\alpha]_{\mathrm{D}}^{25}$ +113·6°, salts), isomeric with glycuronic acid. This is oxidised by bromine water to a gummy product from which *d*-mannosaccharidiamide and diphenylhydrazide were prepared. The presence of *d*-mannuronic acid residues in alginic acid is inferred (cf. Hoagland and Lieb, A., 1916, i, 195; Atsuki and Tomoda, A., 1926, 1280; Schmidt and Vocke, A., 1926, 939). H. E. F. Notton.

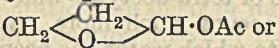
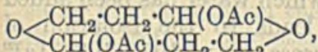
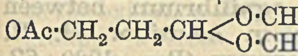
Polyoxymethylenes, a model of cellulose. H. Staudinger (Oesterr. Chem.-Ztg., 1929, **32**, 98—99).—A lecture. H. Wren.

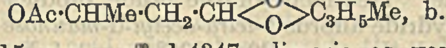
Hexahydrofarnesal and norhexahydrofarnesal. J. von Braun and E. Anton (Ber., 1929, **62**, [*B*], 1489—1491; cf. this vol., 296).—Hexahydrofarnesyl bromide slowly combines with trimethylamine in benzene at 100°, giving the very hygroscopic quaternary *bromide*, which is decomposed by successive treatment with silver oxide and distillation with potassium hydroxide into *hexahydrofarnesyldimethylamine*, b. p. 155—157°/10 mm., and γηλ-*trimethyl*-Δ^{a}-*dodecene*, b. p. 117—120°/12 mm., d_4^{12} 0·7797, n_{D}^{12} 1·4398, converted by ozonolysis into αει-*trimethylundecaldehyde*, b. p. 133—

135°/9 mm., d_4^{12} 0·8452, n_D^{12} 1·4440, the density of which increases on preservation (*semicarbazone*, m. p. 235—237°). *Hexahydrofarnesal*, b. p. 145—147°/11 mm. (*semicarbazone*, m. p. 248—250°), is prepared by oxidation of hexahydrofarnesol. The pleasant odour of the new aldehydes confirms the conclusion (*loc. cit.*) that the structure $CHMe_2·R·CHMe·CHO$ is particularly favourable to the strength and quality of odour.

H. Wren.

Influence of active carbon and of zinc on the formation of complex aldehydes and of sugars from solutions of potassium hydrogen carbonate under the action of ultra-violet rays. G. Mazzadroli and T. Babes.—See this vol., 894.

Associating lactolides. Transformations of aldols. M. Bergmann, A. Miekeley, and E. von Lippmann (Ber., 1929, 62, [*B*], 1467—1474; cf. A., 1924, i, 1042).—β-Hydroxypropaldehyde is transformed by acetic anhydride and pyridine at the ordinary temperature into the corresponding *lactol acetate*  $CH_2<\genfrac{}{}{0pt}{}{CH_2}{O}>CH·OAc$ or  $O<\genfrac{}{}{0pt}{}{CH_2·CH_2·CH(OAc)}{CH(OAc)·CH_2·CH_2}>O$, b. p. 122—123°/0·5 mm., d_4^{20} 1·1795, n_D^{20} 1·4490, monomeric at 180° but dimeric in freezing glacial acetic acid. It is converted by hydrogen in presence of spongy palladium and glacial acetic acid into 2-β-*acetoxyethyl*-1 : 3-*dioxan*,  $OAc·CH_2·CH_2·CH<\genfrac{}{}{0pt}{}{O·CH_2}{O·CH_2}>CH_2$, b. p. 115—118°/12 mm., d_4^{20} 1·0998, n_D^{20} 1·4415, dimeric as vapour at 180°, unimolecular in glacial acetic acid. When hydrolysed by *N*-sodium hydroxide, the acetoxy-compound affords 2-β-*hydroxyethyl*-1 : 3-*dioxan*, b. p. 102—103°/10 mm., d_4^{20} 1·1057, n_D^{20} 1·4566, which does not react with phenylhydrazine or reduce Fehling's solution, whereas acids convert it into trimethylene glycol and acraldehyde. Treatment of 2-β-hydroxyethyl-1 : 3-dioxan with silver oxide and methyl iodide gives 2-β-*methoxyethyl*-1 : 3-*dioxan*, b. p. 70—72°/9 mm., n_D^{20} 1·4334, hydrolysed to methyl alcohol, trimethylene glycol, and acraldehyde under conditions which do not effect the hydrolysis of *trimethylene glycol monomethyl ether*, b. p. 153°/768 mm., n_D^{20} 1·4126. 2-β-Hydroxyethyl-1 : 3-dioxan is prepared synthetically by the action of sodium hydroxide on 2-β-*chloroethyl*-1 : 3-*dioxan*, b. p. 74—75°/9 mm., n_D^{20} 1·4542, obtained by the action of hydrogen chloride on acraldehyde and trimethylene glycol.

Acetyl*cyclo*aldol (*loc. cit.*) is converted similarly by hydrogen into 4-*methyl*-2-β-*acetoxy*-n-*propyl*-1 : 3-*dioxan*,  $OAc·CHMe·CH_2·CH<\genfrac{}{}{0pt}{}{O}{O}>C_3H_5Me$, b. p. 114—116°/15 mm., n_D^{20} 1·4347, dimeric as vapour, also obtained when the monomeric acetyl*cyclo*aldol is passed with hydrogen at 200°/22 mm. over palladised asbestos. It is hydrolysed by alkali hydroxide to 4-*methyl*-2-β-*hydroxypropyl*-1 : 3-*dioxan*, b. p. 100°/15 mm., and by acids to crotonaldehyde and butane-αγ-diol, b. p. 108—109°/12 mm., $n_D^{19·5}$ 1·4418.

H. Wren.

Stereoisomerism of oximes. T. P. Raikowa (Ber., 1929, 62, [*B*], 1626—1637).—The observation that those unsymmetrical oximes which form an exception to the Hantzsch–Werner theory are capable of adding hydrogen cyanide directly, whereas those which harmonise with the theory do not possess this ability, shows that addition does not occur, as previously assumed, at the double linking between the C and N atoms, but at some other portion of the oxime molecule. A second double linking can be produced in suitable cases by desmotropic change; $R·C(CH_3){:}N·OH \longrightarrow R·C({:}CH_2)·NH·OH$, thus yielding ψ-oximes which may be produced directly by the oximation of the enolic forms of aldehydes and ketones. The essential condition for the formation of a ψ-oxime is the presence in one at least of the hydrocarbon residues of a mobile hydrogen atom which can wander to the nitrogen atom. This condition is fulfilled by all the oximes of aldehydes and ketones in which one valency of the oximino-group is attached directly to a methyl or methylene residue; a methene group appears incapable of allowing desmotropic change. The transformation of the oximino- to the hydroxylamino-group causes free movement in the nitrogen atom, and the oxime consequently loses its ability to exist in stereoisomeric modifications according to Hantzsch and Werner.

The ψ-oximes, $-C({:}C{:})·NH·OH$, are closely related to the hydroxamic acids $-C({:}O{:})·NH·OH$, with which they share the ability to give intense red colorations with ferric chloride. Examination of a large series of oximes shows that only those members which are constitutionally capable of desmotropic change give a colour with the reagent, whereas those in which such change is impossible do not react. The behaviour of an oxime towards ferric chloride is therefore a ready criterion of its behaviour towards hydrogen cyanide and the Hantzsch–Werner theory. The oximes are tested in alcoholic solution or, if not preformed, it is usually sufficient to boil the carbonyl compound in alcoholic solution with hydroxylamine hydrochloride and to test the cold solution. *cyclo*Pentanone, *cyclo*hexanone, menthone, carvone, pulegone, and camphor in which the methylene group is present in the ring pass into desmotropic ψ-oximes like the purely aliphatic compounds. Caution is required in applying the test to certain aldoximes on account of their ready oxidisability to hydroximic or hydroxamic acids. The group $·C(·NH·){:}N·OH$ does not appear capable of desmotropic change to $·C({:}N·)·NH·OH$, whereas the transition $R·C(NH_2){:}N·OH \rightleftharpoons R·C({:}NH)·NH·OH$ is possible.

H. Wren.

Dioximes. LII. G. B. Semeria and B. Somigliano (Gazzetta, 1929, 59, 258—265).—The rate of formation of methylglyoxime from oximinoacetone and hydroxylamine at different acidities has been studied (cf. Ölander, A., 1927, 1036). Hydroxylamine is determined by adding iodine and determining the excess, making a correction for the reaction between iodine and oximinoacetone, and the results are plotted in the form of curves for 13 different p_H values, from 1·2 to 12. The velocity of reaction increases rapidly as the p_H increases.

E. W. Wignall.

Hydrolysis of acetylated sugars and similar substances. G. Zemplén and E. Pacsu (Ber., 1929, 62, [*B*], 1613—1614).—Acetyl compounds of sugars which do not possess reducing groups after hydrolysis can be hydrolysed in methyl-alcoholic solution on the water-bath with minimal amounts of sodium methoxide. The instances described include mannitol from the hexa-acetate, β-glucosan from the triacetate, sucrose from the octa-acetate, thio*iso*trehalose from the octa-acetate, salicin from its penta-acetate, and α-methylmannoside from the tetra-acetate. The acetates of reducing sugars are similarly hydrolysed, but the solutions become yellowish-brown, so that it is preferable to use the cold chloroform process. H. Wren.

Ultra-violet light, insulin, and amino-acid catalysis [in the oxidation of sugars]. J. M. Ort.—See this vol., 889.

Decomposition of sugars and glucosamines in a dilute alkali solution. R. Masui (Osaka J. Med., 1928, **27**, 1437—1446).—The quantity of methylglucose produced by distillation of a slightly alkaline solution decreases in the order: lævulose, dextrose, glucosamine, the residue being lactic acid. A phosphate buffer retards the decomposition of dextrose. Chemical Abstracts.

Behaviour of dextrose when heated in alkaline solution. F. Fischler, K. Täufel, and S. W. Souci (Biochem. Z., 1929, **208**, 191—211).—The effect of temperature, time of heating, and concentration on the acids produced by the action of alkali hydroxide on dextrose was studied. Rise of temperature up to 140—150° increases the amount of acid formed; above this the amount decreases. Using dilute alkali (0·7*N*) the yield of acid increases with time of reaction at 98·5° and at 140°; in the latter case it reaches a constant value after 4 hrs. With 10*N*-potassium hydroxide the constant value is reached in ½ hr. With increase in the amount of alkali there is a rapid increase in the amount of acid, followed by a slow decrease. In very concentrated solution there is no caramelisation. The lowest sugar concentrations give the highest percentage of acid.

The acids formed were qualitatively investigated; indications of carbon dioxide, acetic, lactic, and glycollic acids were obtained using both 1·2*N*- and 10*N*-alkali, and at the lower concentrations formic and oxalic acids in addition. Using 1·2*N*-alkali, distillation of the acidified product yielded 7·2%, steam distillation 10·1%, ether extraction 49·7% of the total acid and 29·5%, 35·1%, and 8·9%, respectively, with 10*N*-alkali. J. H. Birkinshaw.

Mechanism of tautomeric interchange and the effect of structure on mobility and equilibrium. IV. Mechanism of acid catalysis in the mutarotation of nitrogen derivatives of tetra-acetylglucose. J. W. Baker.—See this vol., 889.

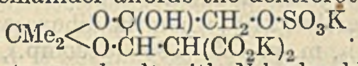
γ-Acetyl-αβ-*iso*propylideneglucose and its rearrangement into ζ-acetyl-αβ-*iso*propylideneglucose. K. Josephson (Svensk Kem. Tidskr., 1929, **41**, 99—106).—Prolonged treatment of γ-acetyldi*iso*propylideneglucose (I) with slightly diluted acetic acid and subsequent removal of volatile products at 30—35°/vac. affords *γ-acetyl*-αβ-iso*propylideneglucose* (II), m. p. 125—126° (corr.), $[\alpha]^{20}_{\text{Hg yellow}}$ −20·1° in water. Treatment of II with acetone and anhydrous copper sulphate at the ordinary temperature regenerates I. The rotation of an aqueous solution of II shows no change after 16 hrs., but when a drop of dilute ammonia is added, isomerisation into ζ-acetyl-αβ-*iso*propylideneglucose, m. p. 144—146° (cf. Fischer and Noth, A., 1918, i, 225), is complete after 5 min. Whilst II is stable in acetic acid solution rearrangement does take place in a slightly acid medium, and the velocity of the change has been measured polarimetrically at p_H 5·81, 6·75, and 7·1. The velocity is approximately proportional to the concentration of hydroxyl ions, and is of the same order as that of mutarotation of a reducing sugar. Rapid isomerisation occurs at about p_H 9. The conversion of Robison's hexosemonophosphate into zymophosphate is considered to involve a similar rearrangement. H. Burton.

Crystalline tetra-acetyl-α-glucose. H. H. Schlubach and I. Wolf [with P. Stadler] (Ber., 1929, **62**, [*B*], 1507—1509).—The action of silver carbonate on β′-acetochloroglucose in moist ether proceeds so slowly that isomerisation of the product to the equilibrium mixture of tetra-acetyl-α- and -β-glucose occurs. Reaction occurs much more rapidly in highly purified acetone to which water has been added in definite amount and leads to the isolation of 2 : 3 : 4 : 6-*tetra-acetyl-α-glucose*, m. p. 107—108°, $[\alpha]^{20}_{D}$ +138·9° in chloroform, $[\alpha]^{20}_{D}$ +139·4° to +83·1° in alcohol within 14 days or immediately on addition of ammonia. H. Wren.

Displacement of the equilibrium between normal and γ-galactose in solution. H. H. Schlubach and V. Prochownick (Ber., 1929, **62**, [*B*], 1502—1507).—The observation of Riiber and Minsaas (A., 1926, 1228) that γ-galactose is formed from the two normal forms of galactose with absorption of heat indicates the probable displacement of the equilibrium in favour of the γ-form as the temperature is raised. This is indicated by observation of the variation of the specific rotation of the equilibrium mixture in pyridine with varying temperature and confirmed by treatment of such mixtures with acetic anhydride and preparation of the β-variety of penta-acetyl-γ-galactose. In boiling pyridine the β-form of γ-galactose appears to be present in 23·4% proportion. H. Wren.

Triphenylmethyl ether of mannose. New tetra-acetylmannose. B. Helferich and J. F. Leete (Ber., 1929, **62**, [*B*], 1549—1554).—*d*-Mannose is converted by triphenylmethyl chloride at the atmospheric temperature into β-d-*mannose* 6-*triphenylmethyl ether*, m. p. 160—170° after softening at 140°, $[\alpha]^{17}_{D}$ −2·0° in chloroform, $[\alpha]^{10}_{D}$ −3·7° to 20·4° in pyridine. Treatment of the crude product with acetic anhydride affords β-*tetra-acetyl*-d-*mannose* 6-*triphenylmethyl ether*, m. p. 204—206° (corr.), $[\alpha]^{23}_{D}$ −2·6° in chloroform, and α-*tetra-acetyl*-d-*mannose* 6-*triphenylmethyl ether*, m. p. 130·5—131·5° (corr.), $[\alpha]^{23}_{D}$ −73·4° in chloroform (possibly accompanied by a second, isomorphous *form*, m. p. 123—124°), separated from one another by crystallisation from alcohol. Either form is hydrolysed to *d*-mannose 6-triphenylmethyl ether described above. Hydrogen bromide in glacial acetic acid transforms the β-tetra-acetate into 1 : 2 : 3 : 4-*tetra-acetyl*-β-d-*mannose*, m. p. 135·5—136·5° (corr.), $[\alpha]^{20}_{D}$ −22·5° in chloroform; in aqueous solution in ordinary glass tubes mutarotation is observed, ascribed, at least in part, to migration of acyl groups catalysed by alkali. Further acetylation gives β-penta-acetyl-*d*-mannose, m. p. 116°, $[\alpha]_D^{20}$ −24·1° in chloroform. The assignation of the triphenylmethyl group to the position 6 is based on the conversion of the tetra-acetylmannose by phosphoryl chloride in pyridine into *tetra-acetyl*-β-d-*mannose*-6-*chlorohydrin*, m. p. 142—143°, $[\alpha]_D^{12}$ −7·6° in chloroform, the chlorine atom of which reacts very sluggishly, whereas in Freudenberg's di*iso*propylidenemannose-1-chlorohydrin it is highly reactive. Similarly, with thionyl chloride *ditetra-acetyl*-β-d-*mannose* 6-*sulphite*, m. p. 173—175° (corr.), $[\alpha]_D^{12}$ −33·1° in chloroform, is obtained. H. WREN.

Model experiments based on the theory of alcoholic fermentation. I. Degradation of di*iso*propylidenefructose sulphate. H. OHLE and J. NEUSCHELLER (Ber., 1929, **62**, [*B*], 1651—1658).—It is assumed that in the initial stage of alcoholic fermentation the sugar or its phosphate must undergo dehydrogenation to yield reactive compounds which suffer fission between the γ- and δ-carbon atoms and that therefore oxidation products of dextrose or lævulose must exist which, under very mild conditions, decompose into three-carbon or simpler products. With di*iso*propylideneglucose or α-di*iso*propylidenefructose it does not appear possible to limit the action to the oxidation of the *sec.*-carbinol group 3 to the keto-group, whereas β-di*iso*propylidenefructose gives 2-ketodi*iso*propylidenegluconic acid. *Potassium* β-*di*-iso*propylidenefructose sulphate hemihydrate*, incipient decomp. about 210°, $[\alpha]_D^{20}$ −21·91° (also *anhydrous*; corresponding *sodium* salt, incipient decomp. about 200°, $[\alpha]_D^{20}$ −22·53°), is oxidised by potassium permanganate at 100° without marked production of sulphate ions if the oxygen used does not exceed 2 atoms, but much material remains unchanged. With increasing amounts of oxygen reaction occurs with formation of a dextrorotatory intermediate, the production of which is at a maximum with 6 atoms of oxygen. Under these conditions about 15% of the material is oxidised to carbon dioxide and sulphuric acid, 15% remains unchanged, about one third is converted into 4 mols. of carbon dioxide and 1 mol. of the *compound*, $CO_2K\cdot CH_2\cdot O\cdot SO_3K$, which darkens at 250° but does not melt below 300° (prepared also from glycollic and chlorosulphonic acids in pyridine), whereas the remainder affords the dextrorotatory *tri-potassium* salt



$\mathrm{CMe_2}<\begin{matrix}\mathrm{O\cdot \underset{|}{C}(OH)\cdot CH_2\cdot O\cdot SO_3K} \\ \mathrm{O\cdot CH\cdot CH(CO_2K)_2}\end{matrix}$

. Hydrolysis of the last-named salt with *N*-hydrochloric acid at 100° yields acetone, sulphuric acid, methylglyoxal, glycollic acid, and carbon dioxide, the yield of methylglyoxal, isolated as the disemicarbazone, being 75—80%. If hydrolysis is effected at about 35° and interrupted as soon as the solution is optically inactive, the yield is only about 30%. It appears therefore that the salt first loses the *iso*propylidene group and yields the sulphuric ester of dihydroxyacetone, which subsequently gives methylglyoxal and sulphuric acid. H. WREN.

Thio-sugars and their derivatives. XIV. α-Glucothiose [α-thioglucose]. W. SCHNEIDER and H. LEONHARDT (Ber., 1929, **62**, [*B*], 1384—1389; cf. A., 1928, 872).—The sodium compound of β-thioglucose is preserved in aqueous acidic solution until mutarotation is complete and the dried product of the reaction is treated with acetic anhydride and pyridine at 0°, thus yielding a mixture of α- and β-thioglucose penta-acetates, separated into its components by fractional crystallisation from alcohol. α-*Thioglucose penta-acetate* has m. p. 128—129°, $[\alpha]_D^{20}$ +132·6° in *s*-tetrachloroethane. It is hydrolysed by sodium methoxide to the *sodium* compound $C_6H_{11}O_5SNa,2H_2O$, m. p. 129—130° (decomp.) after softening at 100° when rapidly heated, $[\alpha]_D^{18}$ +142·93° in water [also *anhydrous*, m. p. 155° (decomp.) after becoming yellow at 130°]. Free α-thioglucose is strongly dextrorotatory in aqueous solution, but the specific rotation slowly diminishes and attains an equilibrium value about 15—20° higher than that observed with the equilibrium mixture from the corresponding β-compound. αα-*Diglucosyl disulphide*, from the sodium compound and iodine, has $[\alpha]_D^{18}$ +535·5°, whereas the value $[\alpha]_D^{18}$ −149·3° is now recorded for the β-derivative. H. WREN.

Synthesis of sucrose. A. PICTET and H. VOGEL (Ber., 1929, **62**, [*B*], 1418—1422; cf. A., 1928, 510, 741; Zemplén, this vol., 683).—Full details are given of the preparation of tetra-acetyl-γ-fructose, the condensation of the tetra-acetates of glucose and γ-fructose, and the isolation and hydrolysis of sucrose octa-acetate. H. WREN.

Unusual course of the solubility of calcium hydroxide in dilute solutions of sucrose. P. FUCHS (Ber., 1929, **62**, [*B*], 1535—1538).—The solubility at 17—17·5° is determined by successive addition to the sugar solution of known concentration of *N*-sodium hydroxide and a slight excess of about 2*N*-calcium chloride solution. After 5 min. the mixture is filtered and the filtrate is titrated with *N*-hydrochloric acid in presence of methyl-orange. The solubility of calcium hydroxide at first increases uniformly with increasing concentration of sucrose, passes through a maximum and minimum, and then again increases uniformly. The curve closely resembles the pressure–volume graph of a non-ideal gas somewhat below its critical temperature. H. WREN.

Optical rotation and atomic dimensions. VIII. Halogenohepta-acetyl derivatives of melibiose and maltose. Structures of bioses and of cellulose. D. H. BRAUNS (J. Amer. Chem. Soc., 1929, **51**, 1820—1831).—The isolation in a pure state of *fluoromelibiose hepta-acetate*, m. p. 135°, $[\alpha]_D^{20}$ +149·7° (all rotations measured in chloroform); *chloromelibiose hepta-acetate*, m. p. 127°, $[\alpha]_D^{20}$ +192·5°; *bromomelibiose hepta-acetate*, m. p. 116°, $[\alpha]_D^{20}$ +209·9°; *fluoromaltose hepta-acetate*, m. p. 174—175°, $[\alpha]_D^{20}$ +111·1°; chloromaltose hepta-acetate, m. p. 125°, $[\alpha]_D^{20}$ +159·5° (cf. Foerg, A., 1902, i, 347), and bromomaltose hepta-acetate, m. p. 112—113°, $[\alpha]_D^{20}$ +180·1°, obtained crystalline with great difficulty (cf. Fischer and Armstrong, A., 1902, i, 746), is described in detail. The specific rotations of these derivatives of α-bioses, unlike those of the β-bioses (cf. A., 1928, 157), show agreement with the regular relationship observed among the corresponding derivatives of the monose sugars. This difference in behaviour is explained by means of models which show that, under certain conditions, the oxide rings of β-bioses may face one another, bringing the halogen atoms under the influence of secondary valencies proceeding from the opposite ring, whereas with α-bioses this is impossible. The models also give formulæ for cellulose and cellobiose in agreement with their chemical properties and *X*-ray diffraction spectra. H. E. F. NOTTON.

Constitution of nodakenin, a new glucoside from *Peucedanum decursivum*, Maxim. II. J. ARIMA (Bull. Chem. Soc. Japan, 1929, 4, 113—119).—Nodakenetin (A., 1927, 599; this vol., 430) treated with bromine in chloroform gives a *bromo*-derivative, m. p. 230—231°, converted by alcoholic potassium hydroxide into *nodakilic acid*, $C_{13}H_{13}O_3 \cdot CO_2H,H_2O$, m. p. 214—215° (*methyl* ester, m. p. 133—134°); the acid is considered analogous to coumarilic acid. Nodakenetin is oxidised by boiling aqueous chromic acid to 7-*hydroxycoumarin*-6-*carboxylic acid*, m. p. 244—246° (decomp.) to 260—261° (decomp.) (according to rate of heating), identified by decarboxylation to umbelliferone, and synthesised by the interaction of 4-resorcylic acid and malic acid in sulphuric acid; *methyl* 7-*methoxycoumarin*-6-*carboxylate*, m. p. 165—166°, is prepared from degradation and synthetical products. E. W. WIGNALL.

Constitution of sinistrin. H. H. SCHLUBACH and W. FLÖRSHEIM (Ber., 1929, 62, [*B*], 1491—1493).—Extraction of the fresh bulbs of *Scilla maritima* with cold water followed by treatment of the extracts with lead acetate and fractional precipitation with alcohol permits the isolation of sinistrin *B*, $(C_6H_{10}O_5)_4$, $[\alpha]_D^{20}$ −30·6° in water, and sinistrin *A*, $(C_6H_{10}O_5)_2$, $[\alpha]_D^{20}$ −25·3° in water. The last-named substance is converted by methyl sulphate and alkali hydroxide into a compound closely resembling methylinulin and converted by oxalic acid into 3 : 4 : 6-trimethylfructose-(2 : 5) (cf. Schlubach and Elsner, this vol., 51; Haworth and Learner, A., 1928, 510). Sinistrin *B* appears to be a tetrafructose anhydride.

H. WREN.

Starch. II. Potato starch. K. HESS and F. A. SMITH (Ber., 1929, 62, [*B*], 1619—1626; cf. 1928, 1225).—The influence of pre-treatment of starch with pyridine on its acetylation depends on the induced swelling of the starch for which the water content of both materials is responsible. Dry starch does not swell in anhydrous pyridine. The ease of acetylation increases with increased degree of swelling. The isolation by Brigl and Schinle (this vol., 299) by the author's process (*loc. cit.*) of a starch acetate " rapidly " soluble in chloroform to a homogeneous viscous solution has led to a repetition of the work with varied amounts of pyridine and acetic anhydride, whereby readily soluble products are not obtained; under similar conditions amylose affords a freely soluble acetate corresponding with Brigl and Schinle's starch acetate. Treatment of starch with warm water below the swelling temperature causes layer-wise dissolution without altering the microscopic appearance of the granules except in regard to diameter. The aqueous solution yields preparations with the properties of starch amylose when treated with alcohol. Prolonged treatment of a fraction thus obtained with boiling water causes increased reducing power and diminished optical activity, whilst the solution becomes markedly more acidic. Treatment of natural starch with warm water causes an irregular development of acidity in the solvent which is not apparently related to the amount of carbohydrate yielded to the water in the corresponding period.

In contrast to natural starch, the product regenerated from starch acetate by hydrolysis with methyl-alcoholic ammonia can be dissolved only with difficulty in cold *N*-sodium hydroxide. Comparison of the optical activities of solutions of the product and natural starch (prepared by protracted heating with 0·81*N*-alkali at 60°) appears to confirm the identity of the substances. The specific rotation of natural starch in solutions of differing concentration with respect to carbohydrate and sodium hydroxide is tabulated. H. WREN.

New series of starch depolymerisation products. A. PICTET and H. VOGEL (Helv. Chim. Acta, 1929, 12, 700—713).—By heating dry starch with 3 parts of dry glycerol at 220° followed by dilution with alcohol etc. iso*trihexosan*, $(C_6H_{10}O_5)_3$, m. p. 260—262° (decomp., after colouring at 235°), $[\alpha]_D$ +166·5° in water, was obtained. It gave the starch–iodine test, and did not reduce Fehling's solution or aqueous potassium permanganate; when warmed with hydrochloric acid it was converted into dextrose. It was unattacked by emulsin but malt-diastase gave dextrinose. Boiling acetic anhydride produced a *monoacetate*, m. p. 156—160°, decomp. 200°, $[\alpha]_D$ +154·8° in chloroform, not coloured by iodine; hydrolysis by sodium methoxide caused regeneration of *iso*trihexosan.

*iso*Trihexosan when treated with concentrated hydrochloric acid under cooling formed iso*trihexose*, $C_{18}H_{32}O_{16}$, decomp. 155—160°, $[\alpha]_D$ +102·1° in water (*osazone*, m. p. 169—170°, decomp. 180°), which reduced Fehling's solution but was not coloured by iodine. Treatment by warm dilute aqueous oxalic acid led to a mixture of dextrose and dextrinose (cf. Syniewski, A., 1900, i, 79), m. p. 67—68°, decomp. 200° (Syniewski gave m. p. 82—85°) [*monohydrate*, m. p. 94—96°, decomp. 200°; osazone, m. p. 167° (lit. 152—153°); octa-acetate, m. p. 157° (identical with maltose octa-acetate, m. p. 158°)].

*iso*Trihexosan was further depolymerised by heating with glycerol at 240°, when the dihexosan *dextrinosan*, $(C_6H_{10}O_5)_2$, m. p. 185—186° (decomp.), $[\alpha]_D$ +151·0° in water (*hexa-acetate*, m. p. 140—143°, $[\alpha]_D$ +145·5° in chloroform), was formed. Iodine coloured dextrinosan a reddish-brown, whilst concentrated hydrochloric acid at the ordinary temperature converted it into dextrinose (above). An attempt to reverse the last change by heating dextrinose at 175° under 12 mm. pressure led only to a *substance*, m. p. 130—140°, $[\alpha]_D$ +149·2° in water, different from the dextrinosan obtained by the depolymerisation of starch, *e.g.*, in not colouring with iodine.

An aqueous solution of *iso*trihexosan, on long keeping at the ordinary temperature, more quickly at 50—60°, deposited the polymeric iso*polyhexosan*, sinters at 235°, decomp. 245°, which, on warming with hydrochloric acid, gave dextrose alone. It was depolymerised by hot water, hence $[\alpha_D]$ +166·7° in water and mol. wt. 486 [corresponding with $(C_6H_{10}O_5)_3$] are untrustworthy. Acetylation by acetic anhydride and pyridine gave a *peracetyl* derivative, $[\alpha]_D$ +177·4° in chloroform, the mol. wt. of which suggested the formula $(C_6H_{10}O_5)_{12}$ for *iso*polyhexosan.

R. J. W. Le Fèvre.

Nature of inulin. H. H. Schlubach and H. Elsner (Ber., 1929, 62, [*B*], 1493—1502).—Examination of the literature discloses the existence of a lengthy series of fructose anhydrides from the simplest member to inulin. With decreasing solubility in water the mol. wt. increases and the specific rotation sinks. There appears to be a polymeric homologous series similar to Staudinger's polyoxymethylenes and for which the nomenclature "polylævans" is proposed. Inulin is to be regarded as a mixture of polymerides of high mol. wt., their nature varying with the botanical origin of the material and the time of harvesting. "Purification" of inulin merely effects the removal of the lower and therefore more freely soluble polymerides. The conflicting evidence does not permit conclusions with regard to the nature of the forces operative within the inulin molecule and the presence of phosphoric and silicic acids is unexplained. Polarimetric observations during the hydrolysis of inulin by acids has led Tanret to regard the product as a mixture of 12 mols. of lævulose with 1 mol. of dextrose, and the last-named sugar has been isolated as such from ψ-inulin. The production of dextrose by the acidic hydrolysis of inulin is established as follows: (1) triacetylinulin is cautiously hydrolysed by acetyl bromide, hydrogen bromide, and glacial acetic acid, the product is debrominated with silver carbonate and acetylated with acetic anhydride and sulphuric acid. Penta-acetyl-α-glucose is thereby obtained crystalline. Intermediately a mixture of acetylated hexoses, probably mainly tetra-acetyl-γ-fructose, is produced. Crystalline penta-acetyl-α-glucose is also obtained by the action of acetic anhydride and sulphuric acid on triacetylinulin. Examination of the reducing power of the mixture obtained by the hydrolysis of inulin with 0·05N-sulphuric acid according to Willstätter, Schudel, and Bertrand discloses the presence of about 8% of aldoses, thus agreeing closely with Tanret's observations. It is not maintained that dextrose is necessarily a constitutive component of inulin, since the partial isomerisation of γ-fructose to dextrose during hydrolysis is not impossible, although it is not observed during the hydrolysis of sucrose under identical conditions. It is possible that the terminal free hydroxyl group which would be present in inulin if a chain structure is assumed is substituted by the glucose residue in such a manner that its reducing group is united to the reducing group of the fructose chain. Inulin would thus resemble a sucrose in which the γ-fructose residue is replaced by a series of these residues.

H. Wren.

Polysaccharides. XXXIX. Enzymic degradation of chitin and chitosan. I. P. Karrer and A. Hofmann (Helv. Chim. Acta, 1929, **12**, 616—637).—Natural chitin is attacked very slowly by enzymes; it is therefore prepared by dissolution in hydrochloric acid and reprecipitation by water. Chitinase decomposes this prepared chitin at the optimum p_H (5·2) and 36° with the formation of N-acetylglucosamine, $[\alpha]_D$ +55·6°, 85% degradation being accomplished in 10 days.

Chitosan at p_H 4·4—4·5 and 36° gives the hydrochloride of a *polyglucosamine* (tri- or tetra-glucosamine compound?), the *base* of which is liberated by treatment of the salt with diethylamine solution; by hydrolysis with hydrochloric acid it gives glucosamine hydrochloride.

R. J. W. Le Fèvre.

Effect of aniline on cellulose triacetate. H. Le B. Gray, T. F. Murray, jun., and C. J. Staud (J. Amer. Chem. Soc., 1929, **51**, 1810—1814).—The reaction of cellulose triacetate with aniline at (*a*) 183°, and (*b*) 148—151°, has been followed polarimetrically and by acetyl determinations [final content: (*a*) 2·0%, (*b*) 10·4% Ac]. The initial and final stages are slow with an intermediate period of rapid change. No appreciable reaction occurs at 20—30°. The changes in composition, solubility, and rotatory power indicate that the triacetate undergoes hydrolysis and not a change analogous to mutarotation (cf. Knoevenagel, B., 1915, 134). The product may be reacetylated to cellulose triacetate.

H. E. F. Notton.

Lignin and cellulose. X. Aromatic nature of lignin. K. Freudenberg, W. Belz, and C. Niemann (Ber., 1929, **62**, [*B*], 1554—1561; cf. A., 1928, 1227).—The investigation is concerned with isolated lignin which may possibly have suffered chemical change during isolation. Bromine in hydrobromic acid causes substitution; there is no evidence of addition. Polymerised coniferyl alcohol behaves similarly in all respects and 5-bromovanillic acid shows close analogy in its behaviour. The similarity is particularly marked in the behaviour of the methyl group during bromination; the aromatic union of the methoxyl group is also indicated by its behaviour towards hydriodic acid. It may therefore be assumed that the 17% of methoxyl present in isolated lignin belongs to a system of the vanillin type; this harmonises with the observation that at least 5—6%, possibly as much as 12%, of the lignin is composed of piperonal components. The vanillin components of lignin are differentiated sharply from polymerised coniferyl alcohol by their insolubility in alkali hydroxide; a part of the methoxyl groups in lignin is transformed by hydriodic acid into phenolic hydroxyl. After deduction of the oxygenated groups, the expression $[CH_{1·4}]_x$ remains for the fundamental hydrocarbon of lignin. For saturated aliphatic or hydroaromatic hydrocarbon residues the terms $[CH_{1·7}]_x$ to $[CH_{2·2}]_x$ must be fulfilled. Since the presence of reactive double linkings is not indicated, the probability of the aromatic nature of lignin is hereby strengthened. The high refractive index (n=about 1·61) is also evidence of its aromatic nature.

Methylcellulose is practically unaffected by bromine in hydrobromic acid.

H. Wren.

Lignin. II. R. O. Herzog and A. Hillmer [with E. Paersch and E. Hellriegel] (Ber., 1929, **62**, [*B*], 1600—1602; cf. A., 1927, 342, 861; Freudenberg, preceding).—It is assumed that atmospheric oxygen plays an essential part in the union of the lignin components in nature. The action of air or oxygen on *iso*eugenol, followed by dissolution of the product in ether and precipitation with light petroleum, yields a *product* differing from vanillin, dehydrovanillin, di*iso*eugenol, and dehydrodi*iso*eugenol. Analyses of the product and its non-crystalline *acetate* indicate the union of 2 mols. of *iso*eugenol with addition of oxygen. The material is not hydrogenated in presence of platinum-black. Its ultra-violet absorption curve has the form typical of *iso*eugenol, coniferyl alcohol, and lignin. It gives a reddish-violet colour with phloroglucinol and hydrochloric acid.

Cautious treatment of rye straw at the ordinary temperature with 2% methyl-alcoholic sodium hydroxide in the absence of light and air yields, after electrodialysis, a lignin soluble in alkali and (colloidally) in water. The mol. wt. in resorcinol indicates the presence of about two coniferyl residues. Its absorption spectrum in the ultra-violet is exactly similar to those of other types of lignin. It is not reduced by hydrogen in presence of platinum-black.

H. Wren.

Free halogenated aliphatic amines. M. de Montmollin and E. Zolliker (Helv. Chim. Acta, 1929, **12**, 610—616).—Treatment of ethyl chlorobutyl ether with alcoholic ammonia gave β-ethoxybutylamine, b. p. 140—145°, accompanied by diethoxydibutylamine, b. p. 225—235°. Displacements of ethoxyl by halogen were accomplished by heating the ethoxy-amines with the appropriate aqueous halogen acid in a sealed tube; β-*chlorobutylamine*, b. p. 50°/40 mm. [hydrochloride; *hydrobromide*; picrate, m. p. 124° (lit. 142°); *benzoyl* derivative, m. p. 69°], and *di*-β-*chlorodibutylamine*, b. p. 91°/11 mm. (*hydrobromide*), were thus prepared.

Reduction of β-ethoxypropionitrile by sodium and alcohol gave γ-*ethoxybutylamine*, b. p. 142—143°, from which γ-*bromobutylamine*, b. p. 57°/18 mm. (*hydrochloride*; *hydrobromide*), was obtained.

Methoxyl and propoxyl groups were not so easily replaced by halogen as ethoxyl. The following compounds were prepared incidentally: γ-*methoxybutylamine*, b. p. 128—130° (*picrate*, m. p. 110—112°; *phenylthiocarbamide* derivative, m. p. 84°), and γ-*propoxybutylamine*, b. p. 160° (*picrate*, m. p. 101°; *phenylthiocarbamide* derivative, m. p. 67°).

R. J. W. Le Fèvre.

Synthesis of ephedrine and structurally similar compounds. II. Ephedrine homologues; resolution of ephedrine. R. H. F. Manske and T. B. Johnson (J. Amer. Chem. Soc., 1929, **51**, 1906—1909).—The new synthesis of ephedrine (this vol., 441) has been extended to other primary aliphatic amines and to β-keto-aldehydes. The simultaneous formation of an isomeride analogous to ψ-ephedrine is not usually observed. *Hydrochlorides* of the following m. p. have been prepared: β-ethylamino-α-phenylpropan-α-ol, m. p. 198° (corr.); β-*ethylamino*-α-*phenylbutan*-α-*ol*, m. p. 226°; β-(β-*hydroxyethylamino*)-α-*phenylpropan*-α-*ol*, m. p. 166°; β-*benzylamino*-α-*phenylpropan*-α-*ol*, m. p. 184—185°; β-(β-*phenylethylamino*)-α-*phenylpropan*-α-*ol*, m. p. 207—208°; β-*ethylamino*-α-p-*ethylphenylpropan*-α-*ol*; m. p. 208°; β-*ethylamino*-α-2 : 5-*dimethylphenylpropan*-α-*ol*, m. p. 221°, and β-*ethylamino*-α-p-*tolylethyl alcohol*, m. p. 208°. *dl*-Ephedrine is conveniently resolved by means of mandelic acid and *vice versa*, d-*ephedrine* d-*mandelate* and l-*ephedrine* l-*mandelate* having m. p. 170°, sintering from 167°. Synthetic *l*-ephedrine is identical with the natural product.

H. E. F. Notton.

Compounds of mono-, di-, and tri-methylamines, ethylenediamine, and choline with flavianic acid. H. Sievers and E. Müller (Z. Biol., 1929, **89**, 37—40).—The following *salts* of flavianic acid are described (the figures in parentheses are the number of mols of acid combined with 1 mol. of base): methylamine (1), decomp. 265—268° after darkening at 230°; dimethylamine (1), decomp. 230—235° after darkening at 200°; trimethylamine (1), decomp. 217—223° after darkening at 210°; ethylenediamine (2), decomp. 265—267°; choline (1), chars when heated. The solubilities of these salts in water and alcohol at 18—19° are given.

H. Burton.

Hydrolysis of polypeptides, their derivatives and amides by *N*-alkali, erepsin, trypsin, and trypsin-kinase. E. Abderhalden and W. Zeisset (Fermentforsch., 1929, **10**, 544—585).—The action of *N*-sodium hydroxide, erepsin, and trypsin-kinase on a large number of polypeptides, their halogenoacyl derivatives and amides has been investigated, comparative experiments with different specimens of enzymes being made. The results are summarised below in groups classified according to the structure of the polypeptides, the order in each class being that of decreasing ease of hydrolysis. Erepsin (at p_H 7·8 and 37°) hydrolyses (*a*) glycylglycine (I), glycylglycylglycine (II), glycyl-di- (III), -tri- (IV), and -tetra- (V) glycylglycine; (*b*) *dl*-valylglycylglycine (VI), *glycyldiglycyl*-dl-*valine* (VII), m. p. 147—149° [from *chloroacetyldiglycyl*-dl-*valine* (VIII), m. p. 169—171° (decomp.)], glycyl-*dl*-valine (IX), *glycylglycyl*-dl-*valine* (X), m. p. 219—221° (decomp.) [from *chloroacetylglycyl*-dl-*valine* (XI), m. p. 170°], dl-*leucylglycyl*-dl-*valine* (XII), m. p. 244—245° (decomp.) [dl-α-*bromoisohexoylglycyl*-dl-*valine* (XIII), m. p. 143—145°], dl-*valyldiglycylglycine* (XIV), decomp. 230—235° [from dl-α-*bromoisovaleryldiglycylglycine* (XV), m. p. 171—173° (decomp.)], *dl*-valylglycine (XVI), *dl*-valylglycyl-*dl*-leucine (XVII), *dl*-valyl-*dl*-alanine (XVIII) and XXX [*dl*-alanyl-*dl*-valine (XIX) is not attacked]; (*c*) glycyl-*dl*-leucine (XX), *glycylglycyl*-dl-*leucine* (XXI), m. p. 240° (decomp.) [from *chloroacetylglycyl*-dl-*leucine*, (XXII), m. p. 153°], *dl*-leucylglycyl-*dl*-leucine (XXIII), *glycyldiglycyl*-dl-*leucine* (XXIV), m. p. 206—208° (decomp.) [from *chloroacetyldiglycyl*-dl-*leucine* (XXV), m. p. 176—177° (decomp.)]; (*d*) *dl*-leucylglycyl-*dl*-valine (XXVI), dl-*valylglycyl*-dl-*leucine* (XXVII), m. p. 242—244° (decomp.) [from dl-α-*bromoisovalerylglycyl*-dl-*leucine* (XXVIII), m. p. 169°], *dl*-leucylglycyl-*dl*-leucine (XXIX), dl-*valylglycyl*-dl-*valine* (XXX), m. p. 233—235° (decomp.) [from dl-α-*bromoisovalerylglycyl*-dl-*valine* (XXXI), m. p. 179—180°]; (*e*) *dl*-leucylamide (XXXII), *dl*-leucylglycylamide (XXXIII). *Glycyl*-dl-*leucylamide* (XXXIV) (*hydrobromide*, m. p. 175—179°) [from *bromoacetyl*-dl-*leucylamide* (XXXV), m. p. 173—174°] and glycylamide (XXXVI) are only slightly attacked by erepsin, whilst dl-*leucyl*-dl-

leucylamide (XXXVII) (*hydrobromide*) [from dl-α-*bromo*iso*hexoyl*-dl-*leucylamide* (XXXVIII), m. p. 141—143°] is not hydrolysed. With trypsin-kinase, at p_H 8·4 and 37°, (*a*) I, II, and III are attacked only slightly, whilst IV and V are unaffected; (*b*) XXX, XIV, VII, X, and VI are slightly hydrolysed, whilst IX and XVI are unattacked; (*c*) XXIV, XXI, and XX suffer slight hydrolysis; (*d*) XXVI, XXVII, XXIX, and XXX are hydrolysed, the last only slightly; (*e*) none of these amides is hydrolysed. The following polypeptides and their amides are hydrolysed by *N*-sodium hydroxide, the order again being that of decreasing degree of hydrolysis: XXIV, VII, XIV, X, XXI, VI, XXXIV, XXXIII, XXXVI, XXXII, XII, XX, XXXVII, XXIII, IX, and XXX, whilst XVI, XVIII, and XIX are unattacked. The specimen of *dl*-valylglycylglycine obtained by Abderhalden, Sah, and Schwab (this vol., 178) was readily hydrolysed by *N*-sodium hydroxide, but another specimen prepared in the same manner and having the same m. p. and mixed m. p. was unattacked, the reason for this difference not being understood. All the halogenoacyl derivatives are hydrolysed by *N*-sodium hydroxide, the order of decreasing ease of hydrolysis being, chloroacetyl-triglycylglycine, -diglycylglycine, XXV, -glycylglycine, VIII, XV, XXII, chloroacetyl-*dl*-leucine, XI, *dl*-α-bromo*iso*valerylglycylglycine, chloroacetyl-*dl*-valine, XXXI, XXVIII, *dl*-α-bromo*iso*valerylglycine, and *dl*-α-bromopropionyl-*dl*-valine. J. W. BAKER.

Specific action of erepsin and trypsin on certain groups in polypeptides. E. ABDERHALDEN and O. HERRMANN (Fermentforsch., 1929, **10**, 586—590).—In the hydrolysis of d-*alanylglycyl*-l-*phenylalanine*, m. p. 220°, $[\alpha]_D^{20}$ +34·02° (from *d*-α-*bromopropionylglycyl*-l-*phenylalanine*, m. p. 150°), in 0·1*M*-solution with erepsin at p_H 7·8 and 37°, the dextrorotation gradually diminishes as hydrolysis proceeds, whilst with trypsin at p_H 8·4 and 37° it rapidly becomes lævorotatory, pointing to the formation of *l*-phenylalanine, $[\alpha]_D$ −35·1°. *l*-Leucylglycyl-*d*-alanine ($[\alpha]_D$ +12·1° and therefore containing a little of the racemic compound) on hydrolysis may yield either *l*-leucylglycine ($[\alpha]_D$ +86°) and *d*-alanine, or glycyl-*d*-alanine ($[\alpha]_D$ −50°) and *l*-leucine. With erepsin, yeast extract, and kidney and liver extracts this tripeptide rapidly becomes lævorotatory, showing that *l*-leucine is formed. With trypsin (which has very little action) and dog's pancreas juice a slight rise in the dextrorotatory value is observed. These results agree with earlier conclusions that erepsin attacks those portions of the polypeptide molecule which contain a free amino-group, and trypsin those containing a free carboxyl group. J. W. BAKER.

Comparative study of the hydrolysis of polypeptides and their derivatives at various hydrogen-ion concentrations, with erepsin and trypsin-kinase. Optimal hydrogen-ion concentration for the action of these enzymes. E. ABDERHALDEN and A. SCHMITZ (Fermentforsch., 1929, **10**, 591—609).—The velocity of hydrolysis of various polypeptides and their derivatives with different concentrations of sodium hydroxide, and with erepsin and trypsin-kinase at various p_H values, has been studied. At a given hydrogen-ion concentration tetrapeptides such as glycyl-*dl*-leucylglycyl-*dl*-leucine (I) (*phenylurethane*, decomp. 144—145°) are more rapidly hydrolysed than tripeptides such as *dl*-leucylglycyl-*dl*-leucine (II), hydrolysis of the former still being possible with 0·2*N*-sodium hydroxide. The phenylurethanes are much more rapidly hydrolysed than the parent polypeptides, suffering considerable hydrolysis even with 0·1*N*-sodium hydroxide. Chloroacetyl-*dl*-leucylglycyl-*dl*-leucine (III) is more rapidly hydrolysed than the free polypeptide, but not so readily as the phenylurethane. Similarly, *dl*-α-bromo*iso*hexoylglycyl-*l*-tyrosine is more rapidly hydrolysed than *dl*-leucylglycyl-*l*-tyrosine (IV) (*phenylurethane*, decomp. 130°). With *N*-hydrochloric acid, which hydrolyses the free polypeptides only very slowly, chloroacetyl-*dl*-alanine and III are hydrolysed, but much more slowly than with *N*-sodium hydroxide. The optimum p_H values for hydrolysis by erepsin or trypsin-kinase differ with various polypeptides. Thus the velocity of hydrolysis of II with erepsin is greater than that of IV, but in both cases the optimal p_H value is 7·8—8·4. With trypsin-kinase, however, the optimal p_H values for II, IV, and I are, respectively, 8·4, 7·8—9·0 (unchanged velocity over this range), and 9·0. Yet another type of curve is obtained with triglycyl-*dl*-phenylalanine. The various halogenoacyl and other derivatives of these polypeptides behave in still another manner towards trypsin-kinase. Although the various curves differ in form (the results being somewhat complicated by the products of the reaction) all show a maximal velocity of hydrolysis at p_H 7·1, that is, at about the neutral point. In the enzymolysis of the halogenoacyl derivatives no fission of the halogenoacyl group occurs. J. W. BAKER.

Influence of α- and β-amino-acids, hippuric acid, sarcosine, aniline, and dipeptides on the velocity of decomposition of polypeptides with erepsin and trypsin-kinase. E. ABDERHALDEN and O. HERRMANN (Fermentforsch., 1929, **10**, 610—616).—The effect of these addenda on the hydrolysis of various polypeptides by erepsin or trypsin-kinase is different with each polypeptide. It was anticipated that substances containing a free amino-group in the α-position would affect erepsin hydrolysis and those with a free carboxyl group would affect hydrolysis by trypsin, but the action is much more complicated. The results do not lend themselves to summarisation. With erepsin, hippuric acid always has a retarding influence the magnitude of which varies with the substrate, but with trypsin-kinase it has an accelerating action except with chloroacetyl-*l*-phenylalanine as substrate. The retarding effect of the addenda varies with the hydrogen-ion concentration, but only with hippuric acid in enzymolysis by erepsin is the maximum effect observed at the optimal p_H hydrolysis value. The addition of various dipeptides, with the exception of *dl*-leucylglycine and glycyl-*dl*-norvaline, which exhibit a strong retarding influence, has no effect on the hydrolysis of *dl*-leucylglycyl-*dl*-leucine with trypsin. J. W. BAKER.

Influence of the free amino-group in polypeptides on their hydrolysis with *N*-alkali, erepsin, and trypsin-kinase. E. ABDERHALDEN,

L. Dinerstein, and S. Genes (Fermentforsch., 1929, **10**, 532—543).—The following polypeptides, prepared by usual methods, suffer enzymolysis with trypsin-kinase (free from erepsin) at p_H 8·4 and 37°: *dl*-α-bromo*iso*hexoylglycylglycine, *dl*-α-bromo*iso*hexoyl-*dl*-leucylglycylglycine, the phenylurethane, naphthalene-2-sulphonyl, p-*chlorobenzoyl*, m. p. 183°, and p-*nitrobenzoyl*, m. p. 163—165°, derivatives of *dl*-leucylglycylglycine, p-*chlorobenzoyl*, m. p. 246—247° (I), and p-*nitrobenzoyl* (II), m. p. 232° (decomp. corr.), derivatives of *dl*-alanylglycylglycine, but *dl*-α-bromopropionylglycylglycine, *dl*-leucylglycylglycine (III), *dl*-alanylglycylglycine (IV), and its *naphthalene-2-sulphonyl* derivative are unattacked. With the exception of III and IV none of these is attacked by trypsin-free erepsin at p_H 7·8 and 37°. All are readily hydrolysed by *N*-sodium hydroxide at 37° in 0·1*M*-solution. Of the derivatives of IV, II is the most rapidly and V the most slowly hydrolysed with alkali. J. W. Baker.

Derivatives of cyanomalonic acid. F. Pabst (Arch. Pharm., 1929, **267**, 325—352).—Ethyl cyanoacetate reacts with potassium cyanate giving ethyl cyanocarboxylamidoacetate, m. p. 162—163° (decomp.) (corresponding *methyl* ester, m. p. 128°; $+1\frac{1}{3}H_2O$, m. p. 116°) (cf. Frerichs and Hartwig, A., 1906, i, 74), strongly acidic substances, which form salts with metallic carbonates, weakly basic amines, and alkaloids. They are converted into carbon dioxide and cyanoacetamide when boiled with water, whilst when heated near their m. p. they undergo further condensation, forming the *monomethyl* and the *monoethyl* ester amides of dicyanomalonimide [*ferric*, *silver*, and *barium* (+1 and $6H_2O$) salts] which are stronger acids than acetic acid. When treated with alcoholic potassium hydroxide and benzyl chloride, the *monomethyl* ester (m. p. 103°) and the *monoethyl* ester amides (m. p. 86°) of benzylcyanomalonic acid are obtained, whilst hot benzyl alcohol affords the corresponding *monobenzyl* ester amide, m. p. 148° (*silver* salt), and *dibenzyl cyanomalonate*, m. p. 73—74° (*sodium*, m. p. 267°, *potassium*, and *silver* salts). The mono-ester anilides of cyanomalonic acid are obtained when a sodiocyanoacetic ester is treated with phenylcarbimide (cf. Micheal and Cobb, A., 1908, i, 947); ethyl ester anilide, m. p. 145° (*silver* salt); *methyl* ester anilide, m. p. 146° (*silver* salt). The corresponding *methyl* (m. p. 103°) and *ethyl* (m. p. 104·5°) ester anilides of benzylcyanomalonic acid do not form salts. *Cyanomalondianilide*, m. p. 192°, obtained when the ester amides or ester anilides are heated with aniline (*silver* and *ferric* salts), or when sodiocyanoacetanilide is treated with phenylcarbimide, affords *benzylcyanomalondianilide*, m. p. 215°. The following are prepared in a similar manner: *cyanomalondimethylanilide*, m. p. 178°; *cyanomalondi*-p-*anisidide*, m. p. 215° (*silver* salt); *cyanomalondi*-m-*toluidide*, m. p. 186°; *cyanomalondi*-p-*toluidide*, m. p. 221°. S. Coffey.

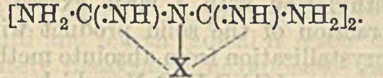
Dicyanic acid. T. L. Davis and K. C. Blanchard (J. Amer. Chem. Soc., 1929, **51**, 1806—1810).—The presence of dicyanic acid in aqueous solutions of cyanic acid is inferred on similar evidence to that adduced in the case of nitrobiuret solutions (cf. this vol., 919). Thus, the formation of allophanates from alcohols and aqueous cyanic acid is due to the direct action of the dicyanic acid (cf. Béhal, A., 1919, ii, 301), and not to a secondary reaction between the carbamate and cyanic acid. Ethyl carbamate is partly converted in presence of alcohol at 100° into ethyl allophanate. In aqueous solution cyanic acid and carbamide do not give biuret. A concentrated solution of potassium cyanate acidified with acetic acid gives, after a few mins., the biuret reaction, but contains no biuret. With aniline this solution gives α-phenylbiuret in addition to phenylcarbamide. H. E. F. Notton.

Dearrangement of nitrocarbamide and its application in syntheses. T. L. Davis and K. C. Blanchard (J. Amer. Chem. Soc., 1929, **51**, 1790—1801).—The primary decomposition of nitrocarbamide at 160—170° (cf. Thiele and Lachman, A., 1896, i, 207) into (*a*) nitroamide and cyanic acid, and (*b*) ammonia and the compound $NO_2\cdot N\!:\!CO$, is inferred from the formation of water, nitrous oxide, cyanic acid, carbon dioxide, ammonia, ammonium cyanurate, and traces of ammelide, carbamide, and biuret. Solutions of nitrocarbamide in warm water or cold concentrated sulphuric acid contain nitroamide; the latter may be used at 0° to effect nitrations (cf. A., 1927, 863). Nitrocarbamide is formed from nitroamide, silver cyanate, and hydrochloric acid at 0°. Air-dried nitrocarbamide, but not that dried over phosphoric oxide, decomposes in presence of traces of alkali. In aqueous solution it forms a convenient source of cyanic acid, giving with primary amines monosubstituted carbamides, *e.g.*, p-*carbamidobenzoic acid*, m. p. above 275°, and *n*-butylcarbamide, m. p. 96° (cf. Werner, J.C.S., 1919, **115**, 1101), and with secondary amines αα-dialkylcarbamides, *e.g.*, oily αα-*di*-n-*butyl*- (*picrate*, m. p. 82—83°) and αα-*di*iso*amyl*- (*oxalate*, m. p. 101·5—102°; *picrate*, m. p. 72·8—73·9°) -*carbamides*. Dipropylamine gives αα-dipropylcarbamide and αα-*di*-n-*propylbiuret*, m. p. 129—129·4°; *n*-propylaniline gives α-*phenyl*-α-n-*propylcarbamide*, m. p. 89·4—89·8° [*picrate*, m. p. 118—118·5°; *oxalate*, m. p. 71—72° (decomp.)], and α-*phenyl*-α-n-*propylbiuret*, m. p. 151°. α-*Phenyl*-α-n-*butylcarbamide* has m. p. 50·5—51·1°. The monoalkyl derivatives may be isolated by evaporating their aqueous solutions, but the dialkyl and arylalkyl derivatives are partly decomposed into amine and cyanic acid. These last also decompose at the m. p. into alkylanilines and cyanuric acid. Nitrocarbamide reacts but slightly with anhydrous alcohols. In presence of water it gives esters of carbamic and allophanic acids. H. E. F. Notton.

Dearrangement of nitrobiuret; application in synthesis. T. L. Davis and K. C. Blanchard (J. Amer. Chem. Soc., 1929, **51**, 1801—1806).—The reactions of nitrobiuret in aqueous solution indicate that it decomposes primarily into nitroamide and dicyanic acid, $NH_2\cdot CO\cdot N\!:\!CO$, and to a smaller extent into carbamide and nitrocyanic acid, $NO_2\cdot N\!:\!CO$. A fresh cold solution does not give the biuret test, but when heated it evolves carbon dioxide and nitrous oxide (cf. Thiele and Uhlfelder, A., 1899, i, 118), forming carbamide and a product which gives the biuret reaction, but leaves only cyanuric acid when evaporated. The reactions of the solution with alcohols and amines indicate that this product is dicyanic acid. Thus, nitrobiuret and potassium hydroxide give in absolute alcohol no reaction, in 80% alcohol potassium allophanate (32% of the theoretical), and in 50% alcohol carbamide but no allophanate. Gradual addition of water to nitrobiuret in ethyl, *n*-propyl, or *n*-butyl alcohol gives mixtures of alkyl carbamates and allophanates; *tert.*-butyl alcohol gives carbamate only, and *iso*amyl alcohol allophanate only. The carbamates are produced by a secondary reaction between the alcohols and allophanates. Nitrobiuret gives with aqueous ammonia at 100° biuret (60% of the theoretical) and with amines in warm aqueous solution good yields of the following substituted biurets: α-methyl-, m. p. 166·5—167°; α-ethyl-, m. p. 154—154·5°; α-n-*propyl*-, m. p. 147·2—147·6°; α-n-*butyl*, m. p. 129·1—129·5°; α-*benzyl*-, m. p. 174·5—175°; α-phenyl-, m. p. 165°; α-p-tolyl-, m. p. 199°; α-(α-*naphthyl*)-, m. p. 217·3—217·6°; αα-*dimethyl*-, m. p. 141—141·5°; αα-*diethyl*-, m. p. 139—139·2°; αα-*di*-n-*propyl*-, m. p. 129—129·4°; αα-*di*-n-*butyl*-, m. p. 144·8—145°; α-*phenyl*-α-*ethyl*-, m. p. 155·2—155·8°; and α-*phenyl*-α-n-*propyl*-, m. p. 151—151·5°. Nitrobiuret does not gives triuret with carbamide in warm water, but with biuret it gives tetruret, $NH_2\cdot[CO\cdot NH]_3\cdot CO\cdot NH_2$. A solution of nitrobiuret in cold concentrated sulphuric acid gives up its nitro-group quantitatively in the nitrometer and may be used at 0° to effect nitrations.

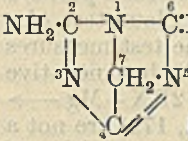
H. E. F. Notton.

Diguanides. I. Constitution of the complex compounds of diguanide with heavy metals. II. Depressing action of diguanides on blood-sugar. K. H. Slotta and R. Tschesche (Ber., 1929, 62, [*B*], 1390—1398, 1398—1405).—I. Examination of a series of substituted diguanides shows that the formation of complex metallic compounds occurs only with derivatives in which the hydrogen atoms of the three imino-groups are not replaced. The complex compounds are therefore formulated



$$[NH_2\cdot C(:NH)\cdot N\cdot C(:NH)\cdot NH_2]_2 \text{ with } X$$

Cyanocarbamide is converted by successive treatment with alcoholic methylamine at 100° and sulphuric acid into *methylguanylcarbamide sulphate*, $[NH_2\cdot CO\cdot NH\cdot C(:NH)\cdot NHMe]_2,H_2SO_4$, m. p. 228—230° (slight decomp.), which does not yield a copper compound. *Carbethoxymethylcyanamide*, b. p. 100°/8 mm., from the sodium derivative of carboethoxycyanamide and methyl sulphate, is converted by concentrated aqueous ammonia into trimethylmelamine, m. p. 115°. Addition of amines to dicyanamide furnishes the following *hydrogen sulphates*: αε-*dimethyldiguanide*, $NHMe\cdot C(:NH)\cdot NH\cdot C(:NH)\cdot NHMe,H_2SO_4$, decomp. 200°; αε-*diallyldiguanide*; ααεε-*tetramethyldiguanide*, decomp. 142° after softening at 133—135°. *N*-Methylguanylthiocarbamide is transformed by boiling ethyl bromide into N-*methyl*-S-*ethylguanylthiocarbamide hydrobromide*, m. p. 173—175° (incipient decomp.), converted by methylamine and dimethylamine into α:N$^{\beta}$-*dimethyldiguanide hydrobromide*, $NHMe\cdot C(:NMe)\cdot NH\cdot C(:NH)\cdot NH_2,HBr$, decomp. 240—245°, and αα:N$^{\beta}$-*trimethyldiguanide hydrobromide*, m. p. 185—190°. *s*-Triphenylguanidine and cyanamide in benzene and ether afford α:N$^{\beta}$:γ-*triphenyldiguanide*, decomp. 118—120°. *s*-Trimethylguanidine (*hydrogen sulphate*) and *s*-triphenetidylguanidine could not be caused to react similarly with cyanamide. The dicyanomethylamide, m. p. 235—238° after softening at 221°, of Madelung and Kern (A., 1922, i, 438) is a polymerised compound. Diguanide, decomp. 142°, is obtained crystalline by treatment of diguanide sulphate with a solution of sodium in boiling ethyl alcohol. The action of ethyl chloroacetate on diguanide affords *diguanido*-ε-*acetic acid hydrochloride*, $NH_2\cdot C(:NH)\cdot NH\cdot C(:NH)\cdot NH\cdot CH_2\cdot CO_2H,HCl$, decomp. 148°, with minor amounts of 2-*amino*-6-*imino*-1 : 4-endo*methylene*-1 : 3 : 5-*triazine hydrochloride* (cf. I), m. p. 215° (decomp.). Similarly, αα-dimethyldiguanide yields αα-*dimethyldiguanido*-ε-*acetic acid hydrochloride*, decomp. 178—180°, and 2-*dimethylamino*-6-*imino*-1 : 4-endo*methylene*-1 : 3 : 5-*triazine hydrochloride*, m. p. 176° (decomp.).



(I.)

II. The physiological action of diguanides depends on the presence of at least one unsubstituted amino-group. In the series α-methyl-, ethyl-, propyl-, *iso*butyl-, *iso*amyl- maximum activity is observed with the methyl derivative; this is also the case with the allyl compound in the sequence allyl-, crotyl-, *iso*-amylenyl-, *iso*hexenyl-. Among αα-di-derivatives the methyl compound is most potent. No advantage is gained by the introduction of the phenyl or anisyl group or the acetic acid residue.

The following substituted diguanides are prepared by addition of the requisite amine to cyanoguanidine: α-*propyldiguanide sulphate*, $[NHPr^{a}\cdot C(:NH)\cdot NH\cdot C(:NH)\cdot NH_2]_2,H_2SO_4$, m. p. 193—196°; α-iso*amyldiguanide sulphate*, m. p. 168—170°; αα-*dimethyldiguanide hydrochloride*, m. p. 235°; αα-diethyldiguanide sulphate, decomp. 202°; very hygroscopic αα-*diallyldiguanide hydrochloride*, m. p. 100—110°; α-*crotyldiguanide sulphate*, m. p. 165—168° [(?)N-*crotylphthalimide*, $C_{12}H_{12}ON_2$, b. p. 178—180°/12 mm., m. p. 76°]; α-iso*amylenyldiguanide sulphate*, m. p. 153—154°; α-α′-*methyl*-Δ$^{\delta'}$-*pentenyldiguanide sulphate*, decomp. 226°; α-p-*anisyldiguanide hydrochloride*, m. p. 235°. Treatment of guanyl-*S*-ethylthiocarbamide (*hydrobromide*, decomp. 166°), prepared from guanylthiocarbamide carbonate and ethyl bromide (preferably in presence of water), with amines leads to loss of ethyl mercaptan and production of the following diguanides: α-β′-*hydroxyethyldiguanide sulphate*, decomp. 148°; α-β′-*thiolethyldiguanide hydrogen sulphate*, decomp. 201°; *ethylenebisdiguanide sulphate*, $[\cdot CH_2\cdot NH\cdot C(:NH)\cdot NH\cdot C(:NH)\cdot NH_2]_2,H_2SO_4$, decomp. 300°; *hexamethylenebisdiguanide hydrogen sulphate*, decomp. 205—210° after softening at 195°; *decamethylenebisdiguanide sulphate*, m. p. 115°, decomp. 122°.

H. Wren.

Organomagnesium halides. H. Gilman, E. L. St. John, and N. B. St. John (Rec. trav. chim., 1929, 48, 593—596).—The optimum conditions for the preparation of organomagnesium halides previously determined (this vol., 800) for small-scale preparations are found to hold for operations on a larger scale, and in some cases better yields are obtained. In general, the halide, in 6 equivalents of ether, can be added to the magnesium in 0·5—0·75 hr. The detailed preparation of Grignard reagents from *n*-butyl bromide (yield 91%), benzyl chloride (yield 91%), bromobenzene (yield 98%), and α-bromonaphthalene (yield 96%), and the yields obtained by conversion with carbon dioxide into the corresponding carboxylic acids, are given. When a solution of magnesium α-naphthyl bromide in ether is cooled, the etherate crystallises. C. W. Shoppee.

Relative reactivities of organic halides. Relative rate of formation of Grignard reagents. H. Gilman and R. J. Vanderwal (Bull. Soc. chim., 1929, [iv], **45**, 344—349).—The relative reactivities of a series of organic halogen compounds have been compared by observing the time required for a positive result with the Gilman and Schulze colour test (A., 1925, ii, 1011; cf. this vol., 303). The test measures the reaction (i) $RX+Mg \longrightarrow R{\cdot}Mg{\cdot}X$, but negative results due to the alternative reaction $2RX+Mg \longrightarrow R{\cdot}R+MgX_2$ preceding (i) (cf. this vol., 179) are not a serious source of error in comparing reactivities of magnesium organohalides of the same class (cf. Gilman, Zoellner, and Dickey, this vol., 800). Among the normal alkyl (propyl to octyl) bromides and iodides the reactivity thus measured decreases as the size of the alkyl group increases. Comparison of the yields of magnesium alkyl bromides indicates an alternating effect in the series ethyl to octyl bromide. The order of reactivity with the butyl bromides is: *n*-<*iso*-<*sec.*<*tert.* Only an approximate result could be obtained with *tert.*-butyl bromide and by noting the time at which ebullition commences. With the bromotoluenes the *para* is the most, the *ortho* the least reactive; measurements were made in presence of iodine as activator. 1-Bromonaphthalene is much less reactive than 2-bromonaphthalene, both in presence and absence of iodine as catalyst, an observation agreeing with the less aromatic and more aliphatic properties shown by β-substituted naphthalene derivatives generally and with the observed order of reactivity: *n*-octyl bromide>bromo*cyclo*hexane> bromobenzene. Comparing the reactivity of alkyl halides with the same alkyl but different halogens, the fluorides are remarkably inert, the chlorides standing midway between these and the bromides or iodides. Aryl iodides are more reactive than the corresponding bromides, but alkyl bromides are slightly more reactive than the iodides, comparison being less exact, since the reaction $2RX+Mg \longrightarrow R{\cdot}R+MgX_2$ is readier with the iodides than with the bromides. Treatment of alkyl iodides with mercury in purification appears to reduce their reactivity slightly. R. Brightman.

Influence of pressure on the formation of Grignard reagents. H. Gilman, R. J. Vanderwal, and F. E. Brown (Bull. Soc. chim., 1929, [iv], **45**, 350—351).—The rate of formation of magnesium *n*-butyl bromide, measured by the technique previously described (cf. this vol., 303), is slightly greater under 2—3 atm. than at atmospheric pressure. No acceleration was observed with chlorobenzene, either on heating for 4½ hrs. at 90° in a sealed tube or under 63—96 atm. at ordinary temperatures. R. Brightman.

Preparation of magnesium *n*-butyl bromide. P. Borgstrom, F. C. Wagner, and H. C. Griffin (J. Amer. Chem. Soc., 1929, **51**, 1861—1865).—Preparations using 6—10 mols. of *n*-butyl bromide are described. The highest yields are obtained when the bromide is added to the magnesium at such a rate (1 mol. in 40 min.) that the concentration of unchanged bromide is always very small. It is unnecessary to use more than the theoretical amount of magnesium. The yield of Grignard reagent, 92·5% of the theoretical, or 94·3% allowing for recovered bromide, is in good agreement with that given by Gilman and McCracken (A., 1924, i, 23). H. E. F. Notton.

Alkylation of tetra- and tri-cyanocadmic acid. F. Hölzl (Monatsh., 1929, **51**, 397—419).—The action of silver nitrate on potassium cadmicyanide, $K_2[Cd(CN)_4]$, yields a mixture of the complex salts $Ag[Cd(CN)_3]$ and $Ag_2[Cd(CN)_4]$, which dissolves in water at 60° with precipitation of silver cyanide, the pure salt $Ag[Cd(CN)_3]$ crystallising from the aqueous solution. When this salt is methylated with methyl iodide a series of complex methylated derivatives of the acid $H[Cd(CN)_3]$ containing only methylcarbylamine groups, are obtained, the unmethylated cyano-groups undergoing partial, stepwise hydrolysis to yield complex salts containing several atoms of tervalent cadmium united by single cyano-bridges. These compounds, however, are unstable and readily react with water to yield derivatives of quadrivalent cadmium. Thus the action of an excess of methyl iodide on the salt $Ag[Cd(CN)_3]$ for 10 days in the dark, extraction of the solid product with chloroform, and crystallisation from dilute methyl alcohol yields the *compound* $C_6H_{15}O_8N_5Cd_4$ (I), which has a weakly alkaline reaction in aqueous solution and yields carbylamine when heated alone or with alkali. Alternative structures for this compound are suggested, the most probable being $[NC{\cdot}Cd(OH)(OH_2){\cdot}\{CN{\cdot}Cd(OH)(OH_2)\}_3{\cdot}CNMe]$. Similar methylation with a large excess of methyl iodide, extraction of the solid product with chloroform, and crystallisation from absolute methyl alcohol yields the *compound* $Cd_2C_4H_5O_2N_3$, which qualitatively resembles I: the most probable formula is $[Cd(OH)(CN){\cdot}CN{\cdot}Cd(OH)(CNMe)]$. Alkylation of potassium cadmicyanide with methyl sulphate yields complex salts of quadrivalent cadmium containing 3 or 6 cadmium atoms united by a double cyano-bridge derived similarly by partial hydrolysis of the simple compound $[Cd(CN)_2(CNMe)_2]$. Thus the action of a large excess of methyl sulphate on finely-powdered, dry potassium cadmicyanide in the dark for 8 days, filtering from the solid product (II), removal of the excess of methyl sulphate from the filtrate by distillation in a vacuum, and extraction of the residue with methyl alcohol yields a *compound* which gives carbylamine with alkali, and barium sulphate on prolonged heating with barium chloride and hydrochloric acid, and is probably $[Cd(CNMe)_{3\,\mathrm{or}\,4}](Me_2SO_4)_2$. Extraction of the solid product II with methyl alcohol and fractional crystallisation from this solvent to remove potassium methyl sulphate yields the compound $[Cd(OH)(CNMe){\cdot}(CN)_2{\cdot}Cd{\cdot}(CN)_2{\cdot}Cd(CN)(CNMe)]$. The action of methyl sulphate on a saturated aqueous solution of potassium cadmicyanide for 2 days, extraction of the solution with ether, and crystallisation of the residue from the ether from methyl alcohol yields the *compound* $Cd_6(CN)_{11}(CNMe)(OH)$, for which three possible formulæ are given among which decision cannot be made. In all these complex salts (the mechanism of the formation of which is discussed) a quantitative determination of nitrile and carbylamine groups by Guillemard's method (A., 1908, i, 718) proves that in every case only methylcarbylamine and no nitrile groups are present. The relation of these results to those of Enklaar (A., 1925, i, 1394) is discussed and it is suggested that the liberation of normal (stable) hydrogen cyanide by the action of hydrogen sulphide on potassium cadmicyanide and similar complex cyanides is no evidence of its existence as such in the co-ordination sphere, since the labile (*iso*-)form if liberated would immediately isomerise to the stable form under the influence of hydrogen sulphide (cf. also Slotta and Jacobi, this vol., 304). Alkylation with ethyl iodide was not possible.

J. W. BAKER.

Preparation of pure *cyclo*hexene. H. I. WATERMAN and H. A. VAN WESTEN (Rec. trav. chim., 1929, 48, 637—640).—*cyclo*Hexene, b. p. 83·05—83·15°/758 mm., $n_D^{19·9}$ 1·44657, containing a trace of *cyclo*hexanol as the sole impurity, can be obtained by fractional distillation of Poulenc's product. Careful fractionation, followed by treatment with sodium under reflux for 7 hrs. and refractionation, afforded pure *cyclo*hexene, b. p. 82·8°/759 mm., $n_D^{20·05}$ 1·44637. The product of the catalytic reduction was pure *cyclo*hexane, $n_C^{19·9}$ 1·42425.

C. W. SHOPPEE.

Ring strain and radical formation. III. G. WITTIG and M. LEO (Ber., 1929, 62, [*B*], 1405—1410; cf. A., 1928, 642, 1233).—In the series, $--CPh_2·C_6H_4·[CH_2]_n·C_6H_4·CPh_2--$ (n=1—4), the position of the very broad absorption band in the spectrum of the first two homologues corresponds with that of the monomeric tridiphenylylmethyl, whereas with the third and fourth radical it resembles that of the moderately dissociated hexaphenylethane. The marked differentiation in the optical properties of the di-radicals is in harmony with expectations based on models; intramolecular union of the terminal radical valencies is impossible in the first two cases, but the ring strain allows such union for a di-radical with a longer methylene bridge.

p-*Benzoylbenzyl bromide*, m. p. 112°, from *p*-methylbenzophenone and bromine at 150°, is converted by ethyl disodiomalonate into *ethyl di*-p-*benzoylbenzylmalonate*, separating according to conditions of crystallisation in two dimorphous, interconvertible forms, m. p. 103—104° and 108—109°, respectively. Hydrolysis and decarboxylation give only resinous products. The ester is transformed by magnesium phenyl bromide into *ethyl di*-p-*hydroxydiphenylmethylbenzylmalonate*, $(OH·CPh_2·C_6H_4·CH_2)_2C(CO_2Et)_2$, m. p. 173·5—174·5°, converted by hydrogen chloride in ether into *ethyl di*-p-*chlorodiphenylmethylbenzylmalonate*, readily hydrolysed to the glycol. Dehalogenation of the chloride by copper powder under nitrogen yields a pale brown solution not at all resembling that of the radicals described previously; exposure of the radical solution to oxygen causes remarkably slow decolorisation to a pale yellow.

αδ-Diphenylbutane is converted by benzoyl chloride and aluminium chloride into *αδ-di*-p-*benzoylphenylbutane*, m. p. 150°, transformed by magnesium phenyl bromide into *αδ-di*-(p-*hydroxydiphenylmethylphenyl*)-*butane*, m. p. 140—145°. *αδ-Di*-p-*chlorodiphenylmethylphenylbutane*, m. p. 159—161°, is transformed by copper powder into the corresponding *di-radical*, which, like its oxidation product, could not be caused to crystallise.

H. WREN.

Reactions of nitrosulphonyl chlorides. I. Reactions of hydrazine hydrate with *o*-nitrosulphonyl chlorides. A. T. DANN and W. DAVIES (J.C.S., 1929, 1050—1055).—The reaction between warm hydrazine hydrate and 2-chloro-5-nitro-*p*-toluenesulphonyl chloride is expressed as follows: $2R·SO_2Cl+2NH_2·NH_2,H_2O=2R·SO_2H+N_2+2H_2O+NH_2·NH_2,2HCl$ and is a general reaction unless the sulphinic acid is too unstable. If carried out in the cold the primary hydrazide can sometimes be isolated. 2-*Chloro*-5-*nitro*-p-*toluenesulphinic acid*, m. p. 131·5°, prepared by the interaction of hydrazine hydrate with 2-chloro-5-nitro-*p*-toluenesulphonyl chloride, on methylation gives 2-*chloro*-5-*nitro*-p-*toluenesulphone*, m. p. 145—146°. 2-*Chloro*-5-*nitro*-p-*toluenesulphonhydrazide*, m. p. 110—113°, was prepared in the cold; it reacts with cinnamaldehyde in warm anisole solution to give *cinnamaldehyde*-2-*chloro*-5-*nitro*-p-*toluenesulphonhydrazone*, dark red, m. p. 95°. o-*Nitrobenzenesulphonhydrazide*, m. p. 110°, can be prepared below 0°; 6-*chloro*-4-*nitro*-o-*toluenesulphonhydrazide*, m. p. 127°, and 2-*chloro*-6-*nitro*-p-*toluenesulphonhydrazide*, m. p. 125°, can be prepared in the usual way. *p*-Nitrobenzoyl chloride reacts with hydrazine hydrate in benzene solution giving *p*-nitrobenzoylhydrazide, m. p. 217°. *Benzaldehyde*-p-*nitrobenzoylhydrazone*, m. p. 259°, may be used as a delicate test for benzaldehyde. s-*Di*-p-*nitrobenzoylhydrazine* has has m. p. 291°.

C. W. GIBBY.

Octahydronaphthalene from tertiary decahydronaphthol. S. NAMETKIN and E. GLAGOLEV (Ber., 1929, 62, [*B*], 1570—1573, and J. Russ. Phys. Chem. Soc., 1929, 61, 535—540; cf. A., 1926, 508).—The octahydronaphthalene, obtained by the action of potassium nitrite on 9-aminodecahydronaphthalene hydrochloride, is converted by perbenzoic acid in chloroform into the corresponding *oxide*, $C_{10}H_{16}O$, b. p. 82—83°/8—9 mm., d_4^{20} 1·003, n^{20} 1·4847, transformed by water into the *glycol*, $C_{10}H_{16}(OH)_2$, isolated as a mixture of isomerides. Dehydration of the glycol affords *hexahydronaphthalene*, b. p. 75—76°/8 mm., d_4^{20} 0·9726, n^{20} 1·5322. The octahydronaphthalene is therefore the Δ^9-compound.

H. WREN.

Behaviour of *cis*- and *trans*-decahydronaphthalene towards bromine and aluminium bromide. Isomerisation of hydrindane. N. D. ZELINSKI and M. B. TUROVA-POLLAK (Ber., 1929, 62, [*B*], 1658—1663; cf. A., 1925, i, 1053).—Treatment of *cis*-decahydronaphthalene, b. p 192·7—193°/755 mm., with excess of bromine gives a *hexabromonaphthalene*, m. p. 312°, whereas the corresponding *trans*-compound yields a *hexabromonaphthalene*, m. p. 269°; the compound of m. p. 311—312° is also obtained by bromination of naphthalene. *cis*-Decahydronaphthalene when treated with aluminium bromide and hydrogen bromide at the ordinary temperature gives mainly an additive *product*, $C_4H_8,AlBr_3$, from which little of the ketone $C_{10}H_{17}\cdot COMe$ [semicarbazone, m. p. 252° (decomp.)] is obtained by treatment with aluminium chloride; the part of the hydrocarbon which does not unite with the aluminium bromide undergoes partial isomerisation to *trans*-decahydronaphthalene. Under similar conditions, aluminium bromide does not appear to react with decahydronaphthalene. Hydrindane, b. p. 166°/758 mm., n^{20} 1·4683, is converted by aluminium bromide at 100° into trans-*hydrindane* mixed with a more fundamentally isomerised hydrocarbon; a *product*, $(C_9H_{14})_3$, m. p. 192—193°, formed by polymerisation of partly dehydrogenated hydrindane, is also produced. H. Wren.

Rubrene. Mechanism of formation, an intermediate chloro-compound. C. Moureu, C. Dufraisse, and J. Robin (Compt. rend., 1929, **188**, 1582—1584).—When an ethereal solution of diphenylphenylacetylenylmethyl chloride is allowed to undergo spontaneous dissociation in the cold (several months), or is heated at 70° for 30 min., an intermediate crystalline *compound*, $C_{42}H_{29}Cl$, m. p. 217°, is formed, which is slowly transformed into rubrene in cold ethereal solution and more rapidly on warming.

C. C. N. Vass.

Rubrene. New oxide of rubrene. C. Moureu, C. Dufraisse, and L. Enderlin (Compt. rend., 1929, **188**, 1528—1530).—In addition to the dissociable peroxide RO_2 (A., 1926, 945; 1928, 53), rubrene forms a stable oxide, RO, m. p. 200° ($+C_6H_6$) and 325°, which is obtained by the action of 15% nitric acid, chromic acid, or permanganate on rubrene, or by reduction of the peroxide by zinc and acetic acid. It is reduced to rubrene by iron and acetic acid or by hydriodic acid. Oxidation yields only dibenzoylbenzene. The relation of rubrene to its oxides is parallel to that of hæmoglobin to its oxides, and suggests that the characteristic properties of the latter are due to the hydrocarbon part of the molecule.

R. K. Callow.

Polynuclear aromatic hydrocarbons and their derivatives. IV. Naphthaphenanthrenes and their quinones. E. Clar (Ber., 1929, **62**, [*B*], 1574—1582; cf. this vol., 435, 689).—The mixture of ketones, mainly *o*-tolyl 9-phenanthryl ketone (*loc. cit.*), is converted by distillation chiefly into 1 : 2 : 3 : 4-dibenzanthracene, whilst from the more sparingly soluble portions *naphtha*-2′ : 3′-1 : 2-*phenanthrene*, m. p. 293—294° in a sealed capillary, is isolated by repeated crystallisation from xylene. The last-named hydrocarbon is also prepared by distillation of 1 : 2-*phthalylphenanthrene*, m. p. 269—270°, with zinc dust. 1 : 2-*Phthalylphenanthraquinone*, its o-*diazine*, not molten below 375°, and 1 : 2-*benzoanthraquinono*-2′ : 1′ : 3 : 4-*phenazine*, subliming at about 300°/vac., are described. α-Naphthoyl chloride and 2-methyl-5 : 6 : 7 : 8-tetrahydronaphthalene are converted by aluminium chloride in benzene into 3-α-*naphthoyl*-2-*methyl*-5 : 6 : 7 : 8-*tetrahydronaphthalene*, b. p. about 265°/13 mm., m. p. 142—143°; 3-β-*naphthoyl*-2-*methyl*-5 : 6 : 7 : 8-*tetrahydronaphthalene*, m. p. 103—104°, is prepared similarly. Either ketone is transformed by distillation with copper powder into *naphtha*-2′ : 3′-2 : 3-*phenanthrene*, m. p. 263—264°. 2 : 3-*Phthalylphenanthrene*, m. p. 272—273°, and 2 : 3-*phthalylphenanthraquinone*, m. p. 318°, are described. The diquinone is converted by phenylhydrazine into the *quinhydrone*, $C_{22}H_{12}O_4$, m. p. about 375° (decomp.), and by *o*-phenylenediamine into the *phenazine*, $C_{28}H_{14}O_2N_2$, subliming at about 300°/vac.

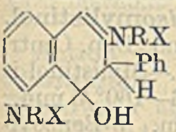
H. Wren.

Phenyl- and *o*-tolyl-thiocarbimides as reagents for primary aromatic amines. T. Otterbacher and F. C. Whitmore (J. Amer. Chem. Soc., 1929, **51**, 1909—1911).—These reagents have the advantage that they may be used in presence of water or alcohol and form no by-products. The following derivatives of *s*-diphenylthiocarbamide were prepared in hot or cold alcoholic solution: p-*methyl*-, m. p. 141°; o-*methyl*-, m. p. 136°; m-*methyl*-, m. p. 94°; p-*bromo*-, m. p. 148°; o-*bromo*-, m. p. 146°; m-*bromo*-, m. p. 97°; p-*chloro*-, m. p. 152°; o-*chloro*-, m. p. 156°; m-*chloro*-, m. p. 116°; p-*iodo*-, m. p. 153°; 2-*bromo*-4-*methyl*-, m. p. 154·5°; 2 : 4-*dimethyl*-, m. p. 133·5°; 4-*hydroxy*-2-*methyl*-, m. p. 167·5°; p-*hydroxy*-, m. p. 150°, also the following derivatives of *p*′-methyl-*s*-diphenylthiocarbamide: p-*methyl*-, m. p. 132°; o-*methyl*-, m. p. 158°; m-*methyl*-, m. p. 140°; p-*bromo*-, m. p. 143°; o-*bromo*-, m. p. 128°; m-*bromo*-, m. p. 101°; p-*chloro*-, m. p. 134·5°; o-*chloro*-, m. p. 140°; m-*chloro*-, m. p. 124°; p-*iodo*-, m. p. 150°; 2-*bromo*-4-*methyl*-, m. p. 132°; 2 : 4-*dimethyl*-, m. p. 143·5°; 4-*hydroxy*-2-*methyl*-, m. p. 182·5°; p-*hydroxy*-, m. p. 158°; p-*methoxy*-, m. p. 138°; and o-*methoxy*-, m. p. 126°. The *diphenylthiourethanes*, m. p. 172° and m. p. 168°, respectively, of phenylhydrazine and hydrazobenzene, and phenyl-, m. p. 154°, and *p*-tolyl-, m. p. 160°, -thiocarbamides were obtained similarly.

H. E. F. Notton.

Steric hindrance and the Grignard reaction. Colour reactions of organometallic compounds. H. Gilman and L. L. Heck (Ber., 1929, **62**, [*B*], 1379—1384; cf. Gilman and others, A., 1925, ii, 1011; 1928, 160; this vol., 303).—The observation of von Braun and others (A., 1918, i, 107; 1920, i, 30) that β-methylanilinoethyl chloride and bromide do not react with ketones appears at variance with the universality of the authors' colour reaction of compounds containing the group C·MgX and Michler's ketone. It is found that in these cases the colour is only slowly developed, thus supporting the hypothesis that the sluggishness is due to steric hindrance. On the other hand, the Grignard reagents from triphenylmethyl chloride and bromomesitylene give an immediate colour. β-Methylanilinoethyl chloride is prepared by the successive addition of magnesium ethyl bromide and β-chloroethyl *p*-toluenesulphonate to methylaniline in ether. Its Grignard derivative is transformed by *n*-butaldehyde into *s*-diphenyldimethyltetramethylenediamine (picrate, m. p. 203°) and the aminocarbinol $NMePh\cdot C_2H_4\cdot CHPr^{\alpha}\cdot OH$ (picrate, m. p. 145; chloroplatinate, m. p. 209°, decomp. 211°) (cf. von Braun and co-workers, A., 1918, i, 107). Magnesium mesityl bromide is converted by carbon dioxide into 2 : 4 : 6-trimethylbenzoic acid in 50% yield. H. Wren.

N-Methyl derivatives of 2-phenylnaphthylene-1 : 3-diamine. W. S. Kentish (J.C.S., 1929, 1169—1175).—The isomerism of the α- and β-*NN'*-dimethyl-2-phenylnaphthylene-1 : 3-diamines (cf. Lees and Thorpe, J.C.S., 1907, **91**, 1282; Gibson, Kentish, and Simonsen, A., 1928, 1128) has been re-examined. The β-dimethyl base (I) is represented as *NN'*-dimethyl-2-phenylnaphthylene-1 : 3-diamine, and the α-dimethyl base (II) as 3-methylamino-1-methylimino-2-phenyl-1 : 2-dihydronaphthalene. By treatment at the ordinary temperature with 1 mol. of nitrous acid, II affords α-3-*nitrosomethylamino*-1-*methylimino*-2-*phenyl*-1 : 2-*dihydronaphthalene* (III), dimorphous (unstable α_1-*form*, yellow needles, m. p. 154°; stable α-form, orange-red prisms, m. p. 154°), reconverted into II by reduction with tin and hydrochloric and acetic acids at 100° in nearly theoretical yield; III can neither be methylated nor condensed with *p*-toluenesulphonyl chloride, but treatment with excess of nitrous acid slowly converts it into β-1 : 3-dinitrosomethylamino-2-phenylnaphthalene, m. p. 179°, which by reduction yields I. α-3-Acetylmethylamino-1-methylimino-2-phenyl-1 : 2-dihydronaphthalene with nitrous acid furnishes β-3-*acetylmethylamino*-1-*nitrosomethylamino*-2-*phenylnaphthalene*, m. p. 198°, reduced by tin and hydrochloric and acetic acids to β-3-*acetylmethylamino*-1-*methylamino*-2-*phenylnaphthalene*, m. p. 147°, which by hydrolysis with concentrated hydrochloric acid yields I. Similarly 3-*p*-toluenesulphonyl-β-*NN'*-dimethyl-2-phenylnaphthylene-1 : 3-diamine affords 1-*nitroso*-3-p-*toluenesulphonyl*-β-NN'-*dimethyl*-2-*phenylnaphthylene*-1 : 3-*diamine*, m. p. 183°, giving I by reduction and hydrolysis. These results show that the α⟶β transformation is effected by nitrous acid and is unassociated with the nature of the substituent in the 3-position. It is suggested that nitrous acid adds on at the methylimino-double linking, giving IV (R=Me; X=NO), which then loses water. In support, it is shown that the " acetyl acetate " of 2-phenylnaphthylene-1 : 3-diamine (V) (Atkinson and Thorpe, J.C.S., 1906, **89**, 1906) has the structure IV (R=Ac; X=H), since, by treatment with cold 5% aqueous sodium hydroxide it loses water, giving diacetyl-2-phenylnaphthylene-1 : 3-diamine, m. p. 272° (cf. lit.). It is concluded that V has a mono-imino-structure.



(IV.)

It is consistent with the suggested structures that β-3-*nitrosomethylamino*-1-*methylamino*-2-*phenylnaphthalene*, m. p. 248°, has a deep red colour and yields highly-coloured solutions, whereas the α-mononitrosoamine (III) gives but slightly coloured solutions. C. W. Shoppee.

Perylene and its derivatives. XXIII. K. Funke and H. Wolf (Monatsh., 1929, **52**, 1—6).—Reduction of 3 : 9-dichloro-4 : 10-dinitroperylene (I) (Zinke, Funke, and Lorber, A., 1927, 350) with phenylhydrazine in boiling xylene takes place through an intermediate compound (constitution not established), and gives 3 : 9-*dichloro*-4 : 10-*diaminoperylene* (II), needles with copper-red metallic lustre (*diacetyl* and *dibenzoyl* derivatives). Nitration of 3 : 9-dibromoperylene suspended in acetic acid with potassium nitrate and sulphuric acid affords 3 : 9-*dibromo*-4 : 10-*dinitroperylene* (III), reduced as above to 3 : 9-*dibromo*-4 : 10-*diaminoperylene* (IV). During acetylation or benzoylation of III and IV a partial (in some cases a total) elimination of halogen occurs (cf. Junghans, A., 1913, i, 1070). Whilst I and II are unaffected by boiling with aniline, III and IV yield 4 : 10-*diaminoperylene*, steel-blue rods (*dibenzoyl* and *di*-p-*bromobenzoyl* derivatives), which differs from the diamino-derivative previously described (this vol., 550). This last compound is postulated as the 3 : 10-derivative, since oxidation of the original dinitro-compound (A., 1927, 350) with concentrated sulphuric acid gives perylene-3 : 4 : 9 : 10-diquinone.
H. Burton.

Catalytic reduction of nitro-compounds. M. Busch and K. Schulz (Ber., 1929, 62, [*B*], 1458—1466).—Reduction is effected in boiling alcoholic 5% potassium hydroxide solution, the hydrogen being obtained by decomposition of hydrazine hydrate under the influence of palladised calcium carbonate. Reaction proceeds more readily in methyl than in ethyl alcohol: thus, under defined conditions, nitrobenzene in ethyl alcohol yields almost exclusively azoxybenzene, whereas in methyl alcohol it gives azobenzene; with increased amounts of catalyst, hydrazobenzene and, finally, aniline are produced. Nitrophenols which can yield pseudo-acids are more readily reduced. *o*- and *p*-Nitrophenols give the corresponding aminophenols; the *m*-compound is reduced similarly in methyl alcohol. *m*-Nitrobenzenesulphonic acid yields the aminobenzenesulphonic acid. The phenylenediamines are obtained from *o*- and *p*-nitroaniline, whereas *m*-nitroaniline yields the azoxy-compound in ethyl alcohol, but *m*-phenylenediamine in methyl alcohol. Under similar conditions, azoxybenzene is reduced almost quantitatively, azobenzene to the extent of 50%, to hydrazobenzene, whereas the last-named compound is almost indifferent. With the nitrotoluenes the absorption of hydrogen increases in the sequence $o > m > p$. In ethyl alcohol azoxy-, azo-, and a mixture of azo- and hydrazotoluenes are obtained in the three cases, whereas in methyl alcohol *o*-nitrotoluene gives *o*-toluidine in excellent yield, *m*-nitrotoluene affords *m*-hydrazotoluene and *m*-toluidine, whereas *p*-nitrotoluene gives a mixture of *p*-azo- and *p*-hydrazo-toluene and *p*-toluidine. With halogenonitrobenzenes the hydrogen first reduces the nitro-group, the activity of which is enhanced by the halogen atom. With the *o*- and *m*-compounds the azoxy-compounds are produced in small yields; only in the case of *p*-bromonitrobenzene is the azoxy-derivative the main product (probably by reason of its sparing solubility in alcohol). In general, halogenoazobenzenes predominate in ethyl alcohol, varying amounts of halogenoanilines and aniline in methyl alcohol. H. Wren.

Action of bromine on mixed ethers. L. C. Raiford and D. M. Birosel (J. Amer. Chem. Soc., 1929, 51, 1776—1778).—Phenyl allyl ether and excess of bromine in chloroform give 2 : 4-*dibromophenyl* βγ-*dibromopropyl ether*, b. p. 220—223°/10 mm., and 2 : 4 : 6-tribromophenol, but no 2 : 4 : 6-*tribromo*-

phenyl βγ-dibromopropyl ether, m. p. 42·5—43·5°, prepared from tribromophenyl allyl ether and bromine. Phenyl methyl, ethyl, *n*-propyl, and *iso*butyl ethers are brominated at the ordinary temperature to 2 : 4 : 6-tribromo-derivatives. 2 : 4 : 6-Tribromophenyl *n*-propyl and *iso*propyl ethers are not attacked by bromine, but phenyl *iso*propyl, *sec.*-butyl, and *tert.*-butyl ethers and 2 : 4-dibromophenyl *iso*propyl ether give tribromophenol, which is also formed to the extent of 10% and 20%, respectively, from anisole and phenetole. The dealkylation is effected by hydrogen bromide formed in the reaction and does not occur (except with the *tert.*-butyl ether) in presence of sodium acetate. 4-*Chloro*-2-*nitrophenyl* and 2 : 4 : 6-*trinitrophenyl βγ-dibromopropyl ethers*, m. p. 55°, and m. p. 102°, were prepared from the corresponding allyl ethers (cf. Fairbourne, A., 1927, 131). 2 : 4-*Dibromophenyl* and 2 : 4 : 6-*tribromophenyl* iso*propyl ethers* have b. p. 156°/18 mm., and b. p. 190°/30 mm., m. p. 40°, respectively. H. E. F. Notton.

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 dissolution in sodium carbonate, separation of the sodium salt, and decomposition of the latter with dilute hydrochloric acid.

C. R. Harington.

Organic compounds of sulphur. XIII. Action of aliphatic diazo-compounds on sulphur aryl chlorides and mercaptans. A. Schönberg, O. Schütz, and J. Peter (Ber., 1929, 62, [*B*], 1663—1670; cf. this vol., 447).—Diphenyldiazomethane and sulphur *o*-nitrophenyl chloride react readily in anhydrous ether, giving nitrogen and o-*nitrophenyl diphenylchloromethyl sulphide*, $CPh_2Cl{\cdot}S{\cdot}C_6H_4{\cdot}NO_2$, decomp. about 137° depending greatly on the rate of heating. It is converted by *o*-nitrophenyl mercaptan in boiling benzene into *di*-o-*nitrophenylthioldiphenylmethane*, $CPh_2(S{\cdot}C_6H_4{\cdot}NO_2)_2$, m. p. (indef.) about 146° (decomp.), and by phenyl mercaptan into *phenylthiol*-o-*nitrophenylthioldiphenylmethane*, m. p. (indef.) 134°. 9-*Chloro*-9-o-*nitrophenylthiolfluorene*, decomp. about 120° according to the rate of heating, from *o*-nitrophenyl mercaptan and diphenylenediazomethane in ether, is converted by phenyl mercaptan in boiling benzene into 9-*phenylthiol*-9-o-*nitrophenylthiolfluorene*, m. p. about 127—129°. Diphenyldiazomethane and sulphur phenyl chloride in ether yield phenylthioldiphenylmethyl chloride, converted by *o*-nitrophenyl mercaptan into phenylthiol-*o*-nitrophenylthioldiphenylmethane. Diphenyldiazomethane and phenyl mercaptan give phenyl diphenylmethyl sulphide, m. p. 78°. α-Naphthyl mercaptan is transformed by diphenyldiazomethane into α-naphthyl diphenylmethyl sulphide, m. p. 77—78°. *Benzyl diphenylmethyl sulphide* has m. p. 70·5°. 9-*Phenylthiolfluorene*, m. p. about 215° (decomp.), is prepared from diphenylenediazomethane and phenyl mercaptan. *Di*-β-*naphthyl ketone hydrazone*, m. p. 148°, is transformed by yellow mercuric oxide into *di*-β-*naphthyldiazomethane*, which passes in boiling benzene into *di*-β-*naphthyl ketazine*, m. p. 263—264° in a closed capillary.

H. Wren.

Nitration of methane- and ethane-sulphon-*p*-phenetidides. F. Reverdin (Helv. Chim. Acta, 1929, 12, 786).—The author acknowledges that ethanesulphonyl-*p*-phenetidine and its 2-nitro- and acetyl derivatives described by him (this vol., 310) as new were first prepared by Autenrieth and Bernheim (A., 1905, i, 47). Two other minor mistakes are rectified. R. J. W. Le Fèvre.

Preparation of aminonaphthols. W. F. Brown, J. C. Hebden, and J. R. Withrow (J. Amer. Chem. Soc., 1929, 51, 1766—1769).—1 : 6- and 1 : 7-Aminonaphthols (*hydrochlorides*) are obtained in about 58% yield, some loss occurring through volatilisation, by fusing the corresponding naphthylaminesulphonic acids in an open vessel with sodium hydroxide at 305° (cf. Cassella, D.R.-P. 69458; Sachs, B., 1906, 369, 1143). Acetylation of 1 : 6-aminonaphthol, m. p. 190·6° (corr.) (picrate, m. p. 170°), by the method of Kehrmann and Engelke (A., 1809, i, 150) gives an impure product, m. p. 195—220°. H. E. F. Notton.

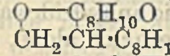
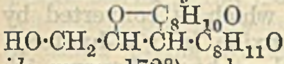
Carbamides and thiocarbamides from vanillylamine; constitution and taste of pungent principles. N. A. Lange, H. L. Ebert, and L. K. Youse (J. Amer. Chem. Soc., 1929, 51, 1911—1914).—The following have been prepared from vanillylamine and the appropriate carbimide or thiocarbimide: 4-*hydroxy*-3-*methoxybenzylcarbamide*, m. p. 178·5° (corr.), and α-*phenyl*-β-4-*hydroxy*-3-*methoxybenzylcarbamide*, m. p. 190·5°; also derivatives of α-p-*hydroxy*-m-*methoxybenzylthiocarbamide*, m. p. 167·5°: β-*phenyl*- (I), m. p. 138—138·5°; β-p-*tolyl*- (II), m. p. 138·5—139°, and β-o-*tolyl*- (III), m. p. 138—138·5°. Compounds I, II, and III have a pungent taste accompanied by slight bitterness; the rest are tasteless.

H. E. F. Notton.

Constitution of mylistinol and *iso*mylistinol. K. Kafuku and N. Ishikawa (Bull. Ind. Dep. Centr. Res. Lab. Formosa, 1928, 24, 27—34).—Mylistinol is 5-hydroxyeugenol ethyl ether, b. p. 156—160°/5 mm.; the methyl ether has b. p. 134°/6 mm. 5-Benzoylmylistinol has m. p. 55·5—57°.

Chemical Abstracts.

Methone as a reagent for aldehydes. D. Vorländer (Z. anal. Chem., 1929, 77, 241—268).—Methone (5 : 5-dimethyldihydroresorcinol) yields characteristic condensation products of the enolic acid type with aqueous or alcoholic solutions of true aldehydes, 2 mols. of methone condensing with 1 mol. of aldehyde with the elimination of 1 mol. of water; in glacial acetic acid 2 mols. of water are removed yielding characteristic anhydrides. Both acids and anhydrides crystallise well, are almost insoluble in the cold solvents used, and have well-defined m. p.; they are thus suitable for the detection and identification of aldehydes. The following compounds are described: *methylenedimethone*, $CH_2(C_8H_{11}O_2)_2$, m. p. 189° (corr.) (*anhydride*, m. p. 171°); *ethylidenedimethone*, $CHMe(C_8H_{11}O_2)_2$, m. p. 139° (*anhydride*, m. p. 173—174°); *propylidenedimethone*, $CH_2Me{\cdot}CH(C_8H_{11}O_2)_2$, m. p. 154—156° [*anhydride*, m. p. 142—143° (corr.)]; iso*valerylidenedimethone*, $CH_2Pr^{\beta}{\cdot}CH(C_8H_{11}O_2)_2$, m. p. 154—155° [*anhydride*, m. p. 172—173° (corr.)]; and *compounds* with the following aldehydes: heptaldehyde,

$Me\cdot[CH_2]_5\cdot CH(C_8H_{11}O_2)_2$, m. p. 103° (*anhydride*, m. p. 112°); acraldehyde, $CH_2\colon CH\cdot CH(C_8H_{11}O_2)_2$, m. p. 192° (*anhydride*, m. p. 162—163°); crotonaldehyde, m. p. 183° (cf. Fricke, 1922, i, 300) (*anhydride*, m. p. 167°); glycollaldehyde,  $\overset{O\text{——}C_8H_{10}O}{CH_2\cdot CH\cdot C_8H_{11}O_2}$, m. p. 237·5° (corr.) [*acetyl* compound, $C_{20}H_{26}O_5$, yellow, m. p. 205—206° (corr.)], also formed by interaction of chloroacetaldehyde and methone; glyceraldehyde,  $HO\cdot CH_2\cdot\overset{O\text{——}C_8H_{10}O}{CH\cdot CH\cdot C_8H_{11}O_2}$, m. p. 197·5° (corr.) (*anhydride*, m. p. 172°); glyoxal, $CHO\cdot CH(C_8H_{11}O_2)_2$, m. p. 186° (corr.) (*anhydride*, m. p. 224°); methylglyoxal, $COMe\cdot CH(C_8H_{11}O_2)_2$, m. p. 164° (corr.); malonaldehyde, m. p. 235—237°; glyoxylic acid (*anhydride*, m. p. 233—234°; *ethyl* ester, m. p. 122—124°); cinnamaldehyde, two isomeric forms, yellow crystals, m. p. 161° (corr.), from cold solutions and white prisms, m. p. 212—214° (corr.), from hot solutions (*anhydride*, m. p. 174—175°); cuminaldehyde, m. p. 170—171° (*anhydride*, 172—173°); *p*-hydroxybenzaldehyde, m. p. 188—190° (corr.) (*anhydride*, m. p. 246°; *acetyl* compound, m. p. 205—206°; *benzoyl* compound, m. p. 204°); *p*-anisaldehyde, m. p. 144—145° (corr.) (*anhydride*, m. p. 243°); salicylaldehyde, *anhydride*, m. p. 208° (corr.); *o*-chlorobenzaldehyde, m. p. 205° (corr.) (*anhydride*, m. p. 224—226°); vanillin, *anhydride*, m. p. 227—228°; piperonaldehyde, *anhydride*, m. p. 219—220°; dimethylaminobenzaldehyde, m. p. 192—194°; furfuraldehyde, m. p. 160° (decomp.) (*anhydride*, m. p. 162—165°). Isatin and methone in glacial acetic acid give a brown solution from which a yellowish flocculent precipitate is obtained on adding water; this *anhydride*, $C_{24}H_{25}O_4N$, has m. p. 283—285°; most other ketones do not react with methone under these conditions.

A. R. POWELL.

Action of aluminium chloride and metallic aluminium on hydroxylic compounds. J. POSTOWSKY and B. LUGOWKIN (J. pr. Chem., 1929, [ii], **122**, 141—146).—When *m*-cresol is boiled with 10% of anhydrous aluminium chloride, 3 : 6-dimethylxanthene is formed in 5% yield, accompanied by di-*m*-tolyl ether. When benzhydrol is boiled with aluminium powder, *s*-tetraphenylethane (30%) and diphenylmethane (5%) are formed. *s*-Tetraphenylethane is evidently formed by way of diphenylmethyl, for diphenylmethane yields only 3% of *s*-tetraphenylethane when heated with aluminium. Benzoin, when boiled with aluminium powder, yields 15% of tetraphenylfuran. The dehydrogenating action of aluminium powder is shown by the conversion of benzylaniline into benzylideneaniline. R. K. CALLOW.

Photochemical activity of various sterols and the nature of their action. L. HUGOUNENQ and E. COUTURE.—See this vol., 895.

Photographic effect produced by sterols after exposure to ultra-violet rays. J. CLUZET and KOFMAN.—See this vol., 895.

Displacement of iodine from an iodide by a solution in oil of cholesterol or ergosterol irradiated by solar light. E. ROUSSEAU.—See this vol., 895.

New photo-reaction with ergosterol. A. STEIGMANN.—See this vol., 895.

Conversion of naphthenic acids into naphthenes. G. KOMPPA (Ber., 1929, **62**, [*B*], 1562—1570).—Fractional distillation of the methyl esters of naphthenic acids derived from Baku petroleum does not lead to the isolation of individuals. Hydrolysis of appropriate fractions followed by distillation of the acids yields only a constant-boiling mixture (b. p. 147—148°/8 mm.) containing about 37% of deca- and 63% of undeca-naphthenic acid, from which suitable crystalline salts or derivatives could not be obtained. The mixed acids are therefore transformed by phosphorus pentachloride into their chlorides, which, when fractionally distilled, afford *undecanaphthenyl chloride*, $C_{10}H_{19}\cdot COCl$, b. p. 106·5—108°/8 mm. (non-crystalline *anilide* and p-*toluidide*). *Ethyl* and *methyl undecanaphthenates* have b. p. 247—248·5°/762 mm., d_4^{20} 0·92356, n_D^{20} 1·44818, and b. p. 236—237°/763 mm., d_4^{20} 0·93528, n_D^{20} 1·44984, respectively. Hydrolysis of the methyl ester affords *undecanaphthenic acid*, b. p. 271—272°/763·5 mm., d_4^{20} 0·9707, n_D^{20} 1·4637 (*silver salt*). Reduction of the ethyl ester with sodium and alcohol yields *undecanaphthenol*, b. p. 236·5—237·5°, d_4^{20} 0·90245, n_D^{20} 1·46469 (*cinnamate*, b. p. 219—220°/7 mm., d_4^{20} 1·00222, n_D^{20} 1·53728, and its non-crystalline *dibromide*), converted by phosphoryl chloride and phosphorus pentachloride into *undecanaphthenyl chloride*, b. p. 74—78°/7 mm., d_4^{20} 0·89318, and thence by sodium and alcohol into undecanaphthene, $C_{11}H_{22}$, b. p. 183·5—184·5°/764·5 mm., d_4^{20} 0·81284, n_D^{20} 1·44834. Since the hydrocarbon thus obtained is identical with that isolated by Markovnikov and Oglobin from Baku naphtha, it follows that the undecanaphthenic acid of the naphtha is a carboxylated derivative of the undecanaphthene present in the same type of petroleum. H. WREN.

Molecular compounds of bile acids with fatty acids and alcohols. II. Hyodeoxycholic acid. III. Cholic acid. H. RHEINBOLDT (Z. physiol. Chem., 1929, **182**, 251—254, 255—258; cf. this vol., 443).—Melting-point curves for binary mixtures of hyodeoxycholic acid and cholic acid with various fatty acids and an alcohol were obtained. There was no evidence of compound formation; the eutectic mixture in each case contained about 1% of the bile acid. The eutectic temperatures determined were: palmitic acid, 59° and 55·5°; stearic acid, 65·5° and 61°; stearolic acid, 45·5° and 44·5°; brassidic acid, 58° and 57·5°; behenolic acid, 54° and 55°; cetyl alcohol, 45·5° and 45°, respectively.

J. H. BIRKINSHAW.

Bufodeoxycholic acid. II. T. OKAMURA (J. Biochem. Japan, 1928, **10**, 5—9; cf. A., 1928, 1272).—Bufodeoxycholic acid (*methyl* ester, m. p. 167°; *ethyl* ester, m. p. 171—173°), when oxidised with chromic acid, affords a *diketo-acid* (α), m. p. 230°, which is quickly converted into an *acid* (β), m. p. 251°, the ethyl ester of which is more stable than that of the α-acid. On reduction, the α-acid affords *bufocholanic acid*, m. p. 236°, $[\alpha]_D^{8.5}$ —20·3° (*ethyl* ester, $C_{26}H_{44}O_2$, m. p. 108—111°). CHEMICAL ABSTRACTS.

Electrochemical reduction of benzoic acid. F. FICHTER and I. STEIN (Helv. Chim. Acta, 1929, **12**, 821—826).—Cathodic reductions of solutions of benzoic acid in sulphuric acid and ethyl alcohol leads only to benzyl alcohol and not to ethyl Δ^{13}-dihydrobenzoate as stated by Somlò (cf. this vol., 776).

R. J. W. Le Fèvre.

Oxidation of toluene to benzoic acid by potassium dichromate and sulphuric acid. O. Y. Magidson and V. I. Maksimov (J. Chem. Ind. Moscow, 1928, **5**, 1102).—At first the product is chiefly benzoic acid, but later this is partly oxidised yielding carbon dioxide. The fall in the yield at the end of the reaction is probably due to increased viscosity interfering with efficient stirring. Rise of temperature increases the yield by decreasing the viscosity, and accelerates the process. An excess of sulphuric acid is favourable, probably owing to decrease of viscosity. The yield, calculated from the dichromate used, is for 60% acid, 25%; for 65% acid, 37%; for 70% acid, 50%; more concentrated acid is unfavourable. Only a large excess of toluene increases the yield. Various salts, particularly those of iron or nickel, accelerate the reaction; sodium chloride causes complete decomposition of the toluene.

Chemical Abstracts.

Identification of *o*-, *m*-, and *p*-hydroxybenzoic acids. F. F. Blicke and F. D. Smith (J. Amer. Chem. Soc., 1929, **51**, 1947—1949).—Application of the method of Lyman and Reid (A., 1917, i, 334) to the preparation of the *p*-nitrobenzyl esters of these acids causes, in addition, partial etherification. The ether-esters, obtained by refluxing the acids in aqueous acetone with excess of *p*-nitrobenzyl bromide and sodium hydroxide, are more suitable for their identification than are the esters, obtained by using 1 mol. of bromide. The 2-, m. p. 166—168° (p-*nitrobenzyl* ester, m. p. 137—139°); 3-, m. p. 193—196° (p-*nitrobenzyl* ester, m. p. 142—144°), and 4-, m. p. 259—261° (p-*nitrobenzyl* ester, m. p. 196—197°, regarded by Lyman and Reid as *p*-nitrobenzyl *p*-hydroxybenzoate, which has actually m. p. 180—182°), -p-*nitrobenzyloxybenzoic acids* are obtained by hydrolysing the ester-ethers with potassium carbonate in 50% aqueous alcohol.

H. E. F. Notton.

Reduction of ethyl diphenylglycidate with sodium and alcohol. (Mme.) P. Billon-Bardon (Compt. rend., 1929, **188**, 1412—1413).—Reduction of ethyl diphenylglycidate with sodium (18 atoms) and alcohol yields α-hydroxy-ββ-diphenylpropionic acid (diphenyl-lactic acid) in 60% yield, together with diphenylethane and a small amount of a *substance*, b. p. 180—215°/15 mm. Attack is thus limited, as in the case of the Grignard reagent (A., 1926, 950), to the oxido-group, and it is suggested that after this initial attack the presence of the group OMgX or ONa on the α-carbon atom greatly reduces the reactivity of the carbethoxyl group.

J. W. Baker.

Phenolhalogenophthaleins. F. F. Blicke and F. D. Smith (J. Amer. Chem. Soc., 1929, **51**, 1865—1875).—Ethyl 4-aminophthalate is converted through 3 : 4-*dicarbethoxybenzenediazonium borofluoride*, decomp. 125° (cf. Balz, A., 1927, 654), into *ethyl* 4-*fluorophthalate*, b. p. 165—170°/25 mm., hydrolysed by sodium hydroxide to 4-*fluorophthalic acid*, m. p. 147—148° in a closed tube. 4-*Fluoro*-, m. p. 76—78°, b. p. 260°/746 mm.; 4-chloro-, m. p. 98°, b. p. 284°/750 mm.; 4-bromo-, m. p. 108—109°, b. p. 290—293°/750 mm.; 4-*iodo*-, m. p. 125—126°, and 3-*iodo*-, m. p. 159—161°, -phthalic anhydrides are prepared by heating the corresponding acids alone, or with acetic anhydride. Crystallographic data are given for the 4-substituted anhydrides. 3-Iodophthalic anhydride, phenol, and zinc chloride at 115—130° give only *phenol*-3-*iodophthalein*, m. p. 252—254°, which is converted by fusion with potassium hydroxide into *m*-hydroxybenzoic acid and *pp'*-dihydroxybenzophenone (cf. Baeyer, A., 1880, 650). The 4-halogenated anhydrides, however, give the following mixtures of phenol-4- and -5-halogenophthaleins: -4- and -5-*fluoro*-, m. p. 230—240°; -4- and -5-*chloro*-, m. p. 214—233°; -4- and -5-*bromo*-, m. p. 226—236°, and -4- and -5-*iodo*-, m. p. 240—255°. These give on alkaline fusion *pp'*-dihydroxybenzophenone and both *m*- and *p*-hydroxybenzoic acids.

H. E. F. Notton.

Grignard reagents from *p*-dibromobenzene. H. Gilman, N. J. Beaber, and H. L. Jones (Rec. trav. chim., 1929, **48**, 597—602).—The formation of the bis-organomagnesium compound (*p*) $C_6H_4(MgBr)_2$, and its conversion by carbon dioxide into terephthalic acid reported by Houben (A., 1906, i, 21; cf. Pink, J.C.S., 1923, **123**, 3418; Quelet, A., 1927, 890) has been confirmed. By employing 15-mesh magnesium and extended refluxing in an ether–benzene mixture, an apparent yield of 4·2% of terephthalic acid was obtained, whilst with several equivalents of a 12·75% copper–magnesium alloy (cf. Gilman, Peterson, and Schulze, A., 1928, 253) the apparent yield was increased to 23·5%. The terephthalic acid yielded methyl terephthalate (mixed m. p.) but was contaminated with *p*-bromobenzoic acid and probably other acids of higher mol. wt. On the assumption that this acid constitutes the sole impurity, titration experiments indicate that the true yield of terephthalic acid is about 7·7%, but the method used to remove the greater part of the *p*-bromobenzoic acid from the reaction product (extraction with chloroform) entails some loss of terephthalic acid. Attention is directed to the theoretical complexity of the reaction between magnesium and simple polyhalogen compounds.

C. W. Shoppee.

***cyclo*Hexyl alkyl phthalates.** R. Adams and J. F. Hyde, Assrs. to Newport Co.—See B., 1929, 511.

Condensation of aromatic aldehydes with nitromethane. M. G. S. Rao, C. Srikantia, and M. S. Iyengar (Helv. Chim. Acta, 1929, **12**, 581—583).—Condensations of vanillin, 2-hydroxy-4-methoxy-, 2 : 4-dimethoxy-, 4-methoxy-2-ethoxy-, and 5-nitro-2 : 4-dimethoxy-benzaldehyde with nitromethane in the presence of ammonium acetate and acetic acid are described. The following compounds were obtained respectively: vanillylidenenitromethane, m. p. 166°; 2-*hydroxy*-4-*methoxy*-, m. p. 171—172°; 2 : 4-*dimethoxy*-, m. p. 104°; 4-*methoxy*-2-*ethoxy*-ω-*nitrostyrene*, m. p. 102°; and 5-ω-*dinitro*-2 : 4-*dimethoxystyrene*, m. p. 214°. The yields were about 80% of the theoretical. R. J. W. Le Fèvre.

Photochemical transformation of *o*-nitrobenzaldehyde. R. Wegscheider.—See this vol., 895.

Mobility of symmetrical triad prototropic systems. V. New triad system (methylene-azomethine). C. K. INGOLD and C. W. SHOPPEE (J.C.S., 1929, 1199—1204).—Condensation of *p*-anisaldehyde with benzylamine in an atmosphere of hydrogen at 100° affords p-*methoxybenzylidenebenzylamine* (I), m. p. 42°, reconverted by hydrolysis with 2*N*-sulphuric acid into its congeners (*benzylamine picrate* has m. p. 198°). A similar condensation yields *benzylidene*-p-*methoxybenzylamine* (II), b. p. 217°/17 mm., giving by hydrolysis benzaldehyde and *p*-methoxybenzylamine [*picrate*, m. p. 188° (decomp.); *benzoate*, m. p. 135°]. Interconversion of I and II occurs in 1·45*N*-alcoholic sodium ethoxide at 85°; at equilibrium the product contains 78·9% of I and 21·1% of II, giving an equilibrium ratio $k_1/k_2=0{\cdot}268$. Methylenebenzylamine, m. p. 48° (cf. lit.), and benzylidenemethylamine, b. p. 90—91°/30 mm. (improved method of preparation described), are stable towards aqueous alkali and towards 1·46*N*- and 2·92*N*-alcoholic sodium ethoxide at 100°, but the former is partly converted into the latter in the presence of potassium hydroxide at about 300° or of 1·45*N*-alcoholic sodium ethoxide at 190°. The present position relating to the study of prototropy is summarised, and the isomeric change undergone by substitution products of benzaldoxime *N*-benzyl ether (lit.) is discussed.

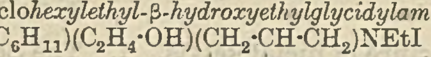
C. W. SHOPPEE.

Catalytic influences in three-carbon tautomerism. I. Sodium alkoxides. G. A. R. KON and R. P. LINSTEAD (J.C.S., 1929, 1269—1282).—Conditions under which mobilities of neutral tautomeric substances are measured have been standardised, and the behaviour of the tautomerides $C_5H_{10}{>}C{:}CHX$ (I) and $C_5H_9{>}C{\cdot}CH_2X$ (II) ($X=COMe$ or CO_2Et) has been studied. In addition to the standard reagent, *N*-sodium ethoxide, the effect of other alkoxides on the ketones I, II has been examined; the order of efficiency is *iso*propoxide>propoxide>ethoxide>methoxide (>hydroxide) (cf. Ingold and Shoppee, this vol., 556), which is the sequence anticipated for an ionic mechanism of tautomeric change (Ingold, Shoppee, and Thorpe, A., 1926, 939). All these catalysts produce the same equilibrium mixture; the presence of water has little effect on the mobility of the ketones, but a considerable retarding influence in the case of the esters I, II owing to greatly increased hydrolysis. The mobility is best measured by the velocity of equilibration of the isomeride II, since there appears to be a small but definite equilibrium between the isomeride I, ethyl or methyl alcohol, and an ethoxy- or methoxy-additive compound; the methoxyl or ethoxyl group is provisionally assumed to occupy the β-position.

*cyclo*Hexylideneacetone (I; X=COMe), b. p. 83—84°/12 mm., $d_4^{15\cdot6}$ 0·95188, $n_D^{15\cdot6}$ 1·49224, and *cyclo*hexenylacetone (II; X=COMe), b. p. 77°/11 mm., $d_4^{19\cdot0}$ 0·93760, $n_D^{19\cdot0}$ 1·47389, both yield the same equilibrium mixture containing 30% of the former (cf. Dickens, Hugh, and Kon, A., 1928, 887); the velocity coefficient $(k_1+k_2)\times10^4$ is 700 min.$^{-1}$, with a half-change period of 9·9 min. Combined high fractions from the distillation of products obtained with sodium ethoxide as catalyst furnish by redistillation a constant-boiling fraction of b. p. 99—101°/9 mm., containing 70% of 1-*ethoxy*cyclo*hexylacetone* (*semicarbazone*, m. p. 174°); experiments with sodium methoxide similarly afford 1-*methoxy*cyclo*hexylacetone* (*semicarbazone*, m. p. 181—182°).

Ethyl *cyclo*hexylideneacetate (I; $X=CO_2Et$) and ethyl *cyclo*hexenylacetate (II; $X=CO_2Et$) yield by treatment with alcoholic sodium ethoxide the same equilibrium mixture, containing 57% of the latter (cf. Birch, Kon, and Norris, J.C.S., 1923, **123**, 1361; Linstead and May, A., 1927, 1167); the coefficient of the velocity of interconversion $(k_1+k_2)\times10^4$ is 8·1 min.$^{-1}$, with a half-change period of 14·1 hrs. The combined fractions from the distillation of equilibrated products by redistillation afford a fraction, b. p. 128°/15 mm., which is *ethyl* 1-*ethoxy*cyclo*hexylacetate*, b. p. 122°/11 mm., $n_D^{17\cdot4}$ 1·45753, $d_4^{17\cdot4}$ 0·9865, hydrolysed by potassium hydroxide to 1-*ethoxy*cyclo*hexylacetic acid*, m. p. 50—51° (*silver* salt, m. p. 216°).

C. W. SHOPPEE.

Isomerism of substituted aromatic phenacylamines. (Stereochemistry of the saturated tervalent nitrogen atom.) E. WEDEKIND and E. BRUCH (Annalen, 1929, 471, 73—112).—The existence of isomerism in various tertiary amines, with and without an asymmetric carbon atom in one of the groups, has been investigated. By the action of ethylene chlorohydrin on benzylethylamine or of ethyl iodide on benzyl-β-hydroxyethylamine the same *benzylethyl*-β-*hydroxyethylamine*, b. p. 134—136°/10 mm. (*methiodide*, m. p. 104°; *ethiodide*, m. p. 106°), is obtained. Similarly from *cyclo*hexylamine by either method the same cyclo*hexylethyl*-β-*hydroxyethylamine* (I), b. p. 119—120°/14 mm., 240—241°/750 mm., results, both specimens giving the same *methiodide*, m. p. 160—161° (Miss, Diss., Kiel, 1922, found one specimen, m. p. 172·5°) (*ethiodide*, m. p. 179—180°; *picrate*, m. p. 78—80°). Epi-iodohydrin reacts with I to yield cyclo*hexylethyl*-β-*hydroxyethylglycidylammonium iodide*,  $(C_6H_{11})(C_2H_4{\cdot}OH)(CH_2{\cdot}\underbrace{CH{\cdot}CH_2}_{O})NEtI$, m. p. 216—217°. Methylaniline and *cyclo*hexylamine react with epichlorohydrin to yield, respectively, *αγ-di*(*phenylmethylamino*)-β-*hydroxypropane*, m. p. 82°, and *αγ-di*(cyclo*hexylamino*)-β-*hydroxypropane*, m. p. 72—73° (*dinitrosoamine*, m. p. 115—116°). By the action of ω-bromoacetophenone and anhydrous potassium hydroxide on γ-chloro-α-*p*-tolylamino-β-hydroxypropane (from *p*-toluidine and epichlorohydrin; Cohn and Friedländer, A., 1904, i, 866) is obtained p-*tolylphenacylglycidylamine* (α-amine), m. p. 145°. The same amine is obtained by the action of epi-iodohydrin on *p*-tolylphenacylamine with anhydrous potassium hydroxide at 120—125°, but is accompanied in this case by the β-*amine*, m. p. 157°. That this isomerism is not dependent on the presence of an asymmetric carbon atom in one of the radicals attached to the tervalent nitrogen atom is shown by the reaction of ω-bromoacetophenone with p-*tolyl*iso*butylamine*, b. p. 135°/19 mm. (from *p*-toluidine and *iso*butyl bromide), in the presence of anhydrous potassium hydroxide, which yields p-*tolylphenacyl*iso*butylamine* (α-amine), m. p. 128° (colourless *oxime*, m. p. 97°). The same α-amine is obtained, together with a *substance* $C_{22}H_{19}O_2N$, m. p. 156°, by the action of *p*-tolylphenacylamine [*oxime*, m. p. 94°; *picrate*, m. p. 108—

109° (decomp.)] on *iso*butyl iodide in the presence of potassium carbonate, but when the latter is replaced by anhydrous potassium hydroxide, a β-amine, m. p. 67° (colourless *oxime*, m. p. 130—131°), is obtained together with *phenacylidene*-p-*toluidine*, $C_6H_4Me{\cdot}N{:}CH{\cdot}COPh$, decomp. 215°. The nature of the isomerism is revealed by heating the α- and β-amines with acetic acid. The α-amine, in agreement with the structure assigned, is converted by loss of 1 mol. of water into 3(?)-*phenyl*-5-*methyl*-1-*isobutylindole*, m. p. 52°, whilst the β-amine suffers fission yielding acet-*p*-toluidide and is therefore a secondary amine, *phenyl* α-(p-*toluidino*)*iso*amyl *ketone*, $C_6H_4Me{\cdot}NH{\cdot}CHBu^{\beta}{\cdot}COPh$, identical with the synthetic product obtained by the action of *p*-toluidine on *phenyl* α-*bromoisoamyl ketone*, b. p. 151—153°/12 mm. (by the Friedel–Crafts reaction from benzene and α-bromo*iso*hexoyl bromide), together with a *substance*, m. p. 111—112°. Hence the β-isomeride is formed by alkylation of the *p*-tolylphenacylamine at the methylene group instead of the imino-group. Similarly p-*chlorophenyl*iso*butylamine*, b. p. 135—136°/12 mm. (from *p*-chloroaniline and *iso*butyl bromide), condenses with ω-bromoacetophenone in the presence of concentrated potassium carbonate solution to yield p-*chlorophenylphenacyl*iso*butylamine*, m. p. 109—110°, but by the action of *iso*butyl iodide on *p*-chlorophenylphenacylamine in the presence of potassium hydroxide the products are *phenyl* α-p-*chloroanilino*-iso*amyl ketone*, m. p. 80·5°, and a *substance*, decomp. 235—236°. The former suffers fission by heating with acetic acid, yielding acet-*p*-chloroanilide. When *p*-chlorophenylphenacylamine and *iso*butyl iodide are heated with an excess of potassium carbonate the product is *phenacylidene*-p-*chloroaniline*, m. p. 196°. By heating β-chloroethyl alcohol with methylaniline in a sealed tube, *NN'*-diphenylpiperazine is obtained.
J. W. Baker.

Structure of metal ketyls. I. The Schmidlin formula. C. B. Wooster (J. Amer. Chem. Soc., 1929, **51**, 1856—1860).—The formula, $R_2C{:}O{\cdots}M$, for the metallic ketyls, proposed by Schmidlin ("Das Triphenylmethyl," 1914, pp. 186—188) to indicate that all the reactions of these substances are preceded by dissociation into ketone and metal, is shown to be incorrect. Addition of ethyl bromide to monosodiobenzophenone in liquid ammonia gives no ethane (cf. A., 1928, 760), whereas sodium liberates the theoretical quantity of ethane from a mixture of ethyl bromide and benzophenone in this solvent, the benzophenone remaining unchanged. As an alternative to Schlenk's mechanism for the reactions of these derivatives (cf. A., 1911, i, 545; 1913, i, 1205), it is suggested that in presence of a substance capable of reacting with the very active disodio-derivative, the reaction, $R_2CNa{\cdot}ONa + R_2CO \longrightarrow 2R_2CONa$, may be completely reversible.
H. E. F. Notton.

Nitration of phenyl *p*-tolyl ketone and phenyl *m*-xylyl ketone. L. Chardonnens (Helv. Chim. Acta, 1929, **12**, 649—662).—3-Nitro-4-methyldiphenyl ketone is produced by the action of nitric acid (*d* 1·4) at 75—80° on 4-methyldiphenyl ketone. The same compound is obtained synthetically from 3-nitro-*p*-toluoyl chloride and benzene. Reduction by iron and glacial acetic acid gives 3-amino-4-methyldiphenyl ketone, m. p. 107·5° (lit. 109°, 108—110°). Nitration of 4-methyldiphenyl ketone by mixed acid at −10° leads to the 3 : 3'-dinitro-derivative, m. p. 133·5—134° (lit. 135°) (also obtained by nitration of 3'- or 3-nitro-4-methyldiphenyl ketone), from which 3 : 3'-*diamino*-4-*methyldiphenyl ketone*, m. p. 130°, is derived by iron–hydrochloric acid reduction. More prolonged nitration by mixed acids gives 3 : 5 : 3'-trinitro-4-methyldiphenyl ketone, m. p. 171° (lit. 173°), also obtained by similar nitration either of 3'-nitro-4-methyldiphenyl ketone or of the condensation product of 3 : 5-dinitro-*p*-toluoyl chloride with benzene in the presence of aluminium chloride.

3 : 5-Dinitrobenzoyl chloride, toluene, and aluminium chloride afford 3' : 5'-dinitro-4-methyldiphenyl ketone, m. p. 135·5—136° (lit. 134°), which gives by long nitration by mixed acids 3 : 5 : 3' : 5'-*tetranitro*-4-*methyldiphenyl ketone*, m. p. 196—198°.

Nitration of 2 : 4-dimethyldiphenyl ketone by nitric acid, *d* 1·4, at 80° gives 5-*nitro*-2 : 4-*dimethyldiphenyl ketone*, m. p. 62—63° (also synthesised from 5-nitro-2 : 4-dimethylbenzoyl chloride, benzene, and aluminium chloride), accompanied by less 3-*nitro*-2 : 4-*dimethyldiphenyl ketone*, m. p. 79·5—80° (similarly synthesised from the analogous 3-nitrobenzoyl chloride). The corresponding 5- and 3-*amino*-2 : 4-*dimethyldiphenyl ketones* have m. p. 103·5—104° and 84°, respectively.

2 : 4-Dimethyldiphenyl ketone is nitrated by nitric acid, *d* 1·5, at −20° to give 5 : 3'-*dinitro*-2 : 4-*dimethyldiphenyl ketone*, m. p. 144·5°, identical with the product of similar nitration of either 3'- or 5-nitro-2 : 4-dimethyldiphenyl ketone, whilst with mixed acids it yields 3 : 5 : 3'-*trinitro*-2 : 4-*dimethyldiphenyl ketone*, m. p. 139—140°, also formed by nitration of 3'-nitro-2 : 4-dimethyldiphenyl ketone or of 3 : 5-*dinitro*-2 : 4-*dimethyldiphenyl ketone*, m. p. 111—112° (synthesised from 3 : 5-dinitro-2 : 4-dimethylbenzoyl chloride, benzene, and aluminium chloride).

3' : 5'-*Dinitro*-2 : 4-*dimethyldiphenyl ketone*, m. p. 110° (prepared from 3 : 5-dinitrobenzoyl chloride, *m*-xylene, and aluminium chloride), is nitrated by mixed acid at the ordinary temperature to 3 : 5 : 3' : 5-*tetranitro*-2 : 4-*dimethyldiphenyl ketone*, m. p. 187—188°.
R. J. W. Le Fèvre.

Reactivity of positive hydrogen atoms. II. Dibenzyl ketone. W. Dilthey and B. Stallmann (Ber., 1929, **62**, [*B*], 1603—1609; cf. A., 1927, 770).—The second methylene group of dibenzyl ketone is capable of reaction with aldehydes in presence of piperidine, but the normal diethylenic compounds are not in general obtained. The course of the change consists in the primary reaction of the aldehyde and piperidine to form the arylidenedipiperidine, $CHR(NC_5H_{10})_2$, which is converted by the ketone into piperidine and the piperidino-compound of the ethylenic compound $CHR(NC_5H_{10}){\cdot}CHPh{\cdot}CO{\cdot}CH_2Ph$ (existing in two racemic forms by reason of the asymmetric carbon atoms); the adduct is transformed by acids into piperidine and the ethylenic compound. Benzaldehyde and dibenzyl ketone react in the presence of 1·25 mols. of piperidine in alcoholic solution at the ordinary temperature to give the two *forms* of γ-*keto*-α-*piperidino*-αβδ-*triphenyl*-n-*butane*, m. p. 147—148° and 121—122°, respectively; a *picrate* of the mixture, m. p. indef. 132—138°, is described. The variety of m. p. 122° is also obtained from benzylidenedipiperidine and dibenzyl ketone in alcohol. The adducts are transformed by warm acids into benzylidenedibenzyl ketone. Similarly anisaldehyde affords the two *γ-keto-α-piperidino-*βδ*-diphenyl-*α-p*-methoxyphenyl-*n*-butanes*, m. p. 126° and 156°, respectively; a *picrate*, m. p. 147—148°, is described. Attempts to resolve the isomeride of m. p. 126° by bromocamphorsulphonic or tartaric acid were unsuccessful. The adducts are converted by acids into anisylidenedibenzyl ketone, m. p. 101—102°. Piperonal gives a *mixture*, m. p. 135—150°, of the isomeric γ-keto-α-piperidino-βδ-diphenyl-α-3 : 4-methylenedioxyphenyl-*n*-butanes from which piperonylidenedibenzyl ketone, m. p. 122—123°, is derived. The mixture of *γ-keto-α-piperidino-*βδ*-diphenyl-α-4′-dimethylaminophenyl-*n*-butanes*, m. p. 143—155°, is converted into p*-dimethylaminobenzylidenedibenzyl ketone*, m. p. 110°. Dibenzyl ketone gives piperidino-adducts with the three nitrobenzaldehydes or their dipiperidino-derivatives, but the yields are smaller, probably by reason of the greater stability of the arylidenepiperidines. Salicylaldehyde, nitro- or bromo-salicylaldehyde, and hydroxynaphthaldehyde do not afford solid piperidino-intermediates, but give chromones by loss of water involving the second methylene group. Cinnamaldehyde gives the two forms of triphenyl*cyclo*hexanone. *Piperonylidenedipiperidine*, m. p. 69—71°, p*-nitrobenzylidenedipiperidine*, m. p. 86—88°, and m*-nitrobenzylidenedipiperidine*, m. p. 93—95°, are described. *o*-Nitrobenzaldehyde gives an unstable *compound*, m. p. 73—75°.

H. WREN.

Reactivity of positive hydrogen atoms. III. Catalytic reactions. W. DILTHEY (Ber., 1929, **62**, [*B*], 1609—1612; cf. preceding abstract).—Since the reaction between benzaldehyde, dibenzyl ketone, and piperidine proceeds in three distinct stages with isolable intermediate products, the action of the secondary base is not regarded as catalytic. The extent to which other bases can be considered to act catalytically in the Knoevenagel reaction is discussed.

H. WREN.

Steric hindrance in Hoesch reaction. I. ORITO (Sci. Rep. Tôhoku, 1929, **18**, 121—128).—*m*-Chlorobenzonitrile condenses with resorcinol in presence of ethereal hydrogen chloride and zinc chloride yielding *3′-chloro-2 : 4-dihydroxybenzophenone* (52% yield), m. p. 197—197·5°, and with phloroglucinol giving *3′-chloro-2 : 4 : 6-trihydroxybenzophenone* (39%), m. p. 169·5—170° after shrinking at about 110°. Similarly, *p*-chlorobenzonitrile and resorcinol or phloroglucinol afford *4′-chloro-2 : 4-dihydroxybenzophenone* (67%), m. p. 151—152°, or *4′-chloro-2 : 4 : 6-trihydroxybenzophenone* (43%), m. p. 169—169·5° (*trimethyl ether*, m. p. 175°), respectively. Whilst *o*-chlorobenzonitrile and *o*-toluonitrile do not undergo the Hoesch reaction, *o*-chlorophenylacetonitrile condenses with the above phenols yielding 18 and 13% of *2 : 4-dihydroxyphenyl 2-chlorobenzyl ketone*, m. p. 142° (*oxime*, m. p. 225—226°), and *2 : 4 : 6-trihydroxyphenyl 2-chlorobenzyl ketone* ($+H_2O$), m. p. (anhydrous) 172—172·5°, respectively. The steric hindrance effect of an *ortho* substituent is partly surmounted by interposing a methylene group between the benzene nucleus and the cyano-group. The above ketones give the Dimroth reaction (A., 1926, 297) with boroacetic anhydride. H. BURTON.

Application of the Hoesch reaction to nitrobenzonitriles. M. YAMASHITA (Sci. Rep. Tôhoku, 1929, **18**, 129—133).—See A., 1928, 1136.

Unusual instance of "pinacolin" transformation. H. KLEINFELLER and F. ECKERT (Ber., 1929, **62**, [*B*], 1598—1600).—Benzil is converted by dimagnesium acetylenyl bromide into αζ*-diketo-*αβεζ*-tetraphenylhexinene-*βε*-diol*, m. p. 154°, transformed by boiling aqueous sodium hydroxide into benzoic acid and αδ-diphenyl-Δ^{β}-butinene-αδ-diol, m. p. 145° (cf. Dupont, A., 1910, i, 379), and by boiling alcoholic hydrogen chloride into αββζ*-tetraphenyl-*Δ^{γ}*-hexinene-*αεζ*-trione*, m. p. 213° (*trioxime*, m. p. 237°).

H. WREN.

Tautomerism of α-diketones. H. MOUREU (Compt. rend., 1929, **188**, 1413—1416).—By determination of the refractive indices it is shown that, at various temperatures, the same position of equilibrium between the A and B forms of methyl- and phenyl-benzylglyoxals (this vol., 449) is reached starting with either pure form. An equilibrium mixture of the former diketone at 70° contains approximately 70% of the A form, whilst one of the latter at 100° contains more than 70% of the B form.

J. W. BAKER.

Perylene and its derivatives. XXIV. A. PONGRATZ (Monatsh., 1929, **52**, 7—12).—Treatment of perylene-3 : 9-dicarboxylic acid (A., 1927, 1190) with thionyl chloride at 100°, or with phosphorus pentachloride in nitrobenzene at 150°, affords the corresponding *chloride*, dark red, which condenses with benzene in presence of aluminium chloride yielding 3 : 9-dibenzoylperylene, m. p. 291—292°. With toluene a *ditoluoylperylene*, m. p. 309—310°, is obtained: this is not identical with the di-*o*-toluoyl derivative previously described (*loc. cit.*). When 3 : 9-*dinaphthoylperylene*, m. p. 321—322° (from naphthalene and the acid chloride in presence of carbon disulphide and aluminium chloride), is treated with manganese dioxide in sulphuric acid solution a dibenz*iso*violanthrone is probably formed (cf. A., 1928, 177). H. BURTON.

Characteristic colour reaction of quinones and the atomic grouping $CH_2(C\colon E)_2$ (E=multivalent element). W. KESTING (Ber., 1929, **62**, [*B*], 1422—1424; cf. A., 1928, 1015).—If alcoholic solutions of *p*-benzoquinone, α- or β-naphthaquinone are mixed with similar solutions of substances containing the group named above and ammonia or alkali is cautiously added, an intense blue colour is developed. The reaction is shown by malononitrile, ethyl cyanoacetate, malonate, acetoacetate, and benzoylacetate, cyanoacetamide, acetylacetone, and benzoylacetone, but not by fluorene, diphenylmethane, indene, or phloroglucinol, in which the group forms part of a ring. Anthraquinone and its derivatives, phenanthraquinone, and anthradiquinone do not react. The solvent must be able to function as a base or, if indifferent, must be treated with a sufficient amount of basic substance. H. WREN.

Anthraquinol-1 : 5-dicarboxydilactone. R. Scholl and L. Wanka [with H. Hähle and W. Leonhardt] (Ber., 1929, 62, [*B*], 1424—1433; cf. this vol., 567).—Anthraquinol-1 : 5-dicarboxydilactone is most conveniently prepared by the action of sulphuric acid and copper powder at the ordinary temperature on anthraquinone-1 : 5-dicarboxylic acid; short treatment affords the monolactonecarboxylic acid. 1 : 5-Diacetamidoanthraquinone, suspended in acetic acid containing acetic anhydride and sodium acetate, is converted by chlorine at 80° in absence of direct sunlight into 4 : 8-*dichloro*-1 : 5-*diacetamidoanthraquinone*, not molten below 300°, hydrolysed by concentrated sulphuric acid to 4 : 8-*dichloro*-1 : 5-*diaminoanthraquinone*, m. p. 305° (*sulphate*). The diamine is converted through the *diazonium sulphate* and 4 : 8-*dichloro*-1 : 5-*dicyanoanthraquinone*, not molten below 300°, into 4 : 8-*dichloroanthraquinone*-1 : 5-*dicarboxylic acid*, decomp. about 250° (*ethyl* ester, m. p. 154°). The acid is transformed by copper powder and sulphuric acid into 4 : 8-*dichloroanthraquinol*-1 : 5-*dicarboxydilactone*, which behaves towards alcohol and sodium hydroxide in the same manner as the unsubstituted dilactone. The dichloro-acid is transformed by potassium phenoxide at 140—150° into 4 : 8-*diphenoxyanthraquinone*-1 : 5-*dicarboxylic acid*, incipient decomp. about 273° (*potassium* salt; corresponding *chloride*; 4 : 8-*di*-p-*nitrophenoxyanthraquinone*-1 : 5-*dicarboxylic acid*, decomp. 325—326° after darkening); it is reduced by zinc dust and ammonia to 4 : 8-*diphenoxyanthracene*-1 : 5-*dicarboxylic acid*, m. p. 344—345° (*pyridinium* salt; *sulphonic acid*). 4 : 8-*Diphenoxyanthraquinol*-1 : 5-*dicarboxydilactone* is described. 4 : 8-*Di*-p-*tolyloxyanthraquinone*-1 : 5-*dicarboxylic acid* darkens at 280° and blackens at 317°. The 4 : 8-dichloro-acid, thiophenol, and potassium hydroxide in boiling aqueous solution afford 4 : 8-*diphenylthiolanthraquinone*-1 : 5-*dicarboxylic acid*, m. p. about 312° (decomp.), from which 4 : 8-*diphenylthiolanthraquinol*-1 : 5-*dicarboxydilactone* is derived. 4 : 8-*Di*-p-*tolylthiolanthraquinone*-1 : 5-*dicarboxylic acid*, m. p. 308°, decomp. 310° (*potassium* salt), and the corresponding *dilactone* are described. 4 : 8-Dichloroanthraquinone-1 : 5-dicarboxylic acid loses carbon dioxide when heated with aniline, whereas its ethyl ester affords *ethyl* 4 : 8-*dianilinoanthraquinone*-1 : 5-*dicarboxylate*, slowly hydrolysed to 4 : 8-*dianilinoanthraquinone*-1 : 5-*dicarboxylic acid*, m. p. 320° (decomp.) [*potassium* salt], which yields 4 : 8-*dianilinoanthraquinol*-1 : 5-*dicarboxydilactone*, m. p. 348° after softening; *sodium* 4 : 8-*dianilinoanthraquinol*-1 : 5-*dicarboxylate* is described. *Ethyl* 4 : 8-*di*-p-*toluidinoanthraquinone*-1 : 5-*dicarboxylate*, m. p. 248°, the corresponding dicarboxylic *acid*, m. p. 312—313° (decomp.), and 4 : 8-*di*-p-*toluidinoanthraquinol*-1 : 5-*dicarboxydilactone* have been prepared. H. Wren.

Dyes of the anthraquinone series. K. Weinland, Assr. to Grasselli Dyestuff Corp.—See B., 1929, 512.

1 : 2-Phenanthraquinone. L. F. Fieser (J. Amer. Chem. Soc., 1929, 51, 1896—1906).—Reduction with sodium sulphite of the azo-*dye* from *p*-sulphobenzenediazonium chloride and 2-phenanthrol gives 1-*amino*-2-*phenanthrol*, darkening from 210° (*hydrochloride*, decomp. 250°), from which 1-*acetamido*-2-*phenanthrol*, m. p. 295° (all m. p. uncorr.), its *acetate*, m. p. 222°, and 1-*diacetamido*-2-*phenanthryl acetate*, m. p. 125°, are prepared. The last two are converted by distillation at 3 mm. into 2-*methyl*-4 : 5-(1 : 2-*phenanthro*)*oxazole*, m .p. 120°. The hydroxyamine is oxidised by chromic acid to brilliant red 1 : 2-*phenanthraquinone*, m. p. 216° (decomp.), softening at 195°. This is reduced by sodium hyposulphite to 1 : 2-*dihydroxyphenanthrene*, m. p. 178°, the *dimethyl ether*, m. p. 102°, of which is not identical with 2 : 3-dimethoxyphenanthrene (Pschorr, A., 1900, i, 489). 1 : 2 : 4-*Triacetoxyphenanthrene*, m. p. 186°, obtained in poor yield from the quinone, acetic anhydride, and sulphuric acid, is converted by hydrolysis with sodium hydroxide in an atmosphere of nitrogen and aeration of the cold solution into the red *sodium* salt of 2-*hydroxy*-1 : 4-*phenanthraquinone*, m. p. 188° (*methyl ether*, m. p. 172·5°). The *silver* salt of this quinone gives with allyl bromide in benzene 4-*allyloxy*-1 : 2-*phenanthraquinone*, m. p. 128°, and 2-*hydroxy*-3-*allyl*-1 : 4-*phenanthraquinone*, m. p. 157°. 2-Hydroxy-1 : 4-phenanthraquinone is converted by boiling aqueous sodium hydroxide into 1-*acetyl*-2-*naphthylglyoxylic acid*, m. p. 181° (decomp.) (*methyl* ester, m. p. 112°), which gives the same oxidation products in acid and alkaline solutions as does 2-acetyl-1-naphthylglyoxylic acid (this vol., 567). 1 : 2-Phenanthraquinone is converted by sodium hydrogen sulphite into 1 : 2-dihydroxyphenanthrene and *sodium* 1 : 2-*dihydroxyphenanthrene*-4-*sulphonate* (corresponding *potassium* and p-*toluidine*, m. p. 240°, salts), oxidised by chromic and sulphuric acids to *sodium* 1 : 2-*phenanthraquinone*-4-*sulphonate*. With *p*-toluidine hydrochloride in aqueous solution this gives the corresponding p-*toluidine* salt, but with *p*-toluidine itself or sodium hydroxide it undergoes disproportionation, 2 mols. giving 1 : 2-dihydroxyphenanthrene-4-sulphonate (1 mol.) and an unknown oxidation product. The sulphonic radical in the quinone-sulphonate is, thus, attached more firmly than it is in most compounds of this type, since no 4-*p*-toluidinophenanthraquinone is formed. H. E. F. Notton.

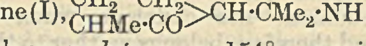
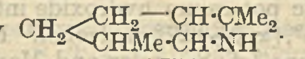
Phenanthraquinones related to alizarin and purpurin. L. F. Fieser (J. Amer. Chem. Soc., 1929, 51, 1935—1942).—1 : 2-Phenanthraquinone (preceding abstract), zinc dust, and sodium acetate in boiling acetic anhydride give 1 : 2-*diacetoxyphenanthrene*, m. p. 146—147°, which is oxidised by chromic and acetic acids to 1 : 2-*diacetoxy*-9 : 10-*phenanthraquinone*, m. p. 257° (corr.), hydrolysed by alcoholic sodium hydroxide to dark red 1 : 2-*dihydroxy*-9 : 10-*phenanthraquinone* (green *chromium* and *aluminium* lakes). 1 : 2 : 4-Triacetoxyphenanthrene is oxidised by chromic and acetic acids at 40° to 1 : 2 : 4-*triacetoxy*-9 : 10-*phenanthraquinone*, m. p. 227—228° (decomp.), which is hydrolysed in an inert atmosphere to the green *sodium* salt of dark red 1 : 2 : 4-*trihydroxy*-9 : 10-*phenanthraquinone* (also +EtOH). Reductive acetylation of 3-hydroxy-1 : 4-phenanthraquinone (this vol., 567) gives 1 : 3 : 4 *triacetoxyphenanthrene*, m. p. 138°, from which dark red 1 : 3 : 4-*triacetoxy*-9 : 10-*phenanthraquinone*, decomp. 240°, softening from 220°, and 1 : 3 : 4-*tri*-

hydroxy-9 : 10-*phenanthraquinone* are prepared. The colour reactions and dyeing properties of the new hydroxyphenanthraquinones are compared with those of related anthraquinone and phenanthraquinone derivatives. They do not assume tautomeric forms, since they are reconvertible into the original acetates. 4-Amino-3-phenanthrol and acetic anhydride in pyridine give 4-*acetamido*-3-*phenanthryl acetate*, m. p. 211°, which gives when distilled at 3 mm. 2-*methyl*-4 : 5-(4 : 3-*phenanthro*)*oxazole*, m. p. 155°, oxidised by chromic acid to the corresponding 9 : 10-phenanthraquinone *derivative*, m. p. 282°. 4-Diacetamido-3-phenanthryl acetate (Werner, A., 1902, i, 437) is oxidised to the 9 : 10-*quinone*, m. p. 207°, hydrolysed by sodium hydroxide in aqueous alcohol in absence of air to 4-*diacetamido*-3-*hydroxy*-9 : 10-*phenanthraquinone*, decomp. 255—260°. Further hydrolysis is accompanied by complete decomposition and the desired 4-amino-3-hydroxyphenanthraquinone is not obtained. H. E. F. Notton.

Perylene and its derivatives. XXV. A. Zinke and W. Hirsch [with H. Kolmayr] (Monatsh., 1929, 52, 13—22).—Treatment of 3 : 4 : 9 : 10-tetrachloroperylene (Zinke, Pongratz, and Funke, A., 1925, i, 384) with concentrated sulphuric acid at 150° in a current of carbon dioxide yields perylene-3 : 4 : 9 : 10-diquinone (I) (this vol., 568). Similar treatment of 3 : 9-dichloro-4 : 10-diacetyl- or 3 : 9-dichloro-4 : 10-dibenzoyl-perylene at 120—130° affords perylene-3 : 9-quinone (II), the acyl group being eliminated as the corresponding acid. Reduction of II with alkaline sodium hyposulphite and subsequent treatment with the appropriate aroyl chloride gives the dibenzoate, m. p. 312—314°, and di-*p*-bromobenzoate, m. p. 359—360°, of 3 : 9-dihydroxyperylene (cf. A., 1926, 71). 3 : 9-Dichloroperylene is oxidised by sulphuric acid at 140—150° to II, in turn partly oxidised at 180° to I. The oxidation product of hexachloroperylene could not be obtained crystalline. The compound $(C_{20}H_{10}O_2)_2,H_2O$, previously described (A., 1926, 71), should be deleted from the literature, as it is essentially II. H. Burton.

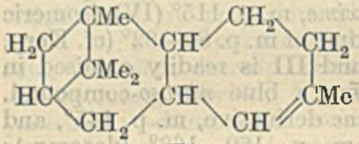
Bixin. I. J. Rinkes (Rec. trav. chim., 1929, 48, 603—606).—The degradation product, $C_8H_{10}O_3$, of methylbixin, considered to be methyl 1-formyl-2- or -3-methyl-1 : 3-pentadienecarboxylate, by oxidation with silver oxide gives methyl hydrogen β-methylmuconate, m. p. 121°, which depresses the m. p. of methyl hydrogen *cis–cis*-β-methyl muconate (m. p. 129°) of Pauly and Will (A., 1918, i, 525), who give m. p. 125°. Subsequent hydrolysis of the ester, m. p. 121°, with 10% alkali affords *trans*-β-methylmuconic acid, m. p. 229°, also obtained by heating *cis–cis*-methylmuconic acid with concentrated sodium hydroxide (cf. *loc. cit.*).

The following attempt to synthesise methylsuccindialdehyde was unsuccessful : the semilactone of β-methylmuconic acid was converted into β-methylmucondiamide, m. p. 218°, by the method of Pauly and Will (*loc. cit.*); treatment of the latter with sodium hypochlorite furnished *isoprenediurethane*, m. p. 160—161°, which by treatment with 5% sulphuric acid yielded, not the foregoing aldehyde, but *methyl* 2-*methylpyrrole*-N-*carboxylate*, b. p. 80°/20 mm., converted by hot 10% potassium hydroxide and subsequent acidification into 2-methylpyrrole, b. p. 142—150°. C. W. Shoppee.

Camphorphorone. I. Action of hydroxylamine. G. Sanna (Gazzetta, 1929, 59, 232—243).—Accounts of the action of hydroxylamine on camphorphorone are discordant (cf. Koenigs and Eppens, A., 1892, 626; 1893, i, 361; Kerp and Müller, A., 1898, i, 265; Harries and Maftus, A., 1899, i, 629; Wallach, A., 1904, i, 752). In agreement with Harries, the action of hydroxylamine hydrochloride and sodium hydrogen carbonate in a boiling mixture of ether and alcohol is found to give dihydrocamphorphoronylhydroxylamine(I),  $\begin{array}{l}CH_2-CH_2\\ CHMe\cdot CO\end{array}>CH\cdot CMe_2\cdot NH\cdot OH$, m. p. 120°, of which an *oxalate*, m. p. 154°, a *semicarbazone*, m. p. 190°, and, by the action of concentrated nitric acid, a *nitro*-derivative, m. p. 50°, are prepared. When the above substances act, however, in boiling aqueous alcohol, a true *camphorphoroneoxime* (II), m. p. 95°, is obtained. Further, when the ketone is heated in methyl alcohol with free hydroxylamine and sodium methoxide, the products are *dihydrocamphorphoronehydroxylamineoxime*, (III), m. p. 160°, and a *camphorphoroneoxime*, m. p. 115° (IV), isomeric with II and with the oxime of m. p. 80—82° (cf. Kerp, *loc. cit.*). The compound III is readily oxidised in alcoholic solution, giving a blue *nitroso*-compound. It furnishes a *benzylidene* derivative, m. p. 145°, and a *benzoyl* derivative, m. p. 160—168° (decomp.); when it is kept in ethereal solution over sulphuric acid, it is converted into yet another *camphorphoroneoxime*, m. p. 40° (V.) When III is reduced by sodium and alcohol, it gives the diamino-derivative, 2-*amino*-3-α-*amino*iso*propyl*-2-*methyl*cyclo*pentane*, of which the *hydrochloride* when distilled loses ammonia to form a *substance*, probably  $CH_2<\begin{array}{l}CH_2-CH\cdot CMe_2\\ CHMe\cdot CH\cdot NH\end{array}$. It was hoped that suitable treatment of III might lead to an *iso*camphorphorone, but the action of acids gave a mixture of products, including 6-*methyl*-3-iso*propylidene*-2-*piperidone*. The structures of the camphorphoroneoximes are discussed. E. W. Wignall.

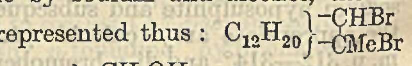
Mono- and sesqui-terpenes. X. Active caryophyllene. E. Deussen and P. Hacker (J. pr. Chem., 1929, [ii], 122, 261—283).—Distillation in steam of the crude ozonide obtained by ozonolysis of γ-caryophyllene in chloroform solution gave (1) in the distillate : formic acid and an *oil* (*semicarbazone*, m. p. 207°), separable by fractionation into two constituents of b. p. 85—90°/11 mm. (*semicarbazone*, m. p. 170°) and 140—145°/11 mm. (*semicarbazone*, m. p. 210°); and (2) in the non-volatile residue : a yellow *oil* [*semicarbazone*, m. p. 120°; *thiosemicarbazone*, m. p. 165° (decomp.)]. Oxidation of the last compound by 27% nitric acid at 90° afforded succinic acid and caryophyllenic acid, α^{13} +5·40° (10% in ethyl acetate) (silver and potassium salts), which was converted into *iso*valeric and acetic acids by alkali fusion and into *dibromocaryophyllenic acid*, $C_9H_{12}O_4Br$, by bromination with phosphorus pentachloride and bromine in a sealed tube. R. J. W. Le Fèvre.

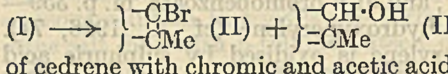
Caryophyllene series. II. Clovene and *iso*clovene. G. G. Henderson, R. O. O. McCrone, and J. M. Robertson (J.C.S., 1929, 1368—1372; cf. A., 1926, 298).—Dehydration of caryophyllene alcohol with anhydrous oxalic acid yields clovene, b. p. 111—113°/10 mm., d_4^{20} 0·924, n_D^{20} 1·4980, identical with that obtained by the use of phosphoric oxide. The liquid hydrocarbon, b. p. 110—114°/9 mm., d_4^{10} 0·926, n_D^{10} 1·5010, obtained as a by-product in the hydration of caryophyllene by Wallach and Walker's method (A., 1893, i, 101), and also the sesquiterpene, b. p. 110—114°/10 mm., d_4^{17} 0·933, n_D^{17} 1·5020, obtained by heating caryophyllene dihydrochloride with quinoline, are probably identical with clovene. Clovene is attacked by potassium permanganate, but no definite oxidation products have been isolated; it gives neither eudalene nor cadalene when heated with sulphur and therefore belongs neither to the eudesmene nor to the cadinene group of sesquiterpenes. By dehydrating caryophyllene alcohol, prepared from caryophyllene and sulphuric acid monohydrate in the presence of dry ether at 0°, by a modification of Wallach and Walker's method (*loc. cit.*), clovene and iso*clovene*, $C_{15}H_{24}$, b. p. 130—131°/12 mm., d_4^{19} 0·943, n_D^{19} 1·5039, $[\alpha]_D^{14}$ −53·6° in alcohol, were obtained. The latter forms a *monohydrochloride*, m. p. 87°, a *monohydrobromide*, m. p. 75° (from which the hydrocarbon may be regenerated), and an unstable *dibromide*, and is more unstable than clovene. *iso*Clovene is completely decomposed by heating to its b. p. with phosphoric oxide. When a solution of *iso*clovene hydrochloride in glacial acetic acid is treated with silver acetate, the *acetate* of iso*clovene alcohol*, m. p. 25—26°, is obtained, which is converted by methyl-alcoholic potassium hydroxide into iso*clovene alcohol*, m. p. 98°, $[\alpha]_D^{20}$ + 227° in alcohol. Formula I is assigned to clovene (cf. Semmler and Mayer, A., 1911, i, 73; Deussen, A., 1926, 1252). A. I. Vogel.


(I.)

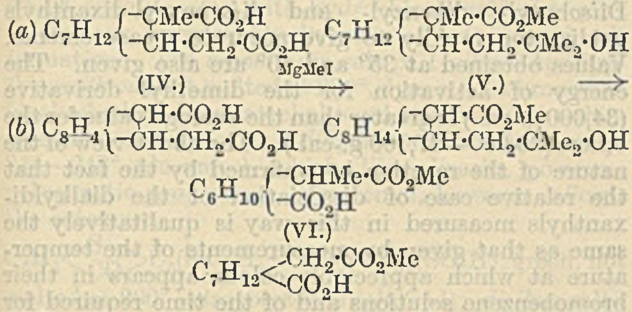
Higher terpene compounds. XXXVIII. Amyrins and lupeol. L. Ruzicka, H. W. Huyser, M. Pfeiffer, and C. F. Seidel (Annalen, 1929, **471**, 21—39).—The conflicting evidence concerning the saturated or unsaturated character of α- and β-amyrin is discussed. Catalytic reduction of the amyrins fails even with hydrogen at 280°/80 atm. with platinum-black or with a platinum oxide catalyst, the original substance being recovered unchanged. With ozone in carbon tetrachloride solution either α- or β-amyrin takes up 5 mols. of ozone to yield an *ozonide*, decomp. about 100°, which was unchanged in composition after keeping for 4 years. On the other hand, with perbenzoic acid it takes up only 0·5 atom of oxygen, behaving like the saturated tetrahydroabietic acid with which it was compared. The molecular refractivity of α-, b. p. 235°/0·1 mm., d_4^{39} 0·9857, n_D 1·5420, and β-, b. p. 235°/0·1 mm., d_4^{38} 0·9807, n_D^{38} 1·5409, -amyrilene, obtained by the action of phosphorus pentachloride and alkali on the parent alcohols, indicates the presence of three double linkings, thus pointing to the presence of two double linkings in the original amyrins. Moreover, the latter readily give a yellow colour with tetranitromethane, a reaction which is never known to occur with a saturated compound, although some unsaturated compounds fail to give this test. The isomeric alcohol lupeol also gives the yellow colour with tetranitromethane, but is readily reduced with hydrogen on a platinum oxide catalyst in acetic acid at 60—70° to *dihydrolupeol*, m. p. 201—202°, $[\alpha]_D$ −17·5°, which fails to give the colour test. Thermal decomposition of the mixed amyrins at 440—460° in a current of carbon dioxide yields a liquid distillate from which a *hydrocarbon*, $C_{15}H_{26}$(?), b. p. 115—125°/15 mm., d_4^{15} 0·924, n_D^{15} 1·500, is isolated. This by catalytic dehydrogenation with selenium yields the same *trimethylnaphthalene*, b. p. 147—148°/16 mm., d_4^{15} 1·008, n_D^{15} 1·6093 (*picrate*, m. p. 127—128°; *styphnate*, m. p. 153—154°), as is obtained by direct dehydrogenation of amyrin itself, and which is possibly identical with the product obtained by Brunner (this vol., 71). When oxidised with potassium ferricyanide this naphthalene derivative gives a *naphthalenetricarboxylic acid*, which is not readily purified, but affords (silver salt method) crystalline *methyl*, m. p. 153—154°, and *ethyl*, m. p. 80—81°, esters. J. W. Baker.

Higher terpene compounds. XXXIX. Cedrene. L. Ruzicka and J. A. van Melsen (Annalen, 1929, **471**, 40—72).—Cedrene (from cedarwood oil) yields a dibromide (I) which is converted by boiling potassium hydroxide partly into the original cedrene and partly into a mixture, b. p. 155—160°/12 mm., of bromocedrene (II) and hydroxy*iso*cedrene (III). The bromocedrene is stable to alkalis, but is reduced to cedrene by sodium and alcohol, the relationships being represented thus:


$C_{12}H_{20}\left\}\begin{array}{l}-\mathrm{CHBr}\\-\mathrm{CMeBr}\end{array}\right.$


(I) $\longrightarrow \left\}\begin{array}{l}-\mathrm{CBr}\\-\mathrm{CMe}\end{array}\right.$ (II) + $\left\}\begin{array}{l}-\mathrm{CH{\cdot}OH}\\=\mathrm{CMe}\end{array}\right.$ (III).

Oxidation of cedrene with chromic and acetic acids yields cedrone (40%) and cedreneketo-acid (10%), which is further oxidised to cedrenedicarboxylic acid, both acids being identical with those obtained by ozonolysis of cedrene (Semmler and Spornitz, A., 1912, i, 573). Ozonolysis of cedrone or oxidation of the ozonide with chromic and acetic acids yields *norcedreneketo-acid*, b. p. 174—175°/0·4 mm., m. p. 113—114° (*semicarbazone*, m. p. 242—244°), oxidised by sodium hypobromite to *norcedrenedicarboxylic acid* (IV*a* or *b*), m. p. 209°. Whereas in cedrenedicarboxylic acid both carboxyl groups are similar and both react in the following series of reactions, in norcedrenedicarboxylic acid they are differently bound in the molecule, one being unreactive. Thus esterification of IV with methyl alcohol and sulphuric acid yields only a *methyl hydrogen* ester, m. p. 97°, and only one ester group in the *dimethyl* ester, b. p. 157°/0·4 mm. (prepared from the *silver* salt), is hydrolysed by 0·1*N*-alcoholic potassium hydroxide. Bromination of IV with phosphorus tribromide and bromine yields only a *mono-bromo-acid*, m. p. 213—214°, which is converted by 10% sodium hydroxide or dilute hydrochloric acid into an unsaturated *acid*, $C_{12}H_{18}O_2$ (IX or X), m. p. 90—91°, d_4^{104} 0·9781, n_D^{104} 1·4637 (crystallographic data by Nannenga) (*ethyl* ester, b. p. 90°/0·5 mm.). Magnesium methyl bromide reacts with only one ester group in methyl norcedrenedicarboxylate to yield an *ester carbinol* (V*a* or *b*), $C_{16}H_{28}O_3$, b. p. 135°/0·4 mm., in which the ester group is resistant to hydrolysis; this is converted by oxidation with chromic and acetic acids into a *hydrogen* ester (VI*a* or *b*), $C_{11}H_{18}O_3$ (not pure, 11·3% OMe instead of 14·5%), in which the ester group is now readily hydrolysed, and which is converted through its *silver* salt into the *dimethyl* ester, b. p. 165—170°/12 mm., d_4^{13} 1·107, n_D^{13} 1·4750, of an *acid*, $C_{10}H_{16}O_4$, which could not be obtained crystalline and for which the name cedrocamphoric acid is suggested. On the basis of these results the ring containing the double linking in cedrene cannot be higher than six-membered, and these reactions may be represented on the basis of two alternative partial formulæ for norcedrenedicarboxylic acid thus :—



$$(a)\ C_7H_{12}\begin{cases}-CMe\cdot CO_2H\\-CH\cdot CH_2\cdot CO_2H\end{cases}\ \ C_7H_{12}\begin{cases}-CMe\cdot CO_2Me\\-CH\cdot CH_2\cdot CMe_2\cdot OH\end{cases}$$

$$\text{(IV.)}\ \xrightarrow{MgMeI}\ \text{(V.)}\ \longrightarrow$$

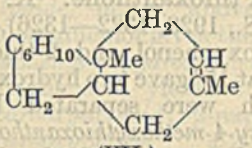
$$(b)\ C_8H_4\begin{cases}-CH\cdot CO_2H\\-CH\cdot CH_2\cdot CO_2H\end{cases}\ \ C_8H_{14}\begin{cases}-CH\cdot CO_2Me\\-CH\cdot CH_2\cdot CMe_2\cdot OH\end{cases}$$

$$C_6H_{10}\begin{cases}-CHMe\cdot CO_2Me\\-CO_2H\end{cases}$$

(VI.)

$$C_7H_{12}{<}\begin{matrix}CH_2\cdot CO_2Me\\CO_2H\end{matrix}$$

Cedrene must be represented by either VII or VIII, neither Semmler's (A., 1915, i, 427) nor Deussen's (A., 1928, 70) formulæ being admissible, the group C_6H_{10} or C_7H_{12} containing the third ring of cedrene which,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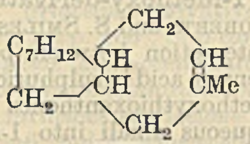
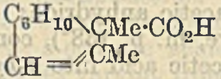
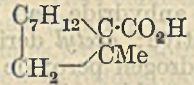
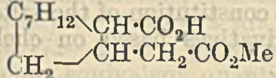

(VIII.)

(IX.)



(X.)

if the second ring is six-membered, can only be a three- or four-membered ring. Ozonolysis of the unsaturated acid IX or X yields a monocarboxylic *acid* $C_{12}H_{18}O_5$, m. p. 166—167°, a *substance*, m. p. 187—189°, and liquid products, oxidation of which has led to no definite results. Catalytic reduction of IX or X (the dimethyl ester of which yields a *diphenylcarbinol*, m. p. 82—83°, with magnesium phenyl bromide) in presence of platinum oxide gives a *dihydro*-acid, b. p. 121°/0·5 mm., m. p. 61—62° (the ester of which does not react with magnesium phenyl bromide), the *ethylamide*, b. p. 122—124°/high vacuum, of which is converted by phosphorus pentachloride into a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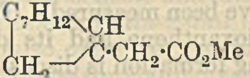
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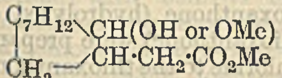
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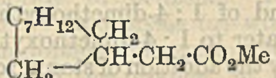
(XIV.)

chlorine-free *nitrile*. Electrolysis of methyl hydrogen norcedrenedicarboxylate (XI) gives a mixture of an unsaturated *ester* (XII), $C_{13}H_{20}O_2$, and the corresponding saturated hydroxy- and methoxy-esters (XIII), from which after heating with alcoholic potassium hydroxide, hydrolysis with hydrogen iodide, and ozonolysis of the product to destroy the unsaturated acid, is obtained a saturated *acid* (XIV) $C_{12}H_{20}O_2$, m. p. 61—62°, which, however, depresses the m. p. of the isomeric dihydro-acid (above). J. W. BAKER.

Photo-bromination of coumarin. D. M. WILLIAMS.—See this vol., 895.

Rotenone, the active principle of Derris root. III. Molecular formula of rotenone. S. TAKEI (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 369—371; see A., 1928, 765).—Rotenone and *iso*rotenone are considered to be *cis-trans* ethylenic isomerides.
E. W. WIGNALL.

Rotenone, the active constituent of Derris root. IV. Rotenic acid. S. TAKEI and S. MIYAJIMA (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 510—518; see preceding abstract).—Consideration of the reactions of rotenic acid suggest two possible formulæ (I or II).

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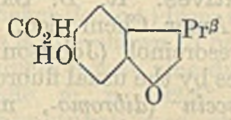
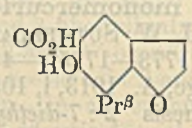
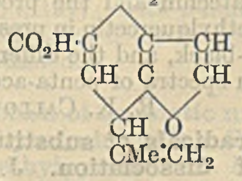
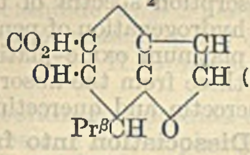



(II.)

By the action of magnesium *iso*propyl bromide on 5-methoxycoumaran-2-one, 5-*methoxy*-2-*hydroxy*iso-*propylcoumaran*, m. p. 70°, was obtained, and from this 5-*methoxy*-2-iso*propylcoumarone*, which formed a resin, m. p. about 150°. This product should be identical with rotenol monomethyl ether (A., 1928, 765) if I were the formula for rotenic acid. As the two substances differ widely, II is more probably the formula. B. W. ANDERSON.

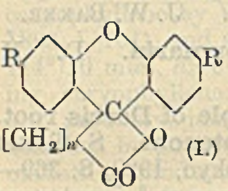
Rotenone, the active constituent of Derris root. V. Tubaic acid. S. TAKEI and M. KOIDA (Bull. Inst. Phys. Chem. Res. Tokyo, 1929, 8, 519—524; cf. preceding abstract, also A., 1928, 1017).—Tubaic acid and dihydrotubaic acid, unlike rotenic acid, are optically active, having $[\alpha]_D^{18}$ −76·0° and $[\alpha]_D^{20}$ −82·2°, respectively. Both acids are easily converted into their respective phenols, *tubanol* and *dihydrotubanol*. *Tubanol methyl ether* is oxidised by ozone to a sweet-smelling *oil* which reduces Fehling's solution, gives the iodoform reaction, and forms a p-*nitrophenylhydrazone*, m. p. 156°. The oil therefore contains the group ·COMe; on further oxidation with iodine and potassium hydroxide it forms a methoxy-carboxylic *acid*, $C_{10}H_9O_4I$, m. p. 140°. The ethylene linking in tubaic acid is thus probably in a 2-allyl group, and this acid and dihydrotubaic acid may be represented by I and II, respectively.

(I.)



(II.)

Fusion with alkali converts tubaic acid into its more stable isomeride, rotenic acid. B. W. ANDERSON.

Colour on the basis of molecular strain. VII. Effect of polymembered ring formation. A. N. Dey and S. Dutt (J. Indian Chem. Soc., 1929, **6**, 289—293).—Condensation of adipic acid with resorcinol in presence of sulphuric acid at 170—180° affords the *fluorescein* (I) (R=OH, n=4), m. p. above 286°, whilst with m-diethylaminophenol at 120—130°, the *rhodamine* (I) (R=NEt$_2$, n=4), sinters at 168°, is obtained. The corresponding *fluoresceins* from pimelic, m. p. 164°, suberic, m. p. 140°, azelaic, m. p. 172°, and sebacic acids, sinters at 166°, and the *rhodamines* from suberic, m. p. 147°, azelaic, m. p. 126°, and sebacic acids, m. p. 142°, are obtained similarly. The intensity of the colour of these dyes in solution is inversely proportional to the stability of the ring systems of the anhydrides of the acids used (cf. Dutt and Thorpe, A., 1925, i, 141; Dutt, A., 1926, 830; 1927, 1006). H. Burton.



(I.)

Diethyl- and dihexyl-fluoresceins; dibromo- and monomercuri-derivatives. R. B. Sandin and J. W. Sutherland (J. Amer. Chem. Soc., 1929, **51**, 1773—1775).—4-Ethylresorcinol (Johnson and Hodge, A., 1913, i, 1055) gives by the usual fluorescein synthesis 2 : 7-*diethylfluorescein* (*dibromo*-, m. p. above 300°, and red *anhydromercuri*-derivatives), and 4-hexylresorcinol (Dohme and others, A., 1926, 838) gives 2 : 7-*dihexylfluorescein* (*dibromo*-, m. p. 180—181°, and *anhydromercuri*-derivatives). The new fluoresceins are precipitated from cold solutions of their sodium salts by acetic acid in a yellow lactonoid form and from boiling solutions by hydrochloric acid in a dark brown quinonoid form (cf. Orndorff and Hemmer, A., 1927, 671). H. E. F. Notton.

Tea catechin from green tea. M. Tsujimura (Sci. Papers Inst. Phys. Chem. Res. Tokyo, 1929, **10**, 252—261).—A new catechin has been isolated in a yield of 0·14% from green tea by extraction with ethyl acetate and fractionation of the extract. *Tea catechin* has m. p. 237—238°, $[\alpha]_D^{25}$ $-69°$ in alcohol, and yields a *penta-acetyl* derivative, m. p. 151—152°, and a *tetramethyl* derivative, m. p. 153—154°. Colour reactions are described. It differs from l-*epi*catechin (Freudenberg and Purrmann, A., 1923, i, 697; 1924, i, 868) only in being anhydrous. Phloroglucinol is obtained by decomposition with 50% potassium hydroxide solution. The formation of phloretic acid, which is obtained from phloretin under these conditions, is not observed. Controlled oxidation of tetramethyl tea catechin by permanganate yields veratric acid. Further support is afforded to the catechin formula of Perkin and Yoshitake (J.C.S., 1902, **81**, 1160) by the close similarity between the absorption spectra of tea catechin and the product of hydrogenation of pentamethylquercetin in presence of platinum oxide–platinum-black, and the difference of these from the absorption spectra of penta-acetylquercetin and quercetin. R. K. Callow.

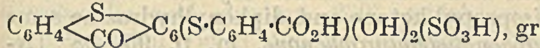
Dissociation into free radicals of substituted dixanthyls. V. Rate of dissociation. J. B. Conant and M. W. Evans (J. Amer. Chem. Soc., 1929, **51**, 1925—1935).—The autoxidation of di-n-butyldixanthyl has been followed in bromobenzene solution. The first 0·6 mol. of oxygen absorbed is apparently used entirely in peroxide formation, but afterwards side reactions occur. In the first stage the reaction is unimolecular, with a high temperature coefficient, and its rate is practically uninfluenced by the substitution of air for oxygen, or by the addition of the usual autoxidative catalysts and antioxygens. This indicates that the rate actually being measured is that of the dissociation of the dixanthyl into free radicals which are then rapidly oxidised. The values of $k \times 10^3$ for some dialkyldixanthyls (cf. A., 1925, i, 955; 1926, 158, 842; 1927, 975) are, at 25°: dimethyl-, 1·79; diethyl-, 1·99; di-n-propyl-, 11·9; di-n-butyl-, 12·6; di*iso*amyl-, 10·0; di-n-amyl-, 6·95. Di*iso*butyl-, dibenzyl-, and di*iso*propyl-dixanthyls oxidise too rapidly to give accurate measurements. Values obtained at 35° and 40° are also given. The energy of activation for the dimethyl derivative (34,000 g.-cal.) is greater than the average value for the others (26,000—27,100 g.-cal.). The above view of the nature of the reaction is confirmed by the fact that the relative ease of dissociation of the dialkyldixanthyls measured in this way is qualitatively the same as that given by measurements of the temperature at which appreciable colour appears in their bromobenzene solutions and of the time required for them to produce a visible amount of Prussian-blue in an aqueous solution of potassium ferricyanide and ferric chloride. H. E. F. Notton.

1-Methoxy-derivatives of thioxanthone. K. C. Roberts and S. Smiles (J.C.S., 1929, 1322—1326).—Interaction between p-methoxyphenol and 2-thiolbenzoic acid in sulphuric acid at 15° gave two hydroxymethoxythioxanthones which were separated by aqueous alkali into 1-*hydroxy*-4-*methoxythioxanthone* (insoluble), m. p. 182° (*diacetoborate*, m. p. 205°, with acetic anhydride and boroacetic anhydride; *sodium* derivative; *acetyl* derivative, m. p. 138°), converted by hydrogen peroxide in acetic acid into 1-*hydroxy*-4-*methoxythioxanthone dioxide*, m. p. 184° (also produced by alkylation of 1 : 4-dihydroxyxanthone), and 4-*hydroxy*-1-*methoxythioxanthone* (soluble), m. p. 270° (decomp.) (*dihydrochloride*; *perchlorate*; *acetyl* derivative only, m. p. 133°, with boroacetic anhydride and acetic anhydride). Aqueous-alkaline methylation of the latter gave 1 : 4-dimethoxythioxanthone, but no sulphone was obtained with hydrogen peroxide and acetic acid. The relative stabilities of the salts of 1-hydroxy-4-methoxy- and 4-hydroxy-1-methoxythioxanthones were measured under the conditions previously described (this vol., 824). The absorption spectra of solutions of the thioxanthones in concentrated hydrochloric acid and in acetic anhydride have been measured. The constitution of the salts of thioxanthone and its derivatives based on chelate ring formation is discussed.

The *chlorostannates* of 2 : 3-dimethoxythioxanthone and of 1 : 4-dimethoxythioxanthone (hydrolysed by water to 1 : 4-dimethoxythioxanthone) were prepared by the addition of stannic chloride to the thioxanthones in benzene solution. A. I. Vogel.

Condensation of di-o-thiobenzoic acid with aromatic hydroxy-compounds. R. N. Sen and

S. C. SEN-GUPTA (J. Indian Chem. Soc., 1929, 6, 267—277).—Treatment of di-*o*-thiobenzoic acid with phenols in presence of sulphuric acid at 100° affords, in the majority of cases studied, hydroxythioxanthones (cf. Smiles, J.C.S., 1910, 97, 1290; 1911, 99, 1533). Thus *o*-, *m*-, and *p*-cresols give 2-*hydroxy*-3-*methylthioxanthone*, m. p. 210—212° (*benzoyl* derivative, m. p. 129—130°), 2-*hydroxy*-4-*methylthioxanthone*, m. p. 190° (decomp.) after shrinking at 170°, and 4-*hydroxy*-1-*methylthioxanthone*, m. p. 234° (decomp.; *sodium* salt; *benzoyl* derivative, m. p. 176—177°), respectively. The *ammonium* salts of these thioxanthones dye wool greenish-yellow shades from an acid bath. Reduction of these ketones with zinc dust and sodium hydroxide solution affords colourless solutions of xanthydrols which when treated with hydrochloric acid give pink colorations, presumably because of *o*-quinonoid salt formation. The *ammonium* salt of 1-*nitro*-4-*hydroxythioxanthone*, not melted at 280°, dyes wool a brownish-black shade. Pyrocatechol condenses with di-*o*-thiobenzoic acid to give 1 : 2-*dihydroxythioxanthone*, m. p. 245—248° (decomp.), which, like alizarin, possesses polygenetic properties. Resorcinol, however, affords the *substance*,

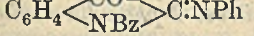


$$C_6H_4{<}{}^{S-}_{CO}{>}C_6(S{\cdot}C_6H_4{\cdot}CO_2H)(OH)_2(SO_3H)$$

, green, not melted at 280° [*tetrapotassium* salt (red); *disilver* salt], whilst resorcinol dimethyl ether yields o-*carboxyphenyl* 1-2 : 4-*dimethoxythioxanthonyl sulphide*, not melted at 280° (*potassium* salt). Pyrogallol furnishes o-*carboxyphenyl* 1-2 : 3 : 4-*trihydroxythioxanthonyl sulphide*, m. p. above 280° (*triacetyl* derivative). Phloroglucinol gives the *lactone*, m. p. 166°, of o-*carboxyphenyl trihydroxyphenyl sulphide* (*ammonium* salt); salicylic acid yields a *sulpho*-2-*hydroxythioxanthone*-3-*carboxylic acid*; β-naphthol furnishes the *lactone* of o-*carboxyphenyl* α-2-*hydroxy*-6 : 8-*disulphonaphthyl sulphide* (*tetrapotassium* salt). The condensation *products* from di-*o*-thiobenzoic acid (1 mol.) and 1:2:3- and 1 : 3 : 5-cresotic acids (2 mols.) dye mordanted wools shades varying from yellow to reddish-brown.

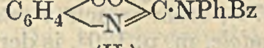
H. BURTON.

Isatin anils. I. Isomerism of isatin-2-anil. R. K. CALLOW and E. HOPE (J.C.S., 1929, 1191—1199).—The existence of two tautomeric forms of isatin-2-anil (Pummerer, A., 1911, i, 231), recently disputed by Rupe and Apotheker (A., 1927, 61), has been confirmed and two benzoyl derivatives, I and II, isolated. When isatin-2-anil, m. p. 126° (decomp.),



$$C_6H_4{<}{}^{CO-}_{NBz}{>}C{:}NPh$$

(I.)



$$C_6H_4{<}{}^{CO}_{-N}{\geqslant}C{\cdot}NPhBz$$

(II.)

best prepared from hydrocyanocarbodiphenylimide and aluminium chloride, is heated with benzoic anhydride (2 mols.) at 100° for 2 hrs. N-*benzoylisatin*-2-*anil* (I), m. p. 172—173°, is produced (also obtained, together with an equivalent quantity of isatin-2-anil hydrochloride, with benzoyl chloride in benzene). Its constitution was established by hydrolysis (*a*) with hydrochloric acid to *o*-benzamidophenylglyoxylic acid, m. p. 192—193·5°, identical with the product, m. p. 196—197° (decomp.; lit. 188°), obtained by warming *N*-benzoylisatin with dilute sodium hydroxide followed by treatment with hydrochloric acid, (*b*) with alkali to aniline, and (*c*) with boiling 50% alcohol and a little hydrochloric acid to *o*-*benzamidophenylglyoxylanilide*, m. p. 183—184°, identical with the compound obtained from *o*-benzamidophenylglyoxylic acid, thionyl chloride, and aniline. The *aniline* salt, m. p. 120—121° (decomp.), from *o*-benzamidophenylglyoxylic acid and aniline in ether, is converted into the acid by phosphorus pentachloride in benzene: *o*-benzamidobenzaldehyde, m. p. 73—74°, is obtained on boiling *o*-benzamidophenylglyoxylic acid with aniline and a little iodine. *N*-Benzoylisatin, m. p. 213—214°, best prepared by heating isatin with benzoic anhydride for 1 hr. at 150—160°, when heated with 50% alcohol and a little hydrochloric acid yielded *o*-benzamidophenylglyoxylic acid and its *ethyl* ester, m. p. 80°. Heating of I with aniline and a little iodine at 100° afforded o-*benzamidophenylglyoxylanilideanil*, m. p. 204—205° (decomp.). Isatin-2-anil reacts with benzoyl chloride in dry pyridine to give *isatin*-2-*benzanilide* (II), m. p. 131°, the constitution of which follows from the production of isatin and benzanilide on boiling with water. The "isatin-β-phenylhydroxylamine" obtained by Rupe and Apotheker (*loc. cit.*) from isatin and β-phenylhydroxylamine is now shown to be isatin-3-anil-*N'*-oxide, since on reduction with zinc dust and acetic acid 3-anilino-oxindole, m. p. 192·5° (decomp., in an evacuated capillary tube), was obtained, identical with the compound obtained by similar reduction of isatin-3-anil.

A. I. VOGEL.

Heterocyclic compounds. IV. Interaction of ethyl *cyclo*hexanone-2-carboxylate with arylamines. I. Synthesis of tetrahydrophenanthridones. H. K. SEN and U. BASU (J. Indian Chem. Soc., 1929, 6, 309—318).—When ethyl *cyclo*hexanone-2-carboxylate is heated with an arylamine at 150—190°, a mixture of diarylcarbamide and *cyclo*hexanone-2-carboxylarylamide results. The following are described: cyclo*hexanone*-2-*carboxy*-*anilide* (I), m. p. 104—105°; -p-*toluidide*, m. p. 108—109°; -m-4-*xylidide*, m. p. 125—126°; -β-*naphthylamide*, m. p. 149°, and -p-*acetamidoanilide*, m. p. 182·5°. These compounds give violet colorations with alcoholic ferric chloride, indicating that they react in the enol form. When I is heated at 100° with concentrated sulphuric acid, 5 : 6 : 7 : 8-*tetrahydrophenanthridone*, m. p. 273°, is produced. The following are prepared similarly: 3-*methyl*-, m. p. 286—288°; 1 : 3-*dimethyl*-, m. p. 270—271°, and 3 : 4-*benzo*-5 : 6 : 7 : 8-*tetrahydrophenanthridones*, m. p. 291—292°.

When ethyl *cyclo*hexanone-2-carboxylate is treated with aniline at the ordinary temperature, reaction occurs between the amino- and keto-groups resulting in the formation of *ethyl* 2-*anilino*-Δ¹-cyclo*hexene*-1-*carboxylate*, m. p. 57·5° (cf. Kötz and Merkel, A., 1909, i, 157): with *p*-aminoacetanilide, *ethyl* 2-p-*acetamidoanilino*-Δ¹-cyclo*hexene*-1-*carboxylate*, m. p. 191·5°, is obtained.

H. BURTON.

Action of aromatic magnesium compounds on methylsuccinimide. Synthesis of 2 : 5-diphenyl-1-methylpyrrole. R. LUKEŠ and V. PRELOG (Coll. Czech. Chem. Comm., 1929, 1, 334—345).—See A., 1928, 897.

Mechanism of Fischer's indole synthesis. P. W. Meber, G. Knöller, K. Herbst, and A. Trissler (Annalen, 1929, **471**, 113—145).—The following mechanism: $\mathrm{C_6H_5{\cdot}NR{\cdot}NH{\cdot}CR{:}CH_2} \longrightarrow \mathrm{C_6H_4}<\substack{\mathrm{CH_2{\cdot}CHR}\\ \mathrm{NR-NH}} \longrightarrow \mathrm{C_6H_4}<\substack{\mathrm{CH}\\ \mathrm{NR}}>\mathrm{CR}$ derives some support from the isolation of oxindole from the reduction of 3-hydroxycinnoline and the formation of 3-phenylindole from 4-phenyltetrahydrocinnoline. Dibenzyl ketone condenses with *as*-phenylmethylhydrazine in acetic acid solution to give 3-*phenyl*-2-*benzyl*-1-*methylindole*, m. p. 129—130°; using the appropriate hydrazines 3-*phenyl*-2-*benzyl*-1-*ethyl*-, and 3-*phenyl*-1 : 2-*dibenzyl-indoles* are obtained, m. p. 106° and 138°, respectively. Amyl nitrite and dibenzyl ketone react in presence of sodium ethoxide and ethyl alcohol to form iso*nitrosodibenzyl ketone*, m. p. 116°, which with *as*-phenylmethylhydrazine gives the *oxime* of 2-*benzoyl*-3-*phenyl*-1-*methylindole*, m. p. 165° (pale yellow needles) and 195° (deep yellow needles) (corresponding 1-*ethyl* compound, m. p. 150°). *iso*-Nitrosodibenzyl ketone forms with phenylhydrazine a *phenylhydrazone*, m. p. 185°, but treatment with hydroxylamine hydrochloride produces αβ-*di*iso*nitroso*-αγ-*diphenylpropane*, m. p. 213°.

Dibenzyl ketone diphenylhydrazone, m. p. 71—72°, affords 1 : 3-*diphenyl*-2-*benzylindole*, m. p. 124°, by boiling with alcoholic hydrogen chloride. *o*-Nitrophenylpyruvic acid underwent the following condensations: (1) by long contact with benzylphenylhydrazine in acetic acid solution 3-o-*nitrophenyl*-1-*benzylindole*-2-*carboxylic acid*, m. p. 186°, is obtained; (2) with boiling alcoholic *as*-phenylmethylhydrazine the *phenylmethylhydrazone* of *o*-nitrophenylpyruvic acid, m. p. 110° with carbon dioxide elimination, is formed; boiling ethyl-alcoholic hydrogen chloride transforms it into 3-o-*nitrophenyl*-1-*methylindole*-2-*carboxylic acid*, m. p. 226°; (3) with diphenylhydrazine the *diphenylhydrazone* of *o*-nitrophenylpyruvic acid, m. p. 125°, is produced, from which 1-*phenyl*-3-o-*nitrophenylindole*-2-*carboxylic acid*, m. p. 220°, is prepared. Ethyl *o*-nitrophenylpyruvate similarly yields a *diphenylhydrazone*, m. p. 107°, and a *phenylmethylhydrazone*, m. p. 99°, from which *ethyl* 3-o-*nitrophenyl*-1-*methylindole*-2-*carboxylate*, m. p. 107°, is derived.

II (with K. Herbst).—3-Hydroxycinnoline, when boiled with red phosphorus and hydrogen iodide, yields oxindole. 3-Hydroxydihydrocinnoline gives a *dibenzoyl* derivative, m. p. 167°.

p-Xylylhydrazine condenses with (1) dibenzyl ketone in alcoholic solution with formation of the *xylylhydrazone*, m. p. 105° (converted by alcoholic hydrogen chloride into 3-*phenyl*-2-*benzyl*-4 : 7-*dimethylindole*, m. p. 139°); (2) with formic acid to produce 2-p-*xylylformhydrazide*, m. p. 135°. This compound treated with methyl sulphate and sodium hydroxide solution gives 2-p-*xylyl*-αβ-*dimethylformhydrazide*, b. p. 172—174°/9 mm., from which, by hydrolysis with concentrated hydrochloric acid, 2-p-*xylyl*-αβ-*dimethylhydrazine*, b. p. 106—108°/9 mm., is obtained. This hydrazine condenses with dibenzyl ketone in acetic acid solution with formation of *dibenzyl ketone* 2-p-*xylyl*-αβ-*dimethylhydrazone* [two stereoisomerides (?), m. p. 86° and 104°], from which 3-*phenyl*-2-*benzyl*-1 : 4 : 7-*trimethylindole*, m. p. 108°, is formed by heating with hydrochloric acid; (3) with pyruvic acid in ethereal solution, to give the *xylylhydrazone*, m. p. 172° (decomp.); (4) with *o*-nitrophenylpyruvic acid in alcoholic solution to produce the *xylylhydrazone*, m. p. 156°.

Diphenylhydrazine reacts with: (1) propiophenone in acetic acid solution yielding the *diphenylhydrazone*, m. p. 83°, and 1 : 2-*diphenyl*-3-*methylindole*, m. p. 116°, successively; (2) phenyl *iso*propyl ketone, under the previous conditions, giving a *diphenylhydrazone*, m. p. 72°, from which is formed by the action of alcoholic hydrogen chloride at 0° 1 : 2-*diphenyl*-3 : 3-*dimethylindolinium chloride*, m. p. 196° (decomp.) [corresponding *perchlorate*, m. p. 209° (decomp.)]. The chloride is hydrolysed by boiling with water, 1 : 2-*diphenyl*-3 : 3-*dimethyl*-2-*indolinol*, $\mathrm{C_6H_4}<\substack{\mathrm{CMe_2}\\ \mathrm{NPh}}>\mathrm{CPh{\cdot}OH}$, m. p. 156° (decomp.) (O-*methyl ether*, obtained by treatment with potassium methoxide and methyl alcohol, m. p. 118°), being produced. 1 : 2-*Diphenyl*-3 : 3-*dimethylindoline*, m. p. 104°, is obtained from the last substance by reduction with acetic acid and zinc dust. By the interaction of phenyl *iso*propyl ketone and diphenylhydrazine some o-*anilinophenyl*iso*butyrophenone*, m. p. 96—98° [*N*-*nitroso*-derivative, m. p. 115° (decomp.), from which the C-*nitroso*-derivative, m. p. 146° (decomp.), is obtained], is isolated.

III (with A. Trissler).—By the action of ethereal hydrogen chloride on ethyl β-phenylazocrotonate a mixture of 1-(o- and p-*chlorophenyl*)-3-*methylpyrazolones*, m. p. 165° after sintering at 160°, is produced. Ethyl acetoacetate forms an o-*chlorophenylhydrazone*, which with aqueous-alcoholic sodium carbonate gives 1-o-*chlorophenyl*-3-*methylpyrazolone*, m. p. 201°.

An acetone solution of pyruvic acid phenylmethylhydrazone, when treated with nitric acid fumes, gives *pyruvic acid* 4-*nitrophenylmethylhydrazone*, decomp. 150°, from which, by treatment with aqueous-alcoholic hydrogen chloride and zinc dust, NN′-*dibenzoyl*-N-*methyl*-p-*phenylenediamine*, m. p. 165°, is obtained.

Methylation of 4-nitro-2-aminostilbene with methyl sulphate and sodium carbonate solution gives 4-*nitro*-2-*dimethylaminostilbene*, m. p. 75°, accompanied by 4-*nitro*-2-*methylaminostilbene*, m. p. 172°. Treatment of the N-*nitroso*-derivative, m. p. 175°, of the last compound with bromine in chloroform solution gives the *hydrobromide* of αβ-*dibromo*-β-(4-*nitro*-3-*nitrosophenyl*)-α-(o-*methylaminophenyl*)*ethane*, m. p. 274°, from which 6-*nitro*-5-*nitroso*-2-*phenyl*-1-*methylindole*, m. p. 170°, is derived.

4-*Hydroxytetrahydrocinnoline* (prepared by reduction with red phosphorus and hydrogen iodide of 4-hydroxycinnoline) has m. p. 220° (decomp.). 4-Phenylcinnoline, by warming with zinc dust, alcohol, and ammonia, gives 4-*phenyldihydrocinnoline*, m. p. 115—116° [treatment of which (or of 4-phenylcinnoline) with water, acetic acid, and amalgamated zinc gives 3-phenylindole], which by catalytic reduction in acetic acid solution (platinum as catalyst) yields 4-*phenyltetrahydrocinnoline*, m. p. 83° (*hydrochloride*, m. p. 201°; *picrate*, m. p. 128°).

o-Nitrophenylacetamide, reduced by hot aqueous ferrous sulphate and ammonia, gives *o*-*aminophenyl*-

acetamide (*monohydrate*, m. p. 93°; *acetyl* derivative, m. p. 130°; o-β-*naphtholazo*-derivative, m. p. 252°).

The following compounds are also described: α-2 : 5-*dichlorophenyl*-β-*formhydrazide*, m. p. 222°; α-2 : 5-*dichlorophenyl*-α-*methyl*-β-*formhydrazide*, m. p. 112°; α-2 : 5-*dichlorophenyl*-α-*methylhydrazine*, b. p. 142—148°/15 mm. (*acetyl* derivative, m. p. 134°); αα-*diphenyl*-β-*formhydrazide*, m. p. 116·5°; and αα-*diphenyl*-β-*methyl*-β-*formhydrazide*, m. p. 68°; b. p. 160—180°/18 mm.

The authors conclude that neither their own theory nor that of Robinson satisfactorily explains the Fischer indole synthesis. R. J. W. Le Fèvre.

Condensation of o-aminobenzaldehyde with ketodicarboxylic and diketocarboxylic esters. G. Koller [with H. Ruppersberg and E. Strang] (Monatsh., 1929, **52**, 59—67; cf. A., 1928, 1024).—Ethyl acetonedicarboxylate condenses with *o*-aminobenzaldehyde in presence of alcohol and a small amount of sodium hydroxide forming *ethyl 2-carbethoxymethylquinoline*-3-*carboxylate*, m. p. 64—66° after sintering. Hydrolysis of this with aqueous-alcoholic potassium hydroxide gives the corresponding *dicarboxylic acid*, decomp. 230°, which on thermal decomposition yields 2-methylquinoline-3-carboxylic acid, m. p. 234°, and when distilled with zinc dust affords 2-methylquinoline. Similar condensation of *o*-aminobenzaldehyde and ethyl acetonemono-oxalate yields an *ester*, $C_{14}H_{13}O_3N$, m. p. 92—93°. The *acid*, $C_{12}H_9O_3N$, m. p. 141° (decomp.), from this eliminates carbon dioxide when heated in a vacuum above its m. p., forming a *ketone* (I) (probably 3-acetylquinoline), $C_{11}H_9ON$, b. p. 182°/12 mm., m. p. 100—101° (*phenylhydrazone*, m. p. 165—166°; *oxime*, m. p. 206—207°). Oxidation of I with chromic oxide and dilute sulphuric acid gives quinoline-3-carboxylic acid, and condensation with benzaldehyde in presence of dilute alcohol and a small amount of potassium hydroxide yields a *benzylidene* derivative, m. p. 223—224°. Methyl 2 : 4-dihydroxyquinoline-3-carboxylate (A., 1927, 674) is converted by heating with alcoholic ammonia into 2 : 4-*dihydroxyquinoline*-3-*carboxylamide*, m. p. 295° (decomp.), which when treated with phosphoryl chloride at 100° affords 2 : 4-dichloro-3-cyanoquinoline, m. p. 167—168° (cf. Gabriel, A., 1919, i, 38). Reduction of this with hydrogen in presence of alcohol, sodium acetate, and palladised charcoal gives 3-*cyanoquinoline* (II), m. p. 108°, which after hydrolysis, conversion into the acid chloride, and subsequent treatment with ammonia in benzene yields *quinoline*-3-*carboxylamide*, m. p. 195°. This is dehydrated by heating with phosphoryl chloride into II. Unlike the 2- and 4-cyano-derivatives, conversion of II into 3-acetylquinoline by the action of magnesium methyl iodide was unsuccessful.

Ethyl acetonedioxalate and *o*-aminobenzaldehyde afford an *ester*, $C_{18}H_{17}O_6N$, m. p. 129°, together with a small amount of a substance, m. p. 142°.

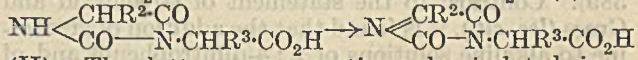
H. Burton.

α-Phenylfluorenoquinoline-γ-carboxylic acid. J. Loevenich and A. Loeser (J. pr. Chem., 1929, [ii], **122**, 285—288).—When an alcoholic solution of 2-aminofluorene, benzaldehyde, and pyruvic acid is boiled, there results 2-*phenylfluorenoquinoline*-4-*carboxylic acid*, m. p. >300° (*sodium*, *ammonium*, *silver* salts; *ethyl* ester, m. p. 174°; *methyl* ester, m. p. 172°). R. J. W. Le Fèvre.

Hydantoins. XLVIII. Polypeptide hydantoins from hydantoin-1-acetic acid. A. G. Renfrew and T. B. Johnson (J. Amer. Chem. Soc., 1929, **51**, 1784—1789).—The effect of substituents on the reactivity of the 5-methylene group in hydantoin towards aldehydes is discussed (cf. this vol., 330). Ethyl hydantoin-1-acetate and anisaldehyde in glacial acetic acid containing sodium acetate and acetic anhydride give the *sodium* salt, decomp. above 300°, of 5-p-*anisylidenehydantoin*-1-*acetic acid*, m. p. 215—216° (also +EtOH). Condensation is not effected by piperidine. The product is reduced by hydriodic acid at 105° to 5-p-*hydroxybenzylhydantoin*-1-*acetic acid*, m. p. 201°, and converted by methyl iodide and potassium hydroxide in methyl alcohol into products which are reduced by hydriodic acid to 5-*p*-hydroxybenzyl-3-methylhydantoin-1-acetic acid (Hahn and Renfrew, A., 1925, i, 581). Ethyl hydantoin-1-acetate and sodium methoxide in methyl alcohol give *ethyl* 3-*methylhydantoin*-1-*acetate*, m. p. 91—92°, which yields with anisaldehyde the two isomeric 5-*p*-anisylidene-3-methylhydantoin-1-acetic acids. No evidence of condensation with aldehydes otherwise than at the 5-methylene group has been obtained.

H. E. F. Notton.

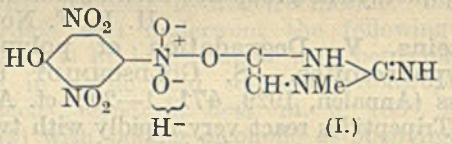
Proteins. V. Degradation of polypeptides by hypobromites. S. Goldschmidt and K. Strauss (Annalen, 1929, **471**, 1—20; cf. A., 1927, 983).—Tripeptides react very rapidly with two mols. of alkali hypobromite and then rather more slowly with a third mol. The initial stages of the reaction are the same as those which occur with a dipeptide (*loc. cit.*), but after elimination of the terminal amino-acid residue as a nitrile, ring formation to a hydantoin derivative occurs, the latter being further oxidised to a dehydrohydantoin (II) by the hypobromite:
$NH_2{\cdot}CHR^1{\cdot}CO{\cdot}NH{\cdot}CHR^2{\cdot}CO{\cdot}NH{\cdot}CHR^3{\cdot}CO_2H \longrightarrow$
$NBr{:}CR^1{\cdot}CO{\cdot}NH{\cdot}CHR^2{\cdot}CO{\cdot}NH{\cdot}CHR^3{\cdot}CO_2H \longrightarrow$
$R^1CN + HO_2C{\cdot}NH{\cdot}CHR^2{\cdot}CO{\cdot}NH{\cdot}CHR^3{\cdot}CO_2H$ (I) $\longrightarrow$



$$NH<\begin{matrix}CHR^2{\cdot}CO\\ CO{-}N{\cdot}CHR^3{\cdot}CO_2H\end{matrix} \longrightarrow N\lessdot\begin{matrix}CR^2{\cdot}CO\\ CO{-}N{\cdot}CHR^3{\cdot}CO_2H\end{matrix}$$

(II). The latter can sometimes be isolated in a crystalline form or as its crystalline potassium salt, but all, on hydrolysis, yield the α-keto-acid $COR^2{\cdot}CO_2H$ (usually isolated as its phenylhydrazone) and the amino-acid $NH_2{\cdot}CHR^3{\cdot}CO_2H$. Thus *alanylvalylglycine*, m. p. 241° (from *bromopropionylvalylglycine*, m. p. 204°), alanyl-leucylglycine, *alanylalanylleucine*, m. p. 246° (from *bromopropionylalanyl leucine*, m. p. 180°), and *dialanylglycine*, m. p. 208° (from the *bromopropionyl* compound, m. p. 194°), all yield acetonitrile and, respectively, 5-iso*propyl*-, m. p. 227°, 5-iso*butyl*-, m. p. 183°, -1 : 5-*dehydrohydantoin*-3-*acetic acid* (II, R^3=H), 5-*methyl*-1 : 5-*dehydrohydantoin*-3-iso*hexoic acid* (II, $R^3=CH_2Pr^\beta$), and 5-*methyl*-1 : 5-*dehydrohydantoin*-3-*acetic acid* (*potassium*+H_2O salt), whilst *valylalanylglycine*, m. p. 220° (from α-*bromo*-iso*valerylalanylglycine*, m. p. 167°), yields the last-named together with *iso*butyronitrile. Alanylglycylleucine, unlike the above tripeptides, takes up 5 mols. of hypobromite, since the carboxylamino-acid (I) loses carbon dioxide to yield glycyl-leucine, which is further degraded to leucine and cyanic acid, the latter being converted by more hypobromite into carbamide. Tetrapeptides react similarly with hypobromite. Thus *trialanylglycine*, m. p. 254° (decomp.) (from *bromopropionyldialanylglycine*, m. p. 217°), and *leucylalanylvalylglycine*, m. p. 250—256° (decomp.) (from the α-*bromo*iso*hexoyl* compound, m. p. 206°), yield, respectively, aceto- and *iso*valero-nitriles and the corresponding *dehydrohydantoins*, which could not be crystallised, but on hydrolysis yield pyruvic acid, glycine, and, respectively, alanine and valine. *Alanylglutamic acid* (*copper* salt) (from α-*bromopropionylglutamic acid*, m. p. 123°) with hypobromite yields acetonitrile and glutamic acid. J. W. Baker.

Constitution of red isomeride of creatinine picrate responsible for Jaffé's colour reaction. W. K. Anslow and H. King (J.C.S., 1929, 1210—1216).—A red isomeric *form* of creatinine picrate, m. p. 213° after turning yellow at 160—170°, is obtained by instantaneous acidification with hydrochloric acid of the red solutions obtained by the addition of alkali to an aqueous suspension of yellow creatinine picrate, m. p. 220—221°. It forms a red *barium* salt (also produced from the yellow compound) and is converted into yellow creatinine picrate when boiled with water. It is concluded that red creatinine picrate is I and



(I.)

that this compound is responsible for the red colour in Jaffé's colour reaction for creatinine (cf. Jaffé, A., 1886, ii, 1056; Folin, A., 1904, ii, 375; Greenwald and Gross, A., 1924, ii, 508; Chapman, A., 1909, ii, 948; Greenwald, A., 1925, i, 839; Weise and Trop, A., 1928, 1267). Support for this formula is given by the isolation of a red *sodium* salt from the interaction of acetone and 2 : 4-dinitrophenol in the presence of sodium ethoxide (cf. Reissert, A., 1904, i, 389). Contrary to the statement of Greenwald and Gross (*loc. cit.*), it is found that the addition of creatinine to alkaline solutions of 2 : 4-dinitrophenol and of 3-methylpicric acid gives orange-red solutions after keeping for several minutes. When alkaline solutions of 2 : 4-dinitrophenol, 2 : 6-dinitrophenol, 3-methylpicric acid, and 2 : 4-dinitro-α-naphthol-7-sulphonic acid containing creatinine are gradually treated with hydrochloric acid, a transient red colour is obtained at neutrality which disappears with excess of acid; the colour is not obtained from the acid side. Ionisation of the enolic form or ionisation of the reactive methylene compound is therefore an essential preliminary to the formation of the co-ordination complex, and this condition is most readily obtained by salt formation in alkaline solution. A. I. Vogel.

Catalytic hydrogenation of cyano-compounds. Reduction of ethyl phenylcyanopyruvate, ethyl benzoylcyanoacetate, and ethyl benzylidenecyanoacetate. H. Rupe and B. Pieper (Helv. Chim. Acta, 1929, 12, 637—649).—Ethyl cyanophenylpyruvate in aqueous alcoholic solution absorbed 2 mols. of hydrogen in 24 hrs. at 50—55° with a nickel catalyst with the formation of 2 : 3-*diketo*-4-*phenylpyrrolidine*, m. p. 295° after colouring at 200° [*benzoyl* derivative, m. p. 218°; *monomethyl* derivative, m. p. 197—198°; *quinoxaline* (from *o*-phenylenediamine), m. p. not given; *phenylhydrazone*, m. p. 224—225°].

Ethyl cyanobenzoylacetate (prepared from ethyl benzoylacetate, sodium, and cyanogen chloride in 70% yield) was reduced in aqueous-alcoholic solution at 68—73° with a nickel catalyst to *ethyl* α-*benzoylpropionate*, b. p. 143—144°/10 mm. The last-named ester formed with semicarbazide hydrochloride, phenylhydrazine, and hydroxylamine hydrochloride, 1-*carbamyl*-3-*phenyl*-4-*methyl*-5-*pyrazolone*, m. p. 193°, 1 : 3-*diphenyl*-4-*methyl*-5-*pyrazolone*, m. p. 195°, and 3-*phenyl*-4-*methyl*isooxazole, m. p. 117°, respectively. When the hydrogenation was interrupted, the *aldimine*, $NH:CH\cdot CHBz\cdot CO_2Et$, m. p. 81—82°, was isolated; by hydrolysis with hydrochloric acid acetophenone was obtained. Catalytic hydrogenation of ethyl benzylidenecyanoacetate led to the *anil* from the half-aldehyde of ethyl hydrogen benzylmalonate and ethyl β-amino-α-benzylpropionate. This, by boiling with alcoholic hydrogen chloride gave the *semi-aldehyde* of *ethyl hydrogen benzylmalonate* (isolated as *semicarbazone*, m. p. 121°; *phenylhydrazone*, m. p. 143°), which, by acid hydrolysis, afforded β-phenylpropaldehyde (*semicarbazone*, m. p. 113°; *oxime*, m. p. 93—94°), accompanied by β-*amino*-α-*benzylpropionic acid*, m. p. 225° (*sulphate*), from which, by treatment with potassium cyanate, 5-*benzylhydrouracil*, m. p. 248°, was prepared. R. J. W. Le Fèvre.

Naphtho*iso*indigotins. A. Wahl and J. Lobeck (Compt. rend., 1929, 188, 1683—1685).—Naphthisatin (benzisatin) and oxindole condense in alcohol containing a trace of ammonia or piperidine, or when ground together, giving α-*benzisatan* (I) and β-*benzisatan* (II). By heating with acetic anhydride containing a few drops of mineral acid I is converted into *benz*iso*indigotin* (also obtained directly from naphthisatin and oxindole by condensation in acetic and hydrochloric acids), which, by reduction with zinc and acetic acid in the presence of acetic anhydride yields a α-*acetyl-leucobenz*iso*indigotin*, m. p. above 300°. *Sodium*, *potassium*, *calcium*, *barium*, and *silver* salts derived from α-*benz*iso*indigotindisulphonic acid* are obtained from the leuco-base by treatment with excess of sulphuric acid, dilution, neutralisation, and addition of the appropriate metallic salt. By heating with acetic anhydride containing a trace of sulphuric acid, II affords β-*benz*iso*indigotin*, converted by zinc and acetic acid into a *diacetyl-leuco*-β-*benz*iso*indigotin*.

The action of hydrogen sulphide in cold methyl-alcoholic solution on naphthisatin furnishes a *dinaphthodisulphisatide* (III), containing 3 atoms of sulphur, the third of which cannot be removed by extraction; the substance nevertheless behaves normally, decomposing in boiling pyridine to yield α-*naphthoxindole* (*benzylidene* derivative, m. p. 241°) and α-*dinaphth*iso*indigotin*; the decomposition is also effected by sodium hydroxide or carbonate or by ammonia. Treatment of III with cuprous chloride affords αα′-*dinaphth*iso*indigotin*, converted by an excess of sulphuric acid into a sulphonic acid.

The α-benz*iso*indigotindisulphonic acid dyes wool a violet-black, not fast to washing, whilst the αα′-dinaphtho-compound gives a fast bluish-black.

C. W. Shoppee.

Reaction between sugars and their degradation products and nitrogenous substances. I. Formation of glyoxalines. K. Bernhauer (Z. physiol. Chem., 1929, **183**, 67—73).—The velocity of formation of methylglyoxaline by the action of zinc hydroxide and ammonia on various sugars increases with rise of temperature. Thus, the separation of the zinc salt is complete after 2 hrs. at 100°, but requires 24 hrs. at 40° and 6 weeks at the ordinary temperature. The concentration of the ammoniacal zinc hydroxide is important, best results being obtained with a 20—25% solution of ammonia saturated with zinc hydroxide. The yield of the methylglyoxaline is somewhat greater with dihydroxyacetone than with dextrose, and is increased by addition of formaldehyde. During the action of ammoniacal zinc hydroxide on methylglyoxal, no separation of the zinc salt of methylglyoxaline occurs unless formaldehyde is present, thus confirming the results of Sjollema and Kam (A., 1916, i, 791); in presence of acetaldehyde dimethylglyoxaline results. The intermediate formation of methylglyoxal during the reaction with dextrose is proved by the isolation of derivatives from the steam distillate of the reaction mixture.

H. Burton.

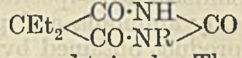
Glyoxaline derivatives. IV. Degradation of histidine to γ-hydroxyornithine. W. Langenbeck and R. Hutschenreuter (Z. physiol. Chem., 1929, **182**, 305—310).—Fission of *l*-histidine methyl ester with sodium hydroxide and benzoyl chloride (cf. Kossel and Edlbacher, A., 1915, i, 295) and subsequent treatment of the product with methyl-alcoholic hydrochloric acid (cf. Windaus, Dörries, and Jensen, A., 1922, i, 60) affords methyl αδ-dibenzamido-γ-keto-*n*-valerate, $[\alpha]_{\mathrm{Hg\ yellow}}^{22}$ —40·4° in pyridine. Reduction of this with hydrogen in presence of platinum oxide and acetic acid yields the *lactone* (I), m. p. 222°, of *αδ-dihexahydrobenzamido-γ-hydroxyvaleric acid* (II), m. p. 236—240°, together with a small amount of an *isomeride*, m. p. 248°. Hydrolysis of I with concentrated hydrochloric acid gives hexahydrobenzoic acid, whilst treatment with 1% sodium hydroxide solution at 0° and subsequent acidification with acetic acid furnishes about 20% of II, the remainder being recovered unchanged by acidifying with hydrochloric acid. When II is heated with acetic acid at 100° a substance, m. p. 245—246°, is produced, indicating that isomerisation of I occurs during the treatment with alkali. Reduction of ethyl benzamidoacetate with hydrogen in presence of platinum oxide and acetic acid yields ethyl hexahydrobenzamidoacetate, m. p. 76°.

H. Burton.

Pyrimidines. CVII. Examination of yeast nucleic acid for 5-methylcytosine. T. B. Johnson and H. H. Harkins (J. Amer. Chem. Soc., 1929, **51**, 1779—1784).—The pyrimidine fraction from protein-free yeast nucleic acid, prepared by a modification of Steudel's method (A., 1924, i, 104), is shown by the acetylcarbinol test (this vol., 705) to be free from thymine and 5-methylcytosine, although a positive reaction may be obtained if the fraction contains nucleosides. 5-Methylcytosine may be completely separated from thymine by two precipitations as the phosphotungstate.

H. E. F. Notton.

Copper compounds of diethylbarbituric acid. N. W. Romanowa (Arch. Pharm., 1929, **267**, 370—372).—When copper sulphate solution is added to a solution of sodium diethylbarbiturate (Medinal), a violet *compound* is first obtained, containing two sodium atoms, one copper atom, and four veronal residues. With a larger proportion of copper acetate or copper sulphate solution until an alkaline reaction is obtained, *cupric acetoveronal*, and *cupric sulphatoveronal*, bright blue compounds,



$CEt_2<{CO\cdot NH \atop CO\cdot NR}>CO$ ($R{=}{-}Cu\cdot CO_2Me$ and ${-}CuSO_4$), are obtained. The addition of still more copper salt solution affords bright blue copper–veronal *compounds* containing 20—26% Cu.

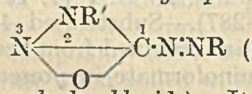
S. Coffey.

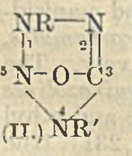
Quinazolines. I. T. Bhattacharyya, P. K. Bose, and J. N. Rây (J. Indian Chem. Soc., 1929, 6, 279—287).—Substituted 4-keto-1 : 4-dihydroquinazolines are obtained from acetylated arylamines and ethyl aminoformate in presence of phosphoric oxide and toluene. They are occasionally formed from the amine and ethyl acetamidoformate, and in this case the acetylcarbamide, $NHAr\cdot CO\cdot NHAc$ (I), is also produced. Thus, *m*-toluidine and ethyl acetamidoformate yield a mixture of *acetyl*-m-*tolylcarbamide* (I, Ar=*m*-$Me\cdot C_6H_4\cdot$), m. p. 123°, and 4-*keto*-2 : 7-*dimethyl*-1 : 4-*dihydroquinazoline*, m. p. 244°, also obtained from *m*-acet-toluidide and ethyl aminoformate. *m*-Anisidine affords *acetyl*-m-*anisylcarbamide*, m. p. 200°, and 4-*keto*-7-*methoxy*-2-*methyl*-1 : 4-*dihydroquinazoline*, m. p. 257°; aniline gives acetylphenylcarbamide and the *amidine*, $NHPh\cdot CMe\colon N\cdot CO_2Et$, whilst *o*-toluidine, *m*-4-xylidine, *o*-phenetidine, and *o*-anisidine afford only the corresponding *acetylcarbamides*, m. p. 168°, 194°, 203°, and 197°, respectively. The following substituted 4-*keto*-1 : 4-*dihydroquinazolines* are obtained from the requisite acylamine and ethyl aminoformate: 2-methyl- (II), m. p. 231° [the 2 : 3-dimethyl derivative, m. p. 112—113° (lit. 110—111°), is obtained by the action of methyl iodide and methyl-alcoholic sodium hydroxide on II, and is formulated as 4-keto-2 : 3-dimethyl-3 : 4-dihydroquinazoline (cf. Bogert and Gotthelf, A., 1900, i, 608; Bogert and Seil, A., 1907, i, 560)]; 2 : 6-*dimethyl*-, m. p. 240° (*picrate*, m. p. 196—198°); 2 : 8-*dimethyl*-, m. p. 240° (*picrate*, m. p. 164°), methylated to the 2 : 3 : 8-*trimethyl* derivative, m. p. 107°; 2 : 6 : 8-trimethyl-, m. p. 266° (lit. 271°; *picrate*, m. p. 197°), methylated to the 2 : 3 : 6 : 8-*tetramethyl* derivative, m. p. 146° (2 : 6 : 8-*trimethyl*-3-*ethyl* derivative, m. p. 190°); 6-*methoxy*-2-*methyl*-, m. p. 257°, methylated to the 6-*methoxy*-2 : 3-*dimethyl* derivative, m. p. 131°; 8-*methoxy*-2-*methyl*-, m. p. 243° (3-*methyl* derivative); 6-*ethoxy*-2-*methyl*-, m. p. 220° (3-*methyl* derivative, m. p. 148°); 8-*ethoxy*-2-*methyl*-, m. p. 225°; 2-phenyl-, m. p. 223° [3-methyl derivative, m. p. 133° (lit. 131°)]; 2-ethyl-, m. p. 227—228° (lit. 225°); 8-*methyl*-2-*ethyl*-, m. p. 215°, and 6-*methyl*-2-*ethyl*-, m. p. 227° (3-*methyl* derivative, m. p. 111°). Acet-α- and -βnaphthalides react with ethyl aminoformate yielding 4-*keto-2-methyl*-7 : 8-*benzo*-, m. p. 322°, and 4-*keto-2-methyl*-5 : 6-*benzo*-1 : 4-*dihydroquinazolines*, m. p. 295° (3-*methyl* derivative, m. p. 156°), respectively.

H. BURTON.

Action of heat on allophanic amides. J. BOUGAULT and J. LEBOUCQ (Compt. rend., 1929, **188**, 1406—1407).—By the action of aniline, *p*-toluidine, and phenylhydrazine on allophanoyl chloride are obtained, respectively, the corresponding anilide, *p*-toluidide, and *phenylhydrazide*, m. p. 218°. When heated at 200—210°, the first two evolve ammonia, yielding, respectively, *s*-diphenyl- and *s*-di-*p*-tolylcarbamide (soluble in alcohol) and cyanuric acid. By similar decomposition the phenylhydrazide yields only ammonia and phenylurazole, identical with the product obtained by Pinner (A., 1888, 687).

J. W. BAKER.

New group of hydrazomethylenes. M. BUSCH and W. SCHMIDT [with P. BOHRISCH and O. LUSCH] (Ber., 1929, **62**, [*B*], 1449—1457).—The product of the action of nitrous acid on αδ-diphenylthiosemicarbazide is shown to be 1 : 3-end*oxy*-1-*phenylazo-2-phenylhydrazomethylene*,  (I) (R=R′=Ph) (colourless *monohydrochloride*). It undergoes complicated hydrolysis by acids, yielding nitrogen, a neutral substance, m. p. 83°, and phenylazocarbanilide. Reduction with aluminium yields αδ-diphenylsemicarbazide, m. p. 176°, and phenylazocarbanilide. With ammonium sulphide αδ-diphenylsemicarbazide is produced, whereas hydrogen sulphide in alcohol affords αδ-diphenylthiosemicarbazide; zinc dust and acetic acid give diphenylsemicarbazide. Treatment of *endo*xyphenylazophenylhydrazomethylene with alcoholic alkali hydroxide gives 3 : 5-end*oxy*-1 : 4-*diphenyltetrazole* (II; R=R′=Ph), which explodes when strongly heated. The new ring is stable towards hydrochloric acid below 220°. It is reduced with difficulty to ammonia, aniline, phenylcarbamide, and small amounts of phenylhydrazine. 1 : 3-end*Oxy*-1-*phenylazo*-2-vic-m-*xylylhydrazomethylene*, m. p. 101°, 3 : 5-end*oxy*-1-*phenyl*-4-vic-m-*xylyltetrazole*, m. p. 174°, 1 : 3-end*oxy*-1-vic-m-*xylylazo-2-phenylhydrazomethylene*, m. p. 91—92°, vic-m-*xylylazocarbanilide*, m. p. 124·5°, and 3 : 5-end*oxy*-4-*phenyl*-1-vic-m-*xylyltetrazole*, m. p. 122—123°, are described. Phenylthiosemicarbazide affords the unstable 1 : 3-end*oxy*-1-*phenylazohydrazomethylene*, m. p. 60—62° (decomp.) [*hydrochloride*, m. p. 189—190°; *benzoyl* derivative, m. p. 166°; *potassium* compound, m. p. 185—190° (decomp.) after darkening at 110°]. The following end*oxyhydrazomethylenes* are described (cf. I): R=*p*-tolyl, R=Ph, m. p. 127°; R=*o*-tolyl, R′=Ph, m. p. 99°; R=R′=*o*-tolyl, m. p. 62°; R=Ph, R′=α-naphthyl, m. p. 125°; R=α-naphthyl, R′=Ph, m. p. 90° (*hydrochloride*); R=Ph, R′=β-naphthyl, m. p. 89—90°; R=Ph, R′=Et, m. p. 45° (*hydrochloride*); R=Ph, R′=allyl, m. p. 43° (*hydrochloride*); R=*p*-tolyl, R′=allyl, m. p. 59° (*hydrochloride*); and the following *tetrazoles* (cf. II): R=*p*-tolyl, R′=Ph, m. p. 158°; R=*o*-tolyl, R′=Ph, m. p. 117°; R=R′=*o*-tolyl, m. p. 128°; R=Ph, R′=α-naphthyl, m. p. 160°; R=α-naphthyl, R′=Ph, m. p. 177—178°; R=Ph, R′=β-naphthyl, m. p. 213—214°.



(II.)

H. WREN.

Porphyrin syntheses. XXIII. Syntheses of coproporphyrins. III and IV. H. FISCHER, K. PLATZ, and K. MORGENROTH (Z. physiol. Chem., 1929, **182**, 265—288).—Two of the four possible coproporphyrins (tetramethyltetra-β-carboxyethylporphins) have been previously synthesised (A., 1928, 1384), and the remaining two are now obtained by similar methods. When bis-(5-carboxy-4-methyl-3-β-carboxyethylpyrryl)methane is brominated in acetic acid solution, carbon dioxide is eliminated and (5-bromo-4-methyl-3-β-carboxyethylpyrryl)-(5-bromo-4-methyl-3-β-carboxyethylpyrrolenyl)methene hydrobromide, m. p. above 250°, results (cf. A., 1927, 1206). Condensation of bis-(2 : 4-dimethyl-3-β-carboxyethylpyrryl)methene hydrobromide with bis-(2-bromo-3-methyl-4-β-carboxyethylpyrryl)methene hydrobromide (I) in presence of hydrobromic and acetic acids or by the succinic acid method gives only small amounts of coproporphyrin IV. With an equimolecular mixture of I and bis-(4-methyl-2-bromomethyl-3-β-carboxymethylpyrryl)methene hydrobromide in presence of succinic acid at 175—180°, about 30% of coproporphyrin IV [*tetramethyl* ester, m. p. 168—169° after sintering at 161° (complex *copper* salt, m. p. 216—217°; *hæmin* derivative); *tetraethyl* ester, m. p. 152° (corr.; complex *copper* salt, m. p. 180—181°)], is obtained. Treatment of hæmopyrrolecarboxylic acid (A., 1928, 902) with hydrogen cyanide and chloride in chloroform solution affords after hydrolysis of the isolated iminochloride *hæmopyrrolecarboxylic acid aldehyde*, m. p. 155° [(corr.); *semicarbazone*, m. p. 190° (corr.) with discoloration at 160°; *oxime*, m. p. 152° (corr.); *methyl* ester (II), m. p. 89°]. This condenses with cryptopyrrole in presence of alcoholic hydrobromic acid yielding (4 : 5-*dimethyl*-3-β-*carboxyethylpyrryl*)-(3 : 5-*dimethyl*-4-*ethylpyrrolenyl*)*methene hydrobromide*, decomp. 217° (corr.) after darkening at 190°, whilst similar condensation of II and cryptopyrrolecarboxylic acid affords (4 : 5-*dimethyl*-3-β-*carbomethoxyethylpyrryl*)-(3 : 5-*dimethyl*-4-β-*carboxyethylpyrrolenyl*)*methene hydrobromide*, m. p. 138° (corr.).

Treatment of a mixture of (2-bromo-3-methyl-4-β-carboxyethylpyrryl)-(2-bromo-3-methyl-4-β-carboxyethylpyrrolenyl)methene hydrobromide and (2 : 3-dimethyl-4-β-carbomethoxypyrryl)-(2 : 4-dimethyl-3-ethylpyrrolenyl)methene hydrobromide with succinic acid at 165—170° affords coproporphyrin III (hydrochloride). The *tetramethyl* ester of this exists in two modifications, m. p. 146—148° (unstable) and 172°, respectively.

[With A. TREIBS.]—The coproporphyrin isolated from the urine and fæces of a case of congenital porphyrism (van den Bergh, Regniers, and Muller, Archiv für Verdauungskrankheiten, 1928, **42**, 306) is shown to be identical with coproporphyrin III.

H. BURTON.

Acetates of porphyrin and hæmin: constitution of rhodoporphyrin. H. FISCHER, G. HUMMEL, and A. TREIBS (Annalen, 1929, **471**, 237—285).—Hæmin extracted with acetic anhydride gives acetic anhydride-hæmin (chlorohæmin diacetate) from which hæmin can be regenerated by treatment of a chloroform solution by boiling acetic acid. Chlorohæmin diacetate when treated with hydrobromic and acetic acids in a sealed tube produces hæmatoporphyrin hydrochloride; when heated with methyl alcohol and a trace of either sulphuric acid or hydrogen chloride it yields a *tetramethylhæmatoporphyrin iron salt*, $C_{38}H_{44}O_6N_4FeCl$; whilst with hot collidine it gives *collidine-hæmin*, $C_{34}H_{32}O_4N_4FeCl,C_8H_{11}N$.

The preparation of the following compounds is described: *pyrroporphyrin acetate*, m. p. 183°; *mesoporphyrin acetate*, m. p. 225° (complex *copper* salt, $C_{38}H_{40}O_6N_4Cu$, m. p. 197°); *mesorhodin acetate*, m. p. 225°; *protoporphyrin acetate*, m. p. 231°; *phylloporphyrin acetate*, m. p. 220°; *rhodoporphyrin diacetate*; *rhodoporphyrin monomethyl* ester, m. p. 330° after sintering at 285° (which by decarboxylation gives pyrroporphyrin) [*acetate*, $C_{30}H_{32}N_4(CO_2Me)(CO_2Ac)$, m. p. 208°; complex *iron* salt]; *coproporphyrin* I-*acetate*, m. p. 182°; *uroporphyrin acetate*; *mesoacetoxyhæmin acetate*, m. p. 235°; *mesochlorohæmin acetate*, m. p. 260°; *mesoacetoxyhæmin dimethyl* ester, m. p. 237°; *protoacetoxyhæmin acetate*, m. p. 204°; *protochlorohæmin acetate*, m. p. 248° (converted into the previous compound by treatment in chloroform solution by 5% sodium hydroxide solution); *protohæmatin acetate*; *dimethylhæmatin*, m. p. 232°; *phylloacetoxyhæmin acetate*, m. p. 327°; *phyllochlorohæmin acetate*, m. p. 329°; *pyrroacetoxyhæmin acetate*; *pyrrochlorohæmin acetate*, m. p. 271°; *coproacetoxyhæmin acetate* I; *ætioacetoxyhæmin*; *rhodoporphyrin anhydride*; *rhodoporphyrin monomethyl ester anhydride*; *phylloporphyrin anhydride*; *pyrroporphyrin anhydride*; *mesoporphyrin anhydride*; *mesochlorohæmin anhydride*; *protoporphyrin anhydride*.
R. J. W. LE FÈVRE.

Synthesis of chlorin. H. FISCHER and H. HELBERGER (Annalen, 1929, **471**, 285—304).—The hæmin resulting from the treatment of porphyrin hydrochloride in acetic acid solution with a solution of ferric acetate and sodium chloride in acetic acid is suspended in *iso*amyl alcohol and sodium added in an atmosphere of hydrogen. From the mixture of porphyrin iron salts, chlorin iron salts, perhydrochlorin, chlorin, and traces of porphyrin, so produced, chlorin and perhydrochlorin are extracted by 18% hydrochloric acid solution. Final separation, by 8% hydrochloric acid solution, gives *chlorinmonocarboxylic acid*, m. p. 217° (corr.) (decomp.) (sodium, potassium, and ammonium *salts*; *methyl* ester, m. p. 152° [corr.]; *methyl ester copper* complex), transformed by 3% oleum at 100° into *anhydride*-a, m. p. 285° (decomp.), and *anhydride*-b, m. p. 282° (decomp.), by saturated methyl-alcoholic potassium hydroxide in a sealed tube at 180° into porphyrinmonocarboxylic acid (methyl ester, m. p. 217°), and by heating with zinc dust and acetic acid into impure porphyrinmonocarboxylic acid. Complex *salts*, $C_{33}H_{40}O_2N_4R$, of chlorinmonocarboxylic acid with iron (R=FeCl), copper (R=Cu), and magnesium are described.
R. J. W. LE FÈVRE.

Degradation of chlorophyll by alkali. A. TREIBS and E. WIEDEMANN (Annalen, 1929, **471**, 146—235).—Phæophytin is a mixture of phæophytin-*a*, m. p. 178—180° (sintering at 150°), and phæophytin-*b*, m. p. 190—195° (sintering at 170°). The analytical figures obtained for chlorin-*e* are in agreement with those previously given for rhodin-*g*. By the action of diazomethane in acetone, chlorin-*e* methyl ester, m. p. 215° (corr.), and rhodin-*g* ester, m. p. 251° (corr.), are obtained; these are hydrolysed by short treatment in pyridine solution with methyl-alcoholic potassium hydroxide, whilst treatment of chloroform solutions with copper acetate in methyl-alcoholic solution yields chlorin-*e* ester and *rhodin*-g *ester* copper salts, both m. p. 225° (corr.).

The actions of the following reagents on chlorin-*e* and rhodin-*g* were examined in detail: (A) 30% methyl-alcoholic potassium hydroxide; (B) A and ½ vol. of pyridine in which the substance is previously dissolved; (C) B with addition of magnesia; (D) ½ vol. of pyridine and 1 vol. of 5% sodium oxide in methyl alcohol; (E) ½ vol. of pyridine and 1 vol. of 25% methyl-alcoholic sodium hydroxide.

Chlorin-*e* treated with reagent E in a silver vessel under pressure at 125°, rhodin-*g* treated with reagent D at 130°, or phæophytin (*a*+*b*) treated with reagent B at 100° all led to the isolation of *verdoporphyrin*, $C_{32}H_{34}O_4N_4$ [*dimethyl* ester, m. p. 280° (corr.); copper *salt*, $C_{32}H_{32}O_4N_4Cu$; magnesium *complex* (*verdophyllin*)], further degradation of which by E, B, D, and sulphuric acid produced rhodoporphyrin, rhodoporphyrin plus a trace of pyrroporphyrin, some phylloporphyrin, and pyrroporphyrin, respectively. By-products in the decomposition of chlorin-*e* include *chlorin*-3 and *chlorin*-10 [identical with phytochlorin-*f* (?) [*methyl* ester, m. p. 203° (corr.); *methyl ester copper* salt, m. p. 210° (corr.)]. Verdoporphyrin is contained in the cyano- and glauco-porphyrins of Willstätter.

Treatment of chlorin-*e* according to conditions C at 150°, rhodin-*g* according to conditions D at 140°, and phæophytin (*a*+*b*) according to conditions B gave rhodoporphyrin [*magnesium* complex (*rhodophyllin*); *dihydrochloride*; *dimethyl* ester, m. p. 268° (corr.); *dimethyl ester copper* complex, $C_{34}H_{36}O_4N_4Cu$, m. p. 243° (corr.); *dimethyl ester iron* complexes: *rhodohæmin* ester, $C_{34}H_{36}O_4N_4FeCl,MeOH$, m. p. 294° (decomp.), and $C_{34}H_{36}O_4N_4FeCl$]. Oxidation of rhodoporphyrin dimethyl ester in chloroform solution by lead dioxide and acetic acid produced a *xanthoporphinogen*, m. p. 284°.

Rhodoporphyrin under conditions E in a sealed tube gave pyrroporphyrin, whilst erythrophyllin and erythroporphyrin (Willstätter) with reagent B gave pyrroporphyrin; it is concluded that erythroporphyrin is very pure rhodoporphyrin.

From rhodin-*g* and reagent D at 150° (in sealed tube) a mixture of phyllo-, pyrro-, and rhodo-porphyrins was obtained. *Phylloporphyrin hydrochloride* and *phylloporphyrin ester copper* salt, m. p. 255° (corr.), are described. Phylloporphyrin when treated with sodium ethoxide in pyridine solution gave *phyllochlorin* [*methyl* ester, m. p. 164° (decomp.)], which by reduction with zinc dust and acetic acid gave a *leuco-compound*. From the porphyrin mixture obtained above from rhodin-*g* pyrroporphyrin [*copper* complex; *pyrroporphyrin ester copper* complex, m. p. 231° (corr.)] was obtained; from it *pyrrochlorin* was prepared analogously to phyllochlorin; when warmed with sulphuric acid it was converted into pyrrorhodin.

Distribution coefficients of, and spectroscopic measurements for, the derivatives described are tabulated. R. J. W. Le Fèvre.

Blood colouring matters. X. Specificity of hæmoglobin and von Krüger's reaction. F. Haurowitz (Z. physiol. Chem., 1929, **183**, 78—87).—The rate of denaturation of oxyhæmoglobins by sodium hydroxide (von Krüger's reaction) depends on the source; thus, human oxyhæmoglobin is transformed into cathæmoglobin in 40—50 sec., whilst the conversion with ox oxyhæmoglobin is not complete until after 24 hrs. The cathæmoglobin formed is precipitable by ammonium sulphate. Spectroscopic investigation of the change shows it to be unimolecular. The characteristic bands of cathæmoglobin are not visible in alkaline solution but appear when carbon dioxide is passed into the solution.

H. Burton.

Action of formic acid on oxy- and chlorohæmins. A. Hamsík (Z. physiol. Chem., 1929, **183**, 103—112).—Treatment of the potassium derivative (I) of oxyhæmin with 95% formic acid in methyl-alcoholic solution affords formylhæmin (cf. A., 1927, 1100). Protoporphyrin is best prepared from oxyhæmin by treatment with 80% formic acid and iron powder. Similar treatment of acetone-chlorohæmin with 85% formic acid also yields protoporphyrin; with more concentrated acid a brown product results. When I is treated with oxalic, 95% formic, or acetic acid in presence of methyl alcohol or acetone, dissolution is greatest with the first and least with the last acid. H. Burton.

Ring openings with benz-αβ-*iso*oxazoles. H. Lindemann and H. Cissée (J. pr. Chem., 1929, [ii], **122**, 232—260).—Methyl 5-nitroindoxazen-2-carboxylate was reduced by stannous chloride and hydrochloric acid to the 5-*amino*-ester, m. p. 206° (*acetyl* derivative, m. p. 210°; *diacetyl* derivative, m. p. 130°), which by hydrolysis with sulphuric acid gave 5-*amino-indoxazen*-2-*carboxylic acid*, decomp. 160° (with formation of 4-amino-2-hydroxybenzonitrile, m. p. 182°) (*acetyl* derivative, decomp. 260—280° with production of acetamidosalicylonitrile, m. p. 288°). The *ethyl* ester, m. p. 147° (*acetyl* derivative, m. p. 186—187°), of the last-named when treated with hydrazine hydrate yielded the *hydrazide* of 5-acetamidoindoxazen-2-carboxylic acid, m. p. 218°, which, with nitrous acid, was transformed into the corresponding *azide*, m. p. 155° (decomp.) [which, by boiling with the appropriate alcohols, afforded the n-*propyl*, n-*butyl*, and iso*amyl* esters of 5-*acetamidoindoxazen*-2-*carbamic acid*, m. p. 205°, 248°, and 215° (decomp.), respectively; the three related *amines*, obtained from these by hydrochloric acid hydrolysis, had m. p. 138° (decomp.), 104° (decomp.), 145°, respectively]. The above azide was boiled with aqueous acetic acid with the production of 2-*amino*-5-*acetamidoindoxazen*, m. p. 222° (*diacetyl* derivative, m. p. 256°; this by warming with 2*N*-sodium hydroxide solution passed into 3-o-*hydroxy*-p-*acetamidophenyl*-5-*methyl*-1 : 2 : 4-*oxdiazole*, m. p. 210°, also obtained by reducing with stannous chloride and hydrochloric acid the analogous nitro-oxdiazole), and either from the hydrolysis of this compound with aqueous sulphuric acid or by reduction of 5-nitro-2-aminoindoxazine with stannous chloride 2 : 5-*diaminoindoxazen*, m. p. 141°, was obtained.

2-Amino-5-acetamidoindoxazen gave 2-*hydroxy*-5-*acetamidoindoxazen*, m. p. 160—165° (decomp.), by diazotisation. This, by heating with formic acid, produced 2-*hydroxy*-4-*acetamidobenzhydroxamic acid*, m. p. 218°. The last two compounds by warming with propionic acid or anhydride respectively afforded 2-*hydroxy*-4-*acetamidobenzpropionylhydroxamic acid*, m. p. 194°, dissolution of which in 2*N*-sodium hydroxide solution led to 5-*acetamido*-1-*benz*iso*oxazolone*, m. p. 320°.

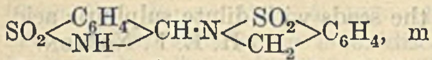
Methyl 5-aminoindoxazen-2-carboxylate was converted by Sandmeyer's reaction into *methyl 5-chloro-indoxazen-2-carboxylate*, which by long contact with 2*N*-sodium hydroxide solution yielded the *acid*, decomp. 171° (with remelting above 300°). Either the previous ester or acid when boiled with 2*N*-sodium hydroxide passed into 4-*chloro*-2-*hydroxybenzonitrile*, m. p. 155° (at 180—200° the clear mass formed a cyaphenin derivative).

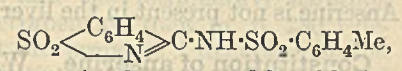
The above 5-chloro-methyl ester when boiled with hydrazine in ethyl-alcoholic solution afforded the *hydrazide* of 5-*chloroindoxazen*-2-*carboxylic acid*, decomp. 192°; this with sodium nitrite produced the corresponding *azide*, m. p. 142° (decomp.). Warming the last compound with acetic acid gave *bis*-(5-*chloro*-2-*indoxazenyl*)*carbamide*, m. p. 260°, whilst boiling with acetic anhydride produced 5-*chloro*-2-*acetamido-indoxazen*, m. p. 186° (corresponding *amine*, m. p. 135°), from which 3-o-*hydroxy*-p-*chlorophenyl*-5-*methyl*-1 : 2 : 4-*oxdiazole*, m. p. 79°, was formed by warming with sodium hydroxide solution.

A parallel series of experiments was performed from *methyl indoxazen*-2-*carboxylate*, m. p. 69° (obtained from the 5-amino-ester by diazotisation), the following compounds being described: *indoxazen*-2-*carboxylic acid*, m. p. 140—141° (with formation of salicylonitrile); the corresponding *hydrazide*, m. p. 143°, and *azide*, m. p. 95°; s-*bis*-2-*indoxazenylcarbamide*, m. p. 244°; 2-*aminoindoxazine*, m. p. 110° (*acetyl* derivative, m. p. 155—156°. R. J. W. Le Fèvre.

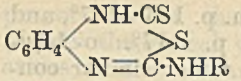
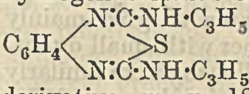
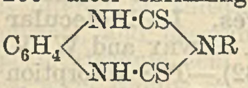
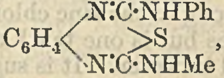
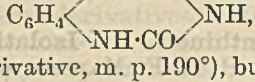
Aromatic sulphonamides. J. Koetschet and P. Koetschet (Helv. Chim. Acta, 1929, **12**, 669—699).—Benzaldehyde-*p*-sulphonamide is prepared in higher yields than by Dakin's method (A., 1917, i, 542) by warming "chloramine-*T*" with a mixture of water, *p*-toluenesulphonamide, and hydrochloric acid. Its α-*naphthyl*- and p-*nitrophenyl-hydrazones* have m. p. 254—255° and 256—257°, respectively. By methylation (alkali and methyl sulphate) it yields the *dimethylsulphonamide*, m. p. 134—137° (*phenylhydrazone*, m. p. 170—171°), accompanied by the *monomethylsulphonamide*, m. p. 119—119·5° (*phenylhydrazone*, m. p. 163—164°). Benzaldehyde-*p*-sulphonamide undergoes Cannizzaro's reaction giving p-*sulphonamidobenzyl alcohol*, m. p. 119—120°, and the corresponding benzoic acid, m. p. above 280°.

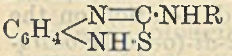
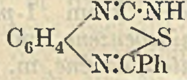
An improved method for the preparation of the *N*-sodium salt of *o*-toluenesulphonchloroamide is described. Treatment of "*o*-chloramine-*T*" with boiling aqueous acetic acid gives a *compound* (I),


$SO_2<\genfrac{}{}{0pt}{}{C_6H_4}{NH-}>CH{\cdot}N<\genfrac{}{}{0pt}{}{SO_2}{CH_2}>C_6H_4$, m. p. 141—142°. This, with the appropriate hydrazines, forms the *phenylhydrazone*, the α-*naphthylhydrazone*, and the p-*nitrophenylhydrazone* of ψ-o-*sulphonamidobenzaldehyde*, m. p. 198°, 206—208°, and 250°, respectively. In the mother-liquors from these condensations is found 1-S-*dioxy*-2 : 3-*dihydro*-αβ-*benzo*iso*thiazole* (internal anhydride of o-*sulphonamidobenzyl alcohol*), m. p. 112·5—113°. The compound I is unaffected by boiling aqueous hydrochloric acid, but is resolved into its constituents (ψ-aldehyde and anhydro-alcohol) by treatment with sodium hydrogen sulphite and sulphur dioxide; methylation (methyl sulphate and alkali) gives *methyl*-ψ-o-*sulphonamidobenzaldehyde* (isolated as the *phenylhydrazone*, m. p. 153—154°), 1-S-*dioxy*-2-*methyl*-2 : 3-*dihydro*-αβ-*benzo*iso*thiazole* (internal anhydride of N-*methyl*-o-*sulphonamidobenzyl alcohol*), m. p. 122—123°, and the true N-*methyl* derivative of I, m. p. 263°.

The compound 
$SO_2<\genfrac{}{}{0pt}{}{C_6H_4}{N}>C{\cdot}NH{\cdot}SO_2{\cdot}C_6H_4Me$, m. p. 225°, may be conveniently prepared by chlorinating a solution of *o*-toluenesulphonamide in aqueous sodium hydroxide. R. J. W. LE FÈVRE.

4-*mp*-Dihydroxyphenylthiazoles. T. B. JOHNSON and E. GATEWOOD (J. Amer. Chem. Soc., 1929, **51**, 1815—1819).—*Acetamidoacetothioamide*, m. p. 123—124°, from acetamidoacetonitrile and ammonium sulphide in alcohol, gives with 3 : 4-dihydroxyphenyl chloromethyl ketone (cf. Stolz, A., 1905, i, 106; Hantzsch, A., 1888, 574) in alcohol 4-mp-*dihydroxyphenyl*-2-*acetamidomethylthiazole hydrochloride*, m. p. 188—190°, which is hydrolysed by hydrochloric acid to 4-mp-*dihydroxyphenyl*-2-*aminomethylthiazole hydrochloride*, m. p. 225—230°. Methylaminoacetonitrile (Heimrod, A., 1914, i, 327) and acetic anhydride in benzene give an acetyl derivative converted by alcoholic ammonium sulphide into *acetmethylamidoacetothioamide*, $NMeAc{\cdot}CH_2{\cdot}CS{\cdot}NH_2$, m. p. 156—157°. This yields with the chloro-ketone 4-mp-*dihydroxyphenyl*-2-*acetmethylamidomethylthiazole hydrochloride*, m. p. 186—188°, hydrolysed to 4-mp-*dihydroxyphenyl*-2-*methylaminomethylthiazole* (+EtOH), m. p. 128—130° (*hydrochloride*, m. p. 220—225°). α-Acetamido*iso*butyrothioamide, m. p. 185—186° (cf. Hellsing, A., 1904, i, 563) is similarly converted into 4-mp-*dihydroxyphenyl*-2-α-*acetamido*iso*propylthiazole*, m. p. 198—200° (*hydrochloride*, m. p. 188—189°), and 4-mp-*dihydroxyphenyl*-2-α-*amino*iso*propylthiazole hydrochloride*, m. p. 210—215°. The following 4-mp-*dihydroxyphenylthiazoles* were also prepared: 2-*thiol*- (+H_2O), m. p. 250°; 2-*phenyl*-, m. p. 164—165°; 2-*amino*-, *hydrochloride*, m. p. 230—235°, and 2-*methylamino*-, *hydrochloride*, m. p. 275—280°. The new thiazoles are all physiologically active. H. E. F. NOTTON.

Lengthened *o*-di-derivatives of benzene and their ring closure. Formation of polymembered heterocyclic compounds from substituted phenylenecarbamides. T. N. GHOSH and P. C. GUHA (J. Indian Chem. Soc., 1929, 6, 181—195).—When 1 : 2-di(phenylthiocarbamido)benzene, $C_6H_4(NH{\cdot}CS{\cdot}NHPh)_2$, is heated with hydrochloric acid (*d* 1·19), aniline and the *compound*, 
$C_6H_4<\genfrac{}{}{0pt}{}{NH{\cdot}CS}{N{=}C{\cdot}NHR}>S$ (I) (R=Ph), m. p. 290—291° (*acetyl* derivative, m. p. 160°; corresponding *disulphide*, m. p. 210°, obtained by oxidation of I with iodine), result; this substance is also formed by the action of 20% potassium hydroxide solution on the thiocarbamide. Similarly, 1 : 2-*di*-(o-*tolylthiocarbamido*)*benzene*, m. p. 161°, yields the *compound* (I, R=o-$Me{\cdot}C_6H_4{\cdot}$), m. p. 300° (*acetyl* derivative, m. p. 200°), also formed from 1-*phenylthiocarbamido*-2-o-*tolylthiocarbamidobenzene*, m. p. 136°; 1 : 2-*di*-(p-*tolylthiocarbamido*)*benzene*, m. p. 178°, gives the *compound* I (R=p-$Me{\cdot}C_6H_4{\cdot}$), m. p. 300° (*acetyl* derivative, m. p. 200°; *disulphide*, m. p. 190°), obtained also from 1-*phenylthiocarbamido*-2-p-*tolylthiocarbamidobenzene*, m. p. 165°; 1 : 2-*di*-(m-4-*xylylthiocarbamido*)*benzene*, m. p. 145°, affords the *compound* I (R=$C_6H_3Me_2$), m. p. 295° (*acetyl* derivative, m. p. 296°; *disulphide*, m. p. 172°); 1 : 2-*di*(*methylthiocarbamido*)*benzene*, m. p. 175°, furnishes the *compound* I (R=Me), m. p. 168° (*disulphide*, m. p. 194°); 1-*phenylthiocarbamido*-2-*allylthiocarbamidobenzene*, m. p. 245°, yields the *compound* I (R=C_3H_5), m. p. 293° (*disulphide*, m. p. above 300°). The *substance* I (R=Ph, C_6H_4=C_6H_3Me), m. p. 265° (*acetyl* derivative, m. p. 185°; *disulphide*, m. p. 137°), is obtained from the *di*(*phenylthiocarbimide*) derivative, m. p. 142°, of *o*-tolylenediamine. When 1 : 2-di(allylthiocarbamido)benzene is treated with concentrated hydrochloric acid, hydrogen sulphide is eliminated and the *substance*, 
$C_6H_4<\genfrac{}{}{0pt}{}{N{:}C{\cdot}NH{\cdot}C_3H_5}{N{:}C{\cdot}NH{\cdot}C_3H_5}>S$, m. p. above 300° (*diacetyl* derivative, m. p. 185°, obtained by the action of acetic anhydride on the thiocarbamide), is formed. 1-*Phenylcarbamido*-2-*phenylthiocarbamidobenzene*, m. p. 200° after shrinking at 140°, yields the *compound*, 
$C_6H_4<\genfrac{}{}{0pt}{}{NH{\cdot}CS}{NH{\cdot}CS}>NR$ (II) (R=Ph), m. p. 185° (*disulphide*, m. p. 128—130°), whilst 1-*phenylcarbamido*-2-p-*tolylthiocarbamidobenzene*, m. p. 165°, gives the *substance* II (R=p-$Me{\cdot}C_6H_4$), m. p. 175—176° (*disulphide*, m. p. 164°). 1-*Phenylcarbamido*-2-*methylthiocarbamidobenzene*, m. p. 98°, loses water, affording the *substance*, 
$C_6H_4<\genfrac{}{}{0pt}{}{N{:}C{\cdot}NHPh}{N{:}C{\cdot}NHMe}>S$, m. p. 195°, whilst 1-*phenylcarbamido*-2-*allylthiocarbamidobenzene*, m. p. 160°, furnishes the *compound* I (R=Ph, CS=CO). Hydrochloric acid converts 1 : 2-dicarbamidobenzene into the *compound*, 
$C_6H_4<\genfrac{}{}{0pt}{}{NH{\cdot}CO}{NH{\cdot}CO}>NH$, sublimes above 300° (*acetyl* derivative, m. p. 190°), but 1 : 2-*di*-(*phenylcarbamido*)*benzene*, m. p. 220°, in unaffected.

When *o*-phenylthiocarbamidoaniline (III) (N-*carbethoxy*-derivative, m. p. 288—290°; o-*nitrobenzylidene* derivative, m. p. 215°; m-*nitrobenzylidene* derivative, m. p. 153—154°; *salicylidene* derivative, m. p. 180°) is heated with concentrated hydrochloric acid, *o*-phenylenethiocarbamide, m. p. 301—302° (lit. 290°; *acetyl* derivative, m. p. 200°; *disulphide*, m. p. 230°), results: this is also formed from the analogous o-*tolyl-*, m. p. 160°, p-*tolyl-* (IV), m. p. 146—147°, and *methyl-thiocarbamidoanilines*, m. p. 117°. o-*Allylthiocarbamidoaniline*, m. p. 115°, under similar conditions, yields 2-*allylaminobenzthiazole*, m. p. 180° (*acetyl* derivative, m. p. 198°). Oxidation of III and IV with ferric chloride solution affords the *compounds*,  $C_6H_4<\begin{matrix}N{=}C\cdot NHR\\ NH\cdot S\end{matrix}$ (R=Ph and *p*-C_6H_4Me, respectively), m. p. 155—156° and 93°, respectively. Similar oxidation of the *benzylidene* derivative, m. p. 265—267°, of III gives the *substance*,  $C_6H_4<\begin{matrix}N{:}C\cdot NHPh\\ \quad >S\\ N{:}CPh\end{matrix}$, m. p. 105°.

H. BURTON.

Nomenclature of alkaloids and alkaloidal derivatives. M. POLONOVSKI and M. POLONOVSKI (Bull. Soc. Chem. biol., 1929, **11**, 521—530).—Present nomenclature is criticised and reforms are suggested.

F. C. HAPPOLD.

Nicotine tetrachloroiodide. F. D. CHATTAWAY and G. D. PARKES (J.C.S., 1929, 1314—1317).—*Nicotine tetrachloroiodide*, $C_{10}H_{14}N_2,2HICl_4$, m. p. 150°, is obtained quantitatively on mixing solutions of nicotine and of iodine trichloride in hydrochloric acid, and may be employed for the preparation of pure nicotine and for its isolation from tobacco, since decomposition with aqueous sodium sulphite, followed by ether extraction, produces the pure base, b. p. 249—250°. Nicotine tetrachloroiodide is stable when kept in a closed vessel, but is decomposed by aqueous alkalis and more slowly by water to give mainly nicotine and nicotinic acid together with small quantities of iodate and iodide. The following were similarly prepared: *nicotinic acid tetrachloroiodide*, m. p. 137°; *methyl* N-*methylnicotinate tetrachloroiodide*, m. p. 110°; *trigonelline tetrachloroiodide*, m. p. 122°.

A. I. VOGEL.

Nicotine and its derivatives. I. Molecular extinction coefficients. T. M. LOWRY and W. V. LLOYD (J.C.S., 1929, 1376—1382).—The absorption spectra of nicotine, the salt $C_{10}H_{14}N_2,2HCl,ZnCl_2,H_2O$, the *iso*methiodide, m. p. 164°, and its hydriodide, m. p. 209°, and of the dimethiodide, m. p. 216°, in water and of nicotine in pure *cyclo*hexane have been measured. They all exhibit a strong absorption band at 2650 Å. which is twice as strong in the zinc chloride compound as in the methiodides but is one tenth as strong when the base is dissolved in water. It is suggested that in aqueous solution a non-ionised hydrate or ψ-base is formed by saturation of a double linking of the pyridine ring (cf. Decker and Kauffmann, A., 1911, i, 807).

A. I. VOGEL.

Calycanthine. I. Isolation from *Meratia præcox*. R. H. F. MANSKE (J. Amer. Chem. Soc., 1929, **51**, 1836—1839).—The seeds of *Meratia præcox*, Rehd. and Wils., an Asiatic shrub, contain 2·5% of calycanthine (cf. Späth and Stroh, A., 1925, i, 1447), which had previously been isolated only from American *Calycanthaceæ*. The seeds also contain dextrose and small quantities of an α-*alkaloid*, m. p. 197—198°, which contains no phenolic groups, and an oily β-*alkaloid* (*hydrochloride*, m. p. 219—220°), both of which give a positive Ehrlich reaction. Hydrolysis of the epicarp of the seeds with dilute sulphuric acid yields *l*-xylose.

H. E. F. NOTTON.

Anserine, new constituent of bird muscle-tissue. D. ACKERMANN, O. TIMPE, and K. POLLER (Z. physiol. Chem., 1929, **183**, 1—10).—Extraction of goose flesh with water and treatment of the extract with mercuric sulphate and sulphuric acid (cf. Dietrich, A., 1914, i, 1104) affords a precipitate from which 0·12% of *anserine*, $C_{10}H_{16}O_3N_4$, m. p. 238—239°, $[\alpha]_D^{16}$ +11·26° in water [*nitrate*, m. p. 216—218° (decomp.); *chloroplatinate*, decomp. 215—220°; *chloroaurate*, m. p. about 90—95°; *picrate*, decomp. 205—208°], was obtained by removal of mercury with hydrogen sulphide and purification through the *copper oxide* compound, $C_{10}H_{16}O_3N_4,CuO$, decomp. 230—232° (two modifications, ultramarine blue and reddish-purple, according to solvent used for purification). The new substance is precipitated from solution by alkaloidal reagents, and it gives the ninhydrin reaction. Anserine is not present in the liver, stomach, or heart.

H. BURTON.

Constitution of anserine. W. LINNEWEH, A. W. KEIL, and F. A. HOPPE-SEYLER (Z. physiol. Chem., 1929, **183**, 11—18; cf. preceding abstract).—Anserine contains a carboxyl group, since it furnishes an *ethyl* ester (*chloroplatinate*, m. p. 225—230°). The presence of amino- and NMe groups is also indicated by the Van Slyke and Zeisel methods. Distillation with soda-lime in a current of hydrogen affords 4(5) : *N*-dimethylglyoxaline, whilst treatment with barium hydroxide and water at 140° yields dl-α-*amino*-β-N-*methyliminazolylpropionic acid*, decomp. 248—252° (*nitrate*, decomp. 144—146°), and β-aminopropionic acid [α-*naphthylcarbimide* derivative, m. p. 230—232° (decomp.)], separable by treatment with phosphotungstic acid. Anserine is, therefore, α-(β′-aminopropion)amido-β-*N*-methyliminazolylpropionic acid.

H. BURTON.

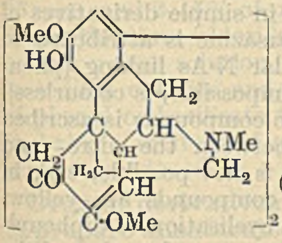
***Strychnos* alkaloids. II. Oxidation by permanganate of the substances $C_{19}H_{22}O_8N_2$ and $C_{19}H_{22}O_9N_2$ obtained from Hanssen's acid.** H. LEUCHS and A. HOFFMANN (Ber., 1929, **62**, [*B*], 1253—1261).—The acid $C_{19}H_{22}O_9N_2$ reduces permanganate in faintly alkaline solution at 0° almost instantaneously until about 4 atoms of oxygen have been absorbed giving oxalic acid and an *acid*, $C_{17}H_{18}O_8N_2$, which becomes brown without softening at about 300° (also *monohydrate*); the corresponding *hydrochloride*, softening at 250—290° with slight darkening, is described. The acid is not affected by yellow mercuric oxide and hydrobromic acid in water or by bromine and hydrobromic acid. It yields an *oxime*, $C_{17}H_{19}O_8N_3$ (also *monohydrate* and *dihydrate*), and a *semicarbazone dihydrate*. With methyl-alcoholic hydrogen chloride it affords the *hydrochloride* of the *dimethyl* ester, $C_{19}H_{23}O_8N_2Cl,H_2O$. Boiling acetic anhydride transforms the acid into the *compound*, $C_{17}H_{14}O_6N_2$,AcOH, which loses acetic acid when heated and leaves the *dianhydride*, $C_{17}H_{14}O_6N_2$, converted by water into the original acid. Oxidation of the acid $C_{19}H_{22}O_8N_2$ by permanganate yields the *acid* $C_{17}H_{18}O_8N_2,H_2O$.

H. WREN.

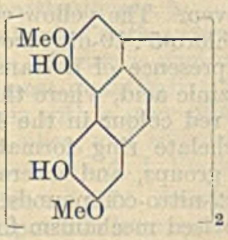
Bimolecular alkaloids. I. Disinomenine and ψ-disinomenine. K. GOTO and H. SUDZUKI (Bull.

Chem. Soc. Japan, 1929, **4**, 107—111; cf. this vol., 830).—When sinomenine is oxidised by potassium ferricyanide, silver nitrate, or similar mild agents, it gives a mixture of bimolecular products, separable by recrystallisation of the hydrochlorides. One substance, *disinomenine*, $(C_{19}H_{22}O_4N)_2$, m. p. 222°, decomp. 245°, $[\alpha]_D$ +149·98°, gives a pink colour with formaldehyde and sulphuric acid, and yields a *hydrochloride*, m. p. above 290°, a *methiodide*, m. p. 263° (decomp.), an *oxime*, m. p. 265° (decomp.), and a *semicarbazone*, m. p. above 290°. Its isomeride, *ψ-disinomenine*, [+MeOH], m. p. 228°, decomp. 245°, $[\alpha]_D$ −127·03°, gives a yellowish-brown colour, and yields a *methiodide*, m. p. 267—268° (decomp.), and a *hydrochloride*, an *oxime*, and a *semicarbazone*, all of which melt above 290°. Acetic anhydride converts either substance into tetra-acetyldisinomenol (cf. A., 1926, 1160; 1927, 146), from which disinomenol, m. p. above 310° (blue colour with ammoniacal silver nitrate in acetone), and the tetramethyl, *tetraethyl* (m. p. 184°), and tetrabenzoyl (new m. p. 280°) derivatives of the last are prepared; disinomenol and its derivatives are distinguished from sinomenol and its derivatives by the fact that the former give with sulphuric acid a brown coloration, changing to a purple flocculation on dilution, whilst the latter give a yellow coloration, destroyed on dilution. The absorption curves of sinomenine, disinomenine, and ψ-disinomenine are given.

Since, like bromosinomenine, in which the bromine atom is considered to occupy the 2-position, the disinomenines give a less intense diazo-coupling reaction than sinomenine itself, and since bromosinomenine does not yield a bimolecular derivative, it is thought that disinomenine and ψ-disinomenine have the formula I, the difference between the two compounds lying possibly in the point of attachment of the bridge linking. Disinomenol is now formulated as II.



(I.)



(II.)

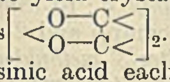
Disinomenine occurs naturally with sinomenine, but ψ-disinomenine has not been isolated from the plant. E. W. Wignall.

Preparation of phosphenyl chloride. J. A. C. Bowles and C. James (J. Amer. Chem. Soc., 1929, **51**, 1406—1408).—Phosphorus trichloride and benzene vapours were passed over a quartz tube sealed in a glass vessel and heated internally by a nichrome winding. The same apparatus may be used to prepare acetamide from ammonia and acetic acid (yield almost theoretical). S. K. Tweedy.

Bromination of *p*-aminophenylarsinic acid. A. Leulier and Y. Dreyfuss (Compt. rend., 1929, **188**, 1416—1418).—Bromination of sodium *p*-aminophenylarsinate with 48% hydrobromic acid and hydrogen peroxide (A., 1924, i, 1297), with varying proportions of these reagents, yields the mono- (nearly theoretical yield) or di-bromo- (85%) derivatives, or tribromoaniline. J. W. Baker.

Reaction between polyhydric alcohols or phenols and arsenic compounds, in particular arsinoacetic acid. B. Englund (J. pr. Chem., 1929, [ii], **122**, 121—140; cf. A., 1928, 1364).—A study has been made of the influence of polyhydroxy-compounds on the solubility of arsenic compounds, from which deductions are made as to the spatial arrangement of the hydroxyl groups. The results are compared with the boric acid and acetone methods of Böeseken, and the possibility of studying molecular configuration by this method is discussed.

Methylarsinic, benzylarsinic, and arsanilic acids each react with two molecules of pyrocatechol in acetic acid to yield crystalline *compounds* containing the group As



$\mathrm{As}\left[<\begin{matrix}\mathrm{O-C<}\\ \mathrm{O-C<}\end{matrix}\right]_2$. Methyl arsinoacetate and resorcinolarsinic acid each react with one molecule of *d*-tartaric acid to yield *compounds* of another type.

By measurement of the solubility of arsinoacetic acid, arsenic trioxide, and resorcinolarsinic acid in acetic acid in presence of hydroxy-compounds it is found that two adjacent hydroxyl groups generally greatly increase the solubility, and this effect is intensified when three or four hydroxyl groups are in a position favourable to the formation of a five-membered ring, as in ethylene glycol, glycerol, erythritol, pyrocatechol, or pyrogallol. β-Glycols, and *m*- and *p*-dihydric phenols, *e.g.*, resorcinol, quinol, and phloroglucinol, have a smaller effect. Stereoisomerides with different spatial configuration of the hydroxyl groups have different effects, *e.g.*, active and *meso*-forms of hydrobenzoin and tartaric acid, *cis*- and *trans*-forms of *cyclo*hexane-, *cyclo*pentane-, and hydrindene-diols. The magnitude of the effect is altered by substitution, *e.g.*, in ethylene glycol, pinacol, and benzpinacol, and in pyrocatechol and protocatechuic acid. The influence of carbonyl or carboxyl groups on the solubility is small, *e.g.*, in succinic acid and benzil. The velocities of the reaction of diols with arsinoacetic acid to form compounds with one and two atoms of arsenic in the molecule have also been investigated both titrimetrically and polarimetrically. Diols with *cis*-hydroxyl groups give consistently greater increases in solubility and higher velocity coefficients than the *trans*-isomerides. R. K. Callow.

10-Chloro-5 : 10-dihydrophenarsazine and its derivatives. IX. Synthesis of nitromethyldiphenylamine-6′-arsinic acids and their conversion into nitromethyl derivatives of 10-chloro-5 : 10-dihydrophenarsazine. Constitution of 10-chloro-5 : 10-dihydrophenarsazine. C. S. Gibson and J. D. A. Johnson (J.C.S., 1929, 1229—1262).—The nitromethyldiphenylamine-6′-arsinic acids were prepared by condensing the appropriate bromonitrotoluenes with *o*-aminophenylarsinic acid or the bromonitrobenzenes with aminotolylarsinic acids (potassium carbonate, amyl alcohol, and copper method). Their ring closure has been studied by conversion into the dichloro- or dibromo-arsine, where isolable, by treating a boiling solution of the arsinic acid in a mixture of alcohol and hydrochloric or hydrobromic acid containing a trace of iodine with sulphur dioxide, followed by boiling in acetic acid solution. The 5 : 10-dihydrophenarsazines formed were oxidised to phenarsazinic acids with hydrogen peroxide in acetic acid. The following compounds were thus prepared : 2-*nitro*-3′-*methyldiphenylamine*-6′-*arsinic acid*, m. p. 215—217° (decomp.); 2-*nitro*-3′-*methyldiphenylamine*-6′-*dichloroarsine*, m. p. 129·5—130°; 10-*chloro*-4-*nitro*-7-*methyl*-5 : 10-*dihydrophenarsazine*, m. p. 201—202°; 4-*nitro*-7-*methylphenarsazinic acid* (I), m. p. 300—303° (decomp.) (*sodium* salt); 4-*amino*-7-*methylphenarsazinic acid* (II), unmelted at 310°, from I and ferrous hydroxide; 10-*chloro*-4-*amino*-7-*methyl*-5 : 10-*dihydrophenarsazine hydrochloride*, m. p. 216—220° (decomp.); 3-*nitro*-3′-*methyldiphenylamine*-6′-*arsinic acid*, m. p. 191—192°; 10-*chloro*- and 10-*bromo*-1(or 3)-*nitro*-7-*methyl*-5 : 10-*dihydrophenarsazine*, m. p. 253—255° (decomp.) and 248—250° (decomp.), respectively : 4-*nitro*-3′-*methyldiphenylamine*-6′-*arsinic acid*, m. p. 276° (decomp.); 2-*nitro*-4′-*methyldiphenylamine*-6′-*arsinic acid*, m. p. 226—227°; 10-*chloro*-4-*nitro*-8-*methyl*-5 : 10-*dihydrophenarsazine*, m. p. 206°; 4-*nitro*-8-*methylphenarsazinic acid*, m. p. 297—300° (decomp.) (*sodium*, *ammonium*, *barium*, *calcium*, and *magnesium* salts); 3-*nitro*-2-*methyldiphenylamine*-6′-*arsinic acid*, m. p. 223—224° (decomp.) (*sodium*, *ammonium*, *barium*, and *calcium* salts); 10-*chloro*- and 10-*bromo*-3-*nitro*-4-*methyl*-5 : 10-*dihydrophenarsazine*, both m. p. 216·5°; 3-*nitro*-4-*methylphenarsazinic acid*, unmelted at 306° (*sodium* salt) : 4-*nitro*-2-*methyldiphenylamine*-6′-*arsinic acid*, m. p. 277° (decomp.) (yield 73%) (*sodium*, *ammonium*, *barium*, *calcium*, *magnesium*, *mercurous*, *mercuric*, *silver*, and *lead* salts); 10-*chloro*- and 10-*bromo*-2-*nitro*-4-*methyl*-5 : 10-*dihydrophenarsazine*, m. p. 303—305° (also produced by reduction of 2-nitro-4-methylphenarsazinic acid) and 301—302°, respectively; 2-*nitro*-4-*methylphenarsazinic acid*, unmelted at 306° (*ammonium*, *barium*, *calcium*, *silver*, *magnesium*, *mercurous*, *mercuric*, *potassium*, and *sodium* salts) : 5-*nitro*-2-*methyldiphenylamine*-6′-*arsinic acid* (III), m. p. 224—226° (decomp.) (*sodium*, *potassium*, *barium*, *lead*, *silver*, *mercurous*, *mercuric*, and *magnesium* salts); 5-*nitro*-2-*methyldiphenylamine*-6′-*dichloroarsine*, m. p. 173°; 10-*chloro*-1-*nitro*-4-*methyl*-5 : 10-*dihydrophenarsazine*, m. p. 258—260°; 5-*nitro*-2-*methyldiphenylamine*-6′-*dibromoarsine*, m. p. 164°, and 10-*bromo*-1-*nitro*-4-*methyl*-5 : 10-*dihydrophenarsazine*, m. p. 272° (decomp.), from III; 1-*nitro*-4-*methylphenarsazinic acid*, unmelted at 305°; 2-*nitro*-6-*methyldiphenylamine*-6′-*arsinic acid*, m. p. 195—197° [from 2-*bromo*-3-*nitrotoluene*, m. p. 41—42°, b. p. 135—136°/8 mm. and 157°/22 mm. (prepared in 67% yield from 2-amino-3-nitrotoluene by the diazo-reaction), and o-aminophenylarsinic acid] (*ammonium*, *sodium*, and *barium* salts); 2-*nitro*-6-*methyldiphenylamine*-6′-*dichloro*- and -6′-*dibromo-arsine*, m. p. 104—105° and 97—98°, respectively : 2-*nitro*-4-*methyldiphenylamine*-6′-*arsinic acid*, m. p. 227—229° (decomp.) (*magnesium* salt); 2-*nitro*-4-*methyldiphenylamine*-6′-*dichloroarsine*, m. p. 91—93°; 10-*chloro*- and 10-*bromo*-4-*nitro*-2-*methyl*-5 : 10-*dihydrophenarsazine*, m. p. 187—188° and 186—188°, respectively; 4-*nitro*-2-*methylphenarsazinic acid*, m. p. 305° (decomp.) (*ammonium*, *sodium*, *silver*, *barium*, and *calcium* salts); 5-*nitro*-3-*methyldiphenylamine*-6′-*arsinic acid*, m. p. 228—230° (decomp.) (*ammonium*, *calcium*, *barium*, *silver*, *mercurous*, *mercuric*, *lead*, *sodium*, and *magnesium* salts); 10-*chloro*- and 10-*bromo*-1(or 3)-*nitro*-3(or 1)-*methyl*-5 : 10-*dihydrophenarsazine*, m. p. 245—247° (decomp.) and 237—242°, respectively; 1(or 3)-*nitro*-3(or 1)-*methylphenarsazinic acid*, unmelted at 300° (*sodium* salt); 3-*nitro*-4-*methyldiphenylamine*-6′-*arsinic acid* (IV), m. p. 165—166° (*barium* salt, $6H_2O$); reduction of IV gave two isomeric ring condensation *products*, $C_{13}H_{10}O_2N_2ClAs$, m. p. 257—258° (decomp.) and 225—226° (decomp.), respectively, oxidation of which yielded two indistinguishable 1- and 3-*nitro*-2-*methylphenarsazinic acids*, unmelted at 297° (*barium* and *sodium* salts); 4-*nitro*-3-*methyldiphenylamine*-6′-*arsinic acid*, m. p. 200° (decomp.) (*sodium* and *ammonium* salts); 10-*chloro*-2-*nitro*-1(or 3)-*methyl*-5 : 10-*dihydrophenarsazine*, m. p. 220—228° (decomp.); 2-*nitro*-1(or 3)-*methylphenarsazinic acid*, unmelted at 308° (*calcium*, *barium*, and *sodium* salts).

The following summarises these and previous results : (1) All substituted nitrodiphenylamine-6′-arsinic acids in which the nitro-group is in the *o*-position to the :NH group yield stable dichloroarsines; when the nitro-group is in the *m*- or *p*-position to the :NH group (exception, 5-nitro-2-methyldiphenylamine-6′-arsinic acid) the corresponding cyclic chloro-compounds are formed on reduction in the presence of hydrochloric acid. (2) All substituted 10-chloro-4-nitro-5 : 10-dihydrophenarsazines are crimson and have lower m. p. and greater solubility in organic solvents than the other nitro-10-chloro-5 : 10-dihydrophenarsazines; the m. p. of the 2-nitro-compounds are very high [exception, 10-chloro-2-nitro-1(or 3)-methyl-5 : 10-dihydrophenarsazine]. (3) 10-Chloro-3-nitro-4-methyl-5 : 10-dihydrophenarsazine is yellow, whereas the 1-nitro-compound is deep red. An explanation of the results based on the electronic theory is given. The yellow colour in simple derivatives of 10-chloro-5 : 10-dihydrophenarsazine is attributed to the presence of a transannular N·As linking (phenarsazinic acid, where this is impossible, is colourless). The red colour in the 4-nitro-compounds is ascribed to chelate ring formation between the nitro- and NH groups, and where this is not possible, *e.g.*, in the 2-nitro-compounds, the compounds are yellow. A revised mechanism for the cyclisation of diphenylamine-6′-arsinic acids, including an explanation of the intermediate formation of dichloroarsines, is given and all the results are interpreted on this basis.

A. I. Vogel.

Meriquinonoid derivatives of dihydrophenarsazine. G. Razubaiev (J. Russ. Phys. Chem. Soc., 1929, 61, 13—26).—See this vol., 585.

***p*-Bromodiethylaniline and mercuric acetate.** F. C. Whitmore, A. R. Cade, and G. J. Leuck (J. Amer. Chem. Soc., 1929, 51, 1952).—Attempts to mercurate *p*-bromodiethylaniline (cf. *p*-bromodimethylaniline, A., 1920, i, 118) under the most varied conditions yielded only ill-defined oxidation products.

H. E. F. Notton.

Mercuration of naphthalic acids. G. J. Leuck, R. P. Perkins, and F. C. Whitmore (J. Amer. Chem.

Soc., 1929, **51**, 1831—1836).—Sodium naphthalate and mercuric acetate in boiling aqueous solution give the *anhydride* of 8-*hydroxymercuri*-1-*naphthoic acid* (*sodium* salt), converted by hydrochloric acid into 1-naphthoic acid. 3-Nitronaphthalic acid gives a mixture (I) of the *anhydrides* of 3-*nitro*- and 6-*nitro*-8-*hydroxymercuri*-1-*naphthoic acids*, the former being the main product. Its *sodium* salt is converted by sodium iodide in alcohol into the *sodium* salt of *mercury bis*-3-*nitro*-8-*naphthyl*-1-*carboxylic acid* (“ No. 93 ”). The mixture, I, gives with hydrochloric acid 3-nitro-1-naphthoic acid, m. p. 270·5—271·5° (*amide*, m. p. 280—280·8°), and 6-nitro-1-naphthoic acid (*amide*, m. p. 216·5°), from which several derivatives were prepared. 4-Nitronaphthalic acid gives on mercuration a mixture of *anhydro*-4-*nitro*-8-*hydroxymercuri*-1-*naphthoic acid* with a little of the 5-*nitro*-derivative, identified by conversion into the 4- and 5-nitro-1-naphthoic acids. 3- and 4-Nitro-1-naphthoic acids are conveniently prepared in this way.

H. E. F. Notton.

Alizarin and mercuric acetate. F. C. Whitmore and G. J. Leuck (J. Amer. Chem. Soc., 1929, **51**, 1951—1952).—Alizarin is converted by excess of (? boiling aqueous) mercuric acetate into (?)1 : 2 : 5 : 8-*tetrahydroxy* - 4 - *acetoxymercurianthraquinone*, which gives with alkali a bluish-red solution and with hydrochloric acid a dye similar to alizarin.

H. E. F. Notton.

Organic derivatives of silicon. XXXIX. Action of sodium on phenoxychlorosilicanes. R. A. Thompson and F. S. Kipping (J.C.S., 1929, 1176—1179).—Interaction of phenol ($2\frac{1}{4}$ mols.) in benzene solution with boiling silicon tetrachloride (1 mol.) and subsequent heating at 200° for 3—4 hrs. gave, on fractionation, *phenoxytrichlorosilicane*, b. p. 183—186°/60 mm., *diphenoxydichlorosilicane*, b. p. 215—218°/60 mm., 199·5—202°/40 mm., *triphenoxychlorosilicane*, b. p. 252—256°/60 mm., 235—239°/25 mm., and 2—5% of phenyl orthosilicate, m. p. 48°. When the three chlorides are heated with sodium in boiling xylene solution, all the chlorine is eliminated as sodium chloride and an almost quantitative yield of phenyl orthosilicate together with a grey powder, probably a mixture of silicon, silica, and silicoformic acid are produced. A. I. Vogel.

Organic derivatives of silicon. XL. Attempts to prepare unsaturated compounds from phenylsilicon trichloride. F. S. Kipping, A. G. Murray, and (in part) J. G. Maltby (J.C.S., 1929, 1180—1191).—Unsuccessful attempts to prepare unsaturated silicon compounds from phenylsilicon trichloride and sodium are described. In all cases a mixture of complex and probably saturated products was obtained. Phenylsilicon trichloride, b. p. 152—153°/200 mm., reacts slowly with sodium in the absence of a solvent at about 190° with the formation of an insoluble powder (25·1—26·8% Si) which is unaffected by alkali hydroxide; in naphthalene solution, a small quantity of an insoluble product (33·9—34·7% Si), yielding hydrogen with alkali hydroxides and giving a residue (13% Si) after evaporation with hydrofluoric acid, together with a large proportion of a benzene-soluble product (Si, 20·1—22·9; C, 61·6—66·8; H, 4·0—4·9%), probably containing naphthyl radicals and $>SiPh_2$ groups, is obtained. Very little interaction occurs in boiling benzene or toluene solutions, but prolonged heating with benzene at about 150° gave an insoluble product similar to that obtained with naphthalene (30—31·5% Si), which gave about 1·35 atoms of hydrogen per atom of silicon on treatment with sodium hydroxide, and a benzene-soluble resin (C, 65·5; H, 4·7; Si, 22·6%) yielding about 2 atoms of hydrogen per atom of silicon when heated with piperidine and sodium hydroxide solution. With boiling xylene as solvent and completion of the reaction by the addition of potassium in a nitrogen atmosphere, a small amount of insoluble product (30·8—33·2% Si) similar to the above, and a xylene-soluble resin, which absorbed about 5% of oxygen on heating at 120° and combined with 1/9—1/4 of its weight of iodine in benzene solution, was obtained. The xylene-soluble resin was systematically fractionated with the aid of acetone and fractions with mol. wts. from about 900 to about 9000 were isolated; the crude product is a mixture of compounds containing from about 6 to at least 50 silicon atoms in the molecule. A. I. Vogel.

Tin tetraphenyl as a phenylating reagent. R. W. Bost and P. Borgstrom (J. Amer. Chem. Soc., 1929, **51**, 1922—1925).—Chlorine, bromine, and iodine monochloride give with tin tetraphenyl high yields of chloro-, bromo-, and iodo-benzenes; alkyl halides give mainly unsaturated hydrocarbons and tin triphenyl halides. *tert.*-Butyl bromide gives a little *tert.*-butylbenzene, and chloroform a little triphenylmethane. Acetyl chloride at 100° gives a little acetophenone, benzoyl chloride at 200° a little benzophenone, and benzenesulphonyl chloride at 200° gives diphenylsulphone (34% of the theoretical). Sulphur and tin tetraphenyl in a sealed tube yield at 170° diphenyl sulphide, at 190° diphenyl disulphide, and at 250° thianthrene. Cold nitric acid gives nitrobenzene, and sulphuryl chloride gives tin triphenyl chloride and tin diphenyl hydroxychloride.

H. E. F. Notton.

Irradiated proteins. VI. Spectroscopic and biological evidence of changes in proteins produced by light. M. Spiegel-Adolf and Z. Oshima. **VII. Ultra-violet absorption of serum- and egg-albumin denatured by heat, ultra-violet-, radium-, and X-rays.** M. Spiegel-Adolf and O. Krumpel (Biochem. Z., 1929, **208**, 32—44, 45—59; cf. this vol., 409).—VI. Egg-albumin and the serum-proteins in feebly alkaline solutions, which prevent visible precipitation, after exposure to a mercury-vapour lamp show increased absorption of the shorter wave-lengths. The absorption increases with the concentration of the alkali (or acid) when this is added before irradiation. Addition of the acid before irradiation produces the same effect as without irradiation, namely an increase in the transparency to ultra-violet rays.

By varying the concentrations of the added electrolytes, the differences in the absorption of serum-albumin and pseudo-globulin can be made to disappear. By the use of irradiated protein solutions or of glass plates of varying transparency as filters for short-wave-length light it is shown that *B. prodigiosus* and *B. coli* exhibit an optimum growth inhibition at different wave-lengths.

VII. Serum- and egg-albumin (with addition of acid or alkali to prevent coagulation) when heated to 100° show an increase in absorption at the shorter wave-lengths from 274·9 μμ. Longer heating of serum-albumin does not increase the absorption, but tends to diminish it. The spectral changes produced by heat are less in amount, but resemble qualitatively those produced by ultra-violet light and by radium irradiation. J. H. Birkinshaw.

Fractionation of partial protein hydrolysates. K. Felix and A. Lang (Z. physiol. Chem., 1929, **182**, 125—140).—The exchange of the sodium of permutite for certain bases (arginine, histidine, ornithine, clupeine) derived from protein hydrolysis follows the law of Rothmund and Kornfeld and is expressed by $(c_1'/c_2')(c_2/c_1)^{\beta}=K$, where c represents the concentration of the bases in solution and c' that in the permutite. The temperature coefficient for arginine is 1·8 per 10°. When arginine and ornithine are present together the latter is selectively taken up. All the bases can be set free from the permutite by ammonia. The method is applied to the partial fractionation of a pepsin hydrolysate of gelatin.
J. H. Birkinshaw.

Micro-determination of sulphur, phosphorus, and arsenic in organic compounds by Gasparini's method. K. Heller (Mikrochem., 1929, **7**, 208—212).—A modified form of Gasparini's method (destruction of organic matter by electrolysis in nitric acid solution) and apparatus suitable for micro-determinations is described. Sulphur, phosphorus, and arsenic are eventually determined, according to established micro-methods, as barium sulphate, ammonium phosphomolybdate, and magnesium pyroarsenate, respectively. The method is unsuitable for the micro-determination of halogens.
J. S. Carter.

Micro-determination of methoxyl and ethoxyl groups. A. Friedrich (Mikrochem., 1929, **7**, 185—194).—The Zeisel determination is modified by replacing the stream of carbon dioxide by an air stream and passing the volatile alkyl iodide through a heated tube packed with copper oxide and lead chromate; the resulting carbon dioxide is determined by absorption. A second determination is then carried out in the normal manner. The constitution of the alkoxy-group is calculable from the weights of carbon dioxide and silver iodide. Complete details are given and sources of error are discussed. J. S. Carter.

Determination of ethylene by absorption in a solution of silver nitrate. V. N. Morris (J. Amer. Chem. Soc., 1929, **51**, 1460—1462).—Silver nitrate solution, preferably concentrated, is suitable for the quantitative absorption of ethylene, which may be recovered by diminishing the pressure.
S. K. Tweedy.

Specific colour reaction for *iso*butyl alcohol. A. Kutzlnigg (Z. anal. Chem., 1929, **77**, 349—352).—Potassium ferrocyanide solution gives with *iso*butyl alcohol an orange coloration, especially in the light. The coloration is not produced by ether, methyl ethyl ketone, ethyleneglycol, glycerol, methyl, ethyl, and *iso*butyl acetates, chloroform, carbon tetrachloride, trichloroethylene, epichlorohydrin, petroleum, benzene and its homologues, phenol, quinoline, tetralin, hexalin, decalin, methylhexalin, *cyclo*hexanone, and methyl*cyclo*hexanone. Amyl acetate gives no coloration on heating, but on irradiation with a quartz–mercury lamp yields a yellow coloration, which, however, may easily be distinguished from that obtained with *iso*butyl alcohol. Although sodium nitroprusside gives no coloration with the alcohol, sodium aminoprusside and aquoprusside are more satisfactory as reagents than potassium ferrocyanide.
H. F. Gillbe.

Reducing power of polyols towards alkaline solutions of potassium iodomercurate. P. Fleury and J. Marque (Compt. rend., 1929, **188**, 1686—1688).—It is found that polyhydric alcohols are able to reduce potassium iodomercurate solution at 100°, the reduction being a function of the alkalinity of the medium and of the duration of the process. With mannitol, dulcitol, inositol, erythritol, glycerol, or glycol the amount of oxygen used is proportional to the number of carbon atoms in the alcohol, and is, in general, a little greater than 1 atom of oxygen per atom of carbon, except in the case of glycerol, where it is nearly 1·5. A similar, but less regular, oxidising action is displayed by potassium iodomercurate towards non-reducing sugars, and becomes less facile with increasing mol. wt. (*e.g.*, towards trioses and tetroses), but is still quite distinct towards a polysaccharide such as glycogen. The activity of the reagent towards acid-alcohols, *i.e.*, the normal products of the oxidation of sugars, is extremely low and in some cases is nil.

Analytical application of the foregoing to the determination of mannitol, inositol, dulcitol, and glycol is described in detail, and compared with the method of Baudouin and Lewin (A., 1927, 476).

The behaviour of the α- and β-glycerophosphoric acid towards potassium iodomercurate is markedly different, and affords a means of distinguishing between them; the α-form is a much more active reducing agent, attributed to the presence of the free secondary alcoholic group, which is not present in the β-form.
C. W. Shoppee.

Iodometric determination of dextrose. V. A. Toscani (Chemist-Analyst, 1929, **18**, No. 2, 7).—Starch paste made by triturating 1 g. of soluble starch with saturated sodium chloride solution, and then adding 100 c.c. of the hot solution, is sensitive and stable. If a reducing sugar is present the solution is made alkaline before adding alkaline ferricyanide solution. To determine dextrose standard potassium ferricyanide solution and 3 c.c. of a mixture of potassium iodide (1 g.), zinc sulphate (2 g.), and sodium chloride (10 g.) in water (40 c.c.) are added, the solution is acidified and titrated with thiosulphate.
Chemical Abstracts.

Micro-potentiometric determination of reducing carbohydrates. J. B. Niederl and R. H. Müller (J. Amer. Chem. Soc., 1929, **51**, 1356—1359).—The potentiometric method of Daggett, Campbell, and Whitman (A., 1923, ii, 345) has been simplified and made suitable for micro- and semi-micro-determinations. S. K. Tweedy.

Reactions of primary arsines. S. S. Nametkin and V. Nekrassov (Z. anal. Chem., 1929, 77, 285—289).—Hydrogen sulphide produces a white amorphous precipitate of the arsine sulphide in aqueous solutions of primary dichloroarsines; from solutions in 96% alcohol the precipitates are crystalline, but the test is not so sensitive. With mercuric nitrate solution the arsines produce a white precipitate of mercurous chloride which rapidly becomes grey in the cases of methyl- and ethyl-dichloroarsines. A. R. Powell.

Determination and separation of formaldehyde and acetaldehyde by means of "methone." D. Vorländer [with C. Ihle and H. Volkholz] (Z. anal. Chem., 1929, 77, 321—327).—"Methone" (5 : 5-dimethyldihydroresorcinol) may be employed for the determination of acetaldehyde and/or formaldehyde by dissolution of the precipitate of methylene- or ethylidene-dimethone in alcohol and titration with sodium hydroxide solution. The methylene compound alone can be dried to constant weight at 90—95°. Alternatively, an excess of standardised methone solution may be added to the aldehyde solution, and the excess of methone titrated with sodium hydroxide solution after removal of the condensation product by filtration. Separation of the two aldehydes may be effected by heating the mixed methone compounds at 100° with four to five times the quantity of acetic acid for 6—7 hrs.; the solution is then precipitated by addition of ice-water, and the precipitate, collected after 12 hrs., is treated with sodium hydroxide solution (*d* 1·095), whereby the formaldehyde compound alone is dissolved, and may be reprecipitated after filtration by acidification with acetic acid. The solubility corrections which must be applied are formaldehydedimethone, 0·001 g., and ethylidenedimethone, 0·008 g. per 100 c.c. of aqueous solution. H. F. Gillbe.

Micro-method for determining semicarbazones and its application to analysis of ketones. R. P. Hobson (J.C.S., 1929, 1384—1385).—Semicarbazide and semicarbazones (the latter after heating for 7—8 hrs.) when heated with a solution containing 15% of hydrochloric acid and 5% of mercuric chloride react thus: $NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2+H_2O=NH_3+CO_2+NH_2{\cdot}NH_2$; $NH_2{\cdot}NH_2+2HgCl_2=N_2+2Hg+4HCl$, yielding one third of their nitrogen as ammonia, the latter being determined by Pregl's modified micro-Kjeldahl method ("Quantitative Organic Microanalysis," 1924, p. 99) with 40% aqueous sodium hydroxide containing an equal volume of a saturated solution of sodium thiosulphate (for the decomposition of the mercury ammonium complex). The application of the method to semicarbazide hydrochloride and the semicarbazones of acetone and *d*-camphor is described. A. I. Vogel.

Micro-determination of methylimides. A. Friedrich (Mikrochem., 1929, 7, 195—201).—The apparatus differs from that customarily used in that condensed hydriodic acid is continuously removed from the gas stream. J. S. Carter.

End-point of the titration in Goldenberg's method of tartaric acid determination. A. Uhl (Z. anal. Chem., 1929, 77, 328—334).—Litmus and azolitmin are not satisfactory indicators on account of the relatively gradual colour change. Electrometric titration is preferable, the best procedure being to titrate to the approximate end-point using azolitmin as indicator, and then to complete the titration (or titrate back) electrometrically. H. F. Gillbe.

Alkalimetric micro-determination of amino-acids and peptides. W. Grassmann and W. Heyde (Z. physiol. Chem., 1929, 183, 32—38).—The method of Willstätter and Waldschmidt-Leitz (A., 1922, ii, 169) has been adapted for use with 0·2 c.c. of an amino-acid solution. Phenolphthalein is replaced by 0·1% alcoholic thymolphthalein and the micro-titration is carried out with 90% alcoholic potassium hydroxide (0·01*N*). The end-point is determined by comparison with the blue colour obtained with 0·0025*M*-copper chloride and excess of ammonia. With pure amino-acids and peptides the method is accurate to ±1% even at a concentration of about 0·002*M*, thus agreeing with the macro-method. Determination of the rate of enzymic hydrolysis of peptides and gelatin by the micro-method compares favourably with the macro-method, but the degree of accuracy is less than with the pure amino-acids: this is attributed to the effect of the buffer solutions and protein on the end-point. H. Burton.

Conditions for the determination of cocaine in physiological material. E. Sadolin (Dansk Tidsskr. Farm., 1929, 3, 188—196; cf. A., 1927, 264).—Owing to the ease with which cocaine is hydrolysed by alkalis, its extraction by ether should be carried out in a solution the p_H value of which is less than 9, *e.g.*, by employing sodium hydrogen carbonate. Of the total cocaine originally present in physiological material 60—80% can thus be recovered, even when a prolonged extraction is necessary on account of emulsification, but with urine a satisfactory determination is practicable only if the urine has an acid reaction. H. F. Harwood.

Determination of urobilin. M. Royer (Compt. rend. Soc. Biol., 1928, 99, 1003—1005; Chem. Zentr., 1929, i, 419).—The fluorescence produced by the addition of zinc salts is compared with that of a solution of trypaflavin (10 mg. per litre corresponding with 0·613 mg. of urobilin per litre of water). A. A. Eldridge.

Biochemistry.

Chemistry of over-ventilation. G. Popoviciu and H. Popescu (Compt. rend. Soc. biol., 1929, 101, 406—408).—In convulsions caused by over-ventilation there is an increase in serum-calcium and a decrease in the serum-phosphate. The decrease in phosphate is reduced by ergotamine and increased by adrenaline and ephetonine. All these drugs tend to reduce the serum-calcium. E. Boyland.

Elimination of carbon dioxide in insects. W. H. Thorpe (Science, 1928, **68**, 433—434).—The elimination of carbon dioxide by various larvæ has been followed by means of a 1% solution of *o*-chlorophenol-indophenol as indicator, and confirmed by means of barium hydroxide. L. S. Theobald.

Determination of the carbon dioxide content of the mixed venous blood. II. Carbon dioxide equilibria between mixed venous blood and re-breathed airs. M. C. G. Israëls and F. W. Lamb (J. Physiol., 1929, **67**, 315—324).—For accurate determination of the carbon dioxide tension of oxygenated blood, the subject should re-breathe into 4 litres of a mixture containing 3·5% of oxygen and 6·5% of carbon dioxide, for 10—12 sec., and the air finally expired should be analysed. E. Boyland.

Effect of temperature on the equilibrium of carbon dioxide and blood, and heat of ionisation of hæmoglobin. G. S. Adair, N. Cordero, and T. C. Shen (J. Physiol., 1929, **67**, 288—298).—The heat of ionisation of hæmoglobin calculated from the carbon dioxide dissociation curves of blood and hæmoglobin at different temperatures is less than that obtained by calorimetric methods. The heat of ionisation of the carboxyl groups varies with $p_{\rm H}$; the calorimetric results are high because the $p_{\rm H}$ at which they are determined is greater than that of the blood. E. Boyland.

Respiratory proteins of the blood. IV. Buffer action of hæmocyanin in blood of *Limulus polyphemus*. A. C. Redfield, G. Humphreys, and E. Ingalls (J. Biol. Chem., 1929, **82**, 759—773).—Titration curves are given for the blood-serum of *Limulus*, and for solutions of the hæmocyanin in distilled water and in presence of salts. The curve given by the blood-serum is closely imitated by a solution of hæmocyanin in water in presence of an amount of magnesium chloride equivalent to that contained in the blood, the ionic strength of the solution being made up to that of the blood by addition of sodium chloride. It thus appears that the buffer value of *Limulus* blood is almost entirely accounted for by the hæmocyanin. The excess base in the normal blood-serum amounts to $18—37\times10^{-5}$ mol. per g. of hæmocyanin. C. R. Harington.

Glycolytic power of polymorphonuclear leucocytes. P. Mauriac (Compt. rend. Soc. Biol., 1929, **101**, 374—376).—Polymorphonuclear leucocytes are much more effective in utilisation of dextrose than are ordinary leucocytes. This glycolysis is unaffected by insulin. E. Boyland.

Micro-determination of blood-sugar. I. Ogawa and K. Kodama (J. Biochem. Japan, 1928, **10**, 1—4).—The blood is deproteinised with acetic acid and potassium ferricyanide and then boiled with sodium carbonate, when the sugar causes reduction to ferrocyanide. The cooled solution is acidified with acetic acid, ferric chloride is added, and the blue coloration is matched against comparison solutions. Chemical Abstracts.

Sugar in blood and cerebrospinal fluid. S. Katzenelbogen (J. Pharm. Exp. Ther., 1929, **36**, 231—234).—The cerebrospinal-fluid-sugar level depends on the level of the blood-sugar. The ratio of the two may vary within wide limits. The meningeal permeability to dextrose may be modified in the same rabbit without apparent change in condition. F. C. Happold.

Participation of a phosphorus compound in glycolysis of blood *in vitro*. A. Roche and J. Roche (Bull. Soc. Chim. biol., 1929, **11**, 549—599).—The blood-sugar undergoes rapid glycolysis *in vitro*; blood-phosphate remains constant, but increases rapidly as glycolysis lags or ceases. The addition of dextrose to a system in which glycolysis is complete revives this process and the increase in the free phosphate content of the blood lags temporarily; such addition to fresh blood increases glycolysis and phosphate fixation. The addition of a certain amount of phosphate hastens glycolysis, but further addition is without effect. Simultaneous addition of both dextrose and phosphate increases the rate of glycolysis and lengthens the period during which phosphate is not liberated. The threshold of activation of glycolysis by phosphate is a function of the concentration of dextrose in the blood. Added calcium chloride increases the liberation of phosphate but does not effect glycolysis, sodium citrate effects neither, potassium oxalate retards glycolysis, whilst sodium fluoride stops it and delays the liberation of phosphate. When calcium chloride is added after 30 min. delay to blood treated with sodium fluoride, glycolysis is activated, whilst addition after 24 hrs. causes an abundant liberation of phosphate but no glycolysis. The degradation of dextrose occurs simultaneously with phosphate fixation. F. C. Happold.

Determination of chloride in serum and red corpuscles. M. M. Levy (Bull. Soc. Chim. biol., 1929, **11**, 633—634).—To 1 c.c. of serum are added 10 c.c. of silver nitrate (2·906 g. per litre), 1·4 c.c. of saturated potassium permanganate solution, and 4 c.c. of nitric acid. The whole is boiled until the precipitate is white, cooled, and 0·5 c.c. of saturated iron alum solution is added. The excess of silver nitrate is titrated against a standard solution of potassium thiocyanate. The method can be applied to the red corpuscles. F. C. Happold.

Micro-determination of chlorides in blood and cerebrospinal fluid. D. S. Schefer (Zhur. exp. Biol. Med., 1928, **10**, 261—265).—The blood (0·1 c.c.) is treated with (1 : 3) nitric acid (3 c.c.) and hydrogen peroxide solution (1 c.c.), heated to coagulate the protein, and centrifuged, the residue being again treated with nitric acid (2 c.c.) and centrifuged. The united liquids are mixed with 0·01N-silver nitrate (2 c.c.), the solution is centrifuged, and the liquid is titrated with 0·01N-ammonium thiocyanate. In the analysis of cerebrospinal fluid the hydrogen peroxide is omitted. Chemical Abstracts.

Determination of sulphur in blood and organic products. A. Lesure and A. Dunez (Bull. Soc. Chim. biol., 1929, **11**, 600—608).—Certain procedures in a previous method are elaborated (A., 1928, 1270). Trichloroacetic acid may be required to remove traces of proteins from serum even after a second treatment with acetic acid. Benzidine hydrochloride is suggested as more suitable than benzidine in the preparation of the sulphate precipitant. In the determinations of free sulphate and of total oxidised sulphur, the deproteinised serum is first dried and extracted with alcohol at 96°. Sera having total sulphur content exceeding 0·18 part per 1000 and ratios of oxidised sulphur to total sulphur less than 1 : 2 are definitely pathological. The total sulphur content of some defatted normal and pathological tissues has been determined. F. C. Happold.

Micelle changes produced by the addition of crystalloids to serum. G. Cluzet (Compt. rend. Soc. Biol., 1929, **101**, 458—461).—The viscosity and refractive index of serum have maxima at p_H 5·5, but the maximum conductivity occurs at p_H 7·0. Electrolytes affect these physical properties but sucrose and dextrose do not. E. Boyland.

Fractionation of water-soluble proteins of blood-serum. S. Goldschmidt and H. Kahn (Z. physiol. Chem., 1929, **183**, 19—31).—Treatment of ox blood-serum with solid ammonium sulphate to give a concentration of 26% causes the precipitation of the globulin. The ammonium sulphate content of the filtrate is increased to 36%, which precipitates an albumin fraction, and subsequent saturation of the filtrate from this yields a further albumin fraction. Purification of these by electrodialysis and subsequent precipitation within the following limits of concentration of ammonium sulphate, 29—33, 33—36, and 37—41%, affords three fractions, the elementary analyses, nitrogen distributions, and histidine and tryptophan contents of which were determined. The most soluble fraction (precipitated by 37—41% ammonium sulphate; 4% of total albumin) contains no tryptophan and the maximum quantity of histidine. H. Burton.

Blood chemistry of rattlesnakes. J. M. Luck and L. Keeler (J. Biol. Chem., 1929, 82, 703—707).—Analytical figures are given for the blood of two species of rattlesnake, *Crotalus atrox* and *C. oregonus*; the blood is chiefly characterised by the almost complete absence of carbamide and by the high content of amino-acids. C. R. Harington.

Blood coagulation. Retardation and acceleration. E. Waldschmidt-Leitz, P. Stadler, and F. Steigerwaldt (Z. physiol. Chem., 1929, **183**, 39—59).—The coagulation of goat's blood, in presence of isotonic sodium chloride solution at 37°, is inhibited by hirudin, and a "hirudin unit" is defined as the amount necessary to prolong the normal period of clotting (5 min.) to 25 min. The number of these units in 1 g. of a preparation is termed the "hirudin value." Extraction of leeches' heads with various solvents and subsequent determination of the hirudin values shows that aqueous glycerol is the best medium. Attempted precipitation of hirudin from an extract by heavy metal salts is unsatisfactory, but adsorption on aluminium hydroxide at p_H 4·7 is almost quantitative, and almost complete elution is obtained using ammonium phosphate solution. The activity of a neutral, aqueous solution is only slightly impaired by boiling for several hours, but in presence of sodium chloride solution it undergoes complete loss of activity after 4 hrs. at 100°. The activity is also destroyed by trypsin-kinase, pepsin, and papain–hydrogen cyanide at their optimum p_H values. Purification of an extract is effected by adsorption of impurities on kaolin, subsequent adsorption on aluminium hydroxide, and elution of the adsorbate. The hirudin is then obtained by precipitation with alcohol and ether.

Heparin (cf. Howell, A., 1925, i, 1346; 1928, 318), obtained from dog liver, affects the coagulation of blood in almost an identical manner to hirudin. It is purified by the above method. The enzymic destruction, however, differs from that of hirudin. Proteolytic substrates (proteoses and peptides) usually retard coagulation, whilst trypsin-kinase causes an acceleration. H. Burton.

Sensitisation of erythrocytes by amboceptors of specific sera. A. P. Konikov (Zhur. exp. Biol. Med., 1928, **10**, 357—366).—Combination of erythrocytes with amboceptors is optimal at p_H 6·0—6·7, and at a definite salt concentration; the presence of an electrolyte is essential. The process of sensitisation is interpreted as an ionic reaction resulting in the formation of a complex containing stroma, amboceptor, and salt. Chemical Abstracts.

Behaviour of hæmolytic, complement-free hæmolytic, and normal sera in presence of chemical hæmolysers. K. C. Sen and N. N. Mitra (J. Indian Chem. Soc., 1929, 6, 155—170).—Hæmolysis of sheep's red blood-corpuscles by saponin, potassium oleate, sodium taurocholate, 0·002*N*-hydrochloric acid, and 0·04*N*-sodium hydroxide, in presence of sodium chloride solution, is inhibited by a low concentration of added hæmolytic serum. With larger concentrations of the serum, in presence of saponin and oleate, the time of hæmolysis is practically the same as with the serum alone, the effect of the chemical hæmolyser being inhibited almost entirely. Under similar conditions, hydrochloric acid and taurocholate cause an inhibition, sodium hydroxide an acceleration. Using complement-free serum, the hæmolysis by saponin and taurocholate is inhibited to a greater extent than with hæmolytic serum. The results previously described (Sen and Sen, A., 1928, 1151) on the inhibition of taurocholate hæmolysis by normal serum are confirmed. Using low concentrations of corpuscles and small amounts of serum inhibition also occurs, but with relatively large quantities of serum there is an acceleration (cf. Ponder, A., 1923, i, 975); a similar phenomenon is observed with oleate. The acceleration depends also on the time interval after which the serum is added to the corpuscle–hæmolyte mixture, since addition before or with the hæmolyte causes inhibition. No acceleration of saponin hæmolysis by normal serum was observed under the conditions studied. H. Burton.

Hæmolysis in sucrose solution and behaviour of normal serum in presence of chemical hæmolytes. A. C. Roy and K. C. Sen (J. Indian Chem. Soc., 1929, 6, 171—180).—The time–dilution curves for the hæmolysis of sheep's red blood-corpuscles by taurocholate, saponin, and oleate in presence of sucrose solution are normal except for high concentrations of taurocholate (cf. this vol., 589). The inhibiting action of the sugar is confirmed. Inhibition or acceleration of the time of hæmolysis by taurocholate or oleate can be obtained by addition of normal serum, depending on the time interval after which the serum is added to the mixture (cf. preceding abstract). With low corpuscle concentration, an increased amount of serum causes an acceleration. The results are analogous to those obtained in presence of sodium chloride solution.

H. Burton.

Effect of p_H on saponin hæmolysis. M. Bodansky (J. Biol. Chem., 1929, 82, 567—577).—The effect of acid on saponin hæmolysis observed by Ponder (A., 1926, 751) is compounded of two effects, (*a*) the formation of an ionisable compound with the saponin which retards hæmolysis and (*b*) the action on the blood-corpuscles themselves, which, as their positive charge increases on the acid side of the isoelectric point, become more sensitive to saponin, and, conversely, are more resistant at alkaline reactions. This effect of p_H on the blood-corpuscles themselves is predominant. C. R. Harington.

Electro-osmosis as the principal factor in specific hæmolysis. A. P. Konikov (Zhur. exp. Biol. Med., 1928, 10, 368—383).—The combination between complement and salt is chemical in nature.

Chemical Abstracts.

Relation of chromatin to hæmoglobin and bilirubin. H. H. Riecker (J. Exp. Med., 1929, 49, 937—943).—The iron content of the spleen and bone-marrow (determined histologically) depends on the chromatin content, being high when hæmoglobin is being formed. E. Boyland.

Structure and composition of hæmosiderin. S. F. Cook (J. Biol. Chem., 1929, 82, 595—609).—Hæmosiderin granules were extracted in an unaltered condition from spleen pulp by digestion of the tissue with dilute potassium hydroxide solution in the cold. Treatment of the granules with hydrochloric acid removed the iron as ferric chloride, leaving colourless stromata. Extraction of the granules with 1% nitric acid gave a brown solution from which, by increasing the acid to 20%, there was precipitated a coloured compound containing only iron (44%), hydrogen, and oxygen; traces of ionised iron were left in the mother-liquor. It appears therefore that the granules consist of a stroma impregnated with a colloidal form of ferric hydroxide, this supposition being confirmed by the fact that the qualitative reactions of the pigment extracted by 1% nitric acid could be imitated by those of a solution of colloidal ferric hydroxide prepared artificially.

C. R. Harington.

Nature of the sugar residue in the hexosemonophosphoric acid of muscle. J. Pryde and E. T. Waters (Biochem J., 1929, 23, 573—582).—The hexosephosphoric acid of normal muscle press-juice from rabbit, goat, and donkey is a monophosphoric acid, $[\alpha]_{5461}$ of brucine salt $-20{\cdot}3°$ in methyl alcohol. The diphosphoric acid, identical with that of yeast fermentation, is obtained only when the fermentative resynthesis using sodium fluoride is employed (cf. Embden and Zimmermann, A., 1925, i, 729; 1927, 749). The carbohydrate residue of muscle hexosemonophosphoric acid consists of 90% of dextrose and 10% of ketose.

S. S. Zilva.

Regularity of variation of characters of oils extracted from an animal as a function of the section used. L. Margaillan (Compt. rend., 1929, 188, 1630—1632; cf. Marcelet, B., 1926, 677).—Oils extracted out of contact with air from the fatty tissues of specific sections of the *Delphinus tursio*, Fabr., show a regular increase in their iodine value proceeding from the head to the tail. In order to characterise the oil it is therefore necessary to define rigorously the section of the tissues extracted.

C. C. N. Vass.

Unsaponifiable material. I. Distribution of unsaponifiable matter in the animal body. E. Igarashi (Sei-I-Kwai Med. J., 1928, 47, No. 9; Abstr. 1—2).—In the rabbit the voluntary muscle contains less cholesterol and more unknown unsaponifiable substance than involuntary muscle; the unknown unsaponifiable substance is present chiefly in the nervous system and endocrine organs. The ratios of fatty acid to cholesterol and to the unknown saponifiable substance are constant in organs of different animals. Chemical Abstracts.

Behaviour of cholesterol in the animal body. I. Determination of cholesterol in tissue. J. Onizawa (J. Biochem. Japan, 1928, 10, 45—61).—The finely-minced tissue is mixed with twice its volume of 2% sodium hydroxide solution; after several hours, the mixture is heated at 100° for 30—60 min. until almost complete dissolution is effected. The liquid and the rinsings (water, acetone, ether) of the vessel are vigorously shaken, the ether layer is separated, and the extraction repeated twice, with careful rinsing (ether). The ethereal solution is washed with dilute alkali, the ether is removed, and the residue dried on a water-bath and then in an oven at 80°. An ethereal solution of the residue is filtered through an asbestos filter; after removal of the ether the substance is treated while warm with acetone and filtered, after 4 hrs., through asbestos. After evaporation of the acetone, the substance is dissolved in chloroform or ether, and the solution is used for the determination, the cholesterol (1—3 mg.) being precipitated with a 1% solution of digitonin in 80% alcohol. After 12 hrs. the mixture is kept for 5—10 min. with acetone (80%) at 40—50°, centrifuged, and the supernatant liquid filtered through asbestos. The precipitate is washed twice with 80% acetone, then transferred to the filter with pure acetone, washed (ether, acetone, water), and dried in a vacuum at 105°. The error for 1 mg. does not exceed 3%. For the determination of cholesteryl esters saponification is effected with saturated alcoholic sodium hydroxide for 6 hrs. at 100°, whereby, however, a loss (2—3%) of the digitonin compound occurs.

Chemical Abstracts.

Spectrographic analysis of the ash of blood and organs. P. Dutoit and C. Zbinden (Compt. rend., 1929, 188, 1628—1629).—By means of the arc spectra the following metals have always been observed in the ash of blood, lightly calcined to avoid any loss of volatile chlorides and phosphorus compounds:

silver, aluminium, calcium, copper, iron, potassium, magnesium, manganese, sodium, phosphorus, silicon, titanium, and zinc. In some samples, cobalt, chromium, germanium, lead, nickel, tin, and strontium were observed. The analysis of the ash of tumours and organs showed a selective adsorption or absence of the heavy metals; thus nickel, cobalt, and lead accumulated in the pancreas, the suprarenal glands retained tin, and zinc predominated in the liver and kidney. Copper and silver appear to be absent from tumours. C. C. N. VASS.

Occurrence of nickel in bones. A. MARTINI (Mikrochem., 1929, 7, 235).—The presence of nickel in gelatin has been traced to the bones used in its manufacture. Nickel is apparently a normal constituent of bones. J. S. CARTER.

Colostrum of East Friesian milch sheep. A. BURR (Landw. Jahrb., 1928, 68, Suppl. I, 176—178; Chem. Zentr., 1929, i, 163).—The dry matter is high, the lactose at first low, rising later from 2 to 5%, the chlorine low (0·07%), and ash content 1%. Nitrogenous substances immediately after lambing are high (17·89—23·12). A. A. ELDRIDGE.

Colostrum. A. L. PROVAN (Welsh J. Agric., 1928, 4, 141—147).—Average values, for shorthorn cows, of colostrum from the second and third milkings, 12 hrs. and 24 hrs., respectively, after calving, and of normal milk were: total solids 20·65, 16·68, 12·63; fat 3·31, 3·50, 3·69; solids not fat 18·26, 13·18, 8·94; protein 13·05, 8·15, 3·41; ash 0·937, 0·817, 0·708; CaO 0·2011, 0·1864, 0·1646; P_2O_5 0·3390, 0·3269, 0·2324; K_2O 0·1902, 0·2005, 0·1952; Cl 0·1323, 0·1135, 0·0962%. Samples of colostrum exhibited considerable individual variations. Analyses of samples of colostrum at different periods after calving showed a rapid diminution of the protein and chloride contents, and a slow diminution of the lime and phosphate contents. The fat content of colostrum decreased with increasing age of the cow. Variations with the number of calvings and with the breed of cows are recorded. CHEMICAL ABSTRACTS.

Inorganic constituents of milk. N. C. WRIGHT and J. PAPISH (Science, 1929, 69, 78).—Spectrographic examination of cow's milk obtained from various localities in Great Britain and the United States showed the presence in small but definite traces of the following elements not previously identified in milk: silicon, boron, titanium, vanadium, rubidium, lithium, and strontium. One sample of dried milk contained more than the usual amount of copper; another sample obtained from cows pasturing near zinc smelters contained an abnormal quantity of zinc. L. S. THEOBALD.

Physiology of the pancreas. IV. Elimination of dyes in the external secretion of the pancreas. L. A. CRANDALL, E. OLDBERG, and A. C. IVY (Amer. J. Physiol., 1929, 89, 223—229).—Sodium thiocyanate and some dyes (*e.g.*, fuchsin, fluorescein, methylene-blue, rhodamine, and safranine) after intravenous injection are excreted to a slight extent in the pancreatic secretion. E. BOYLAND.

Inorganic composition of body fluids of the *Chelonia*. H. W. SMITH [with H. SILVETTE] (J. Biol. Chem., 1929, 82, 651—661).—The pericardial and perivisceral fluids of turtles contain considerably more hydrogen carbonate and correspondingly less chloride than the blood-serum; the potassium, calcium, and magnesium may also be reduced in comparison with the blood, although the total base content of both fluids remains about the same. A transudate which is sometimes to be found in the infra-cardial spaces has the composition of a simple ultrafiltrate of the blood-serum, and is characterised as lymph. The unequal distribution of hydrogen carbonate between the blood and the tissue fluids is ascribed to a secretory activity on the part of the cell membranes determining the transport of certain ions. C. R. HARINGTON.

Fat excretion. VI. Excretion by Thiry-Vella fistulas. R. W. ANGEVINE (J. Biol. Chem., 1929, 82, 559—565).—Figures are given for the composition of the lipins excreted by an isolated loop of small intestine in dogs. Both the total amount and the composition of this lipin fraction were independent of the diet of the animal as well as of the level of the small intestine selected. C. R. HARINGTON.

Loss of water and salts through the skin. W. HANCOCK, A. G. R. WHITEHOUSE, and J. S. HALDANE (Proc. Roy. Soc., 1929, B, 105, 43—59).—Loss of water from the skin in temperate climates is largely due to the evaporation of water passing by osmosis through the skin, and the amount of chloride lost is small. As the loss of water becomes greater due to true sweating the percentage of chloride in the water increases and true sweat contains about nine times as much sodium chloride as potassium chloride. The percentage of chloride in true sweat can increase with duration and rate of sweating from 0·06 to 0·22%. E. A. LUNT.

Nitrogen excretion of fishes. H. DELAUNAY (Compt. rend. Soc. Biol., 1929, 101, 371—372).—Teleosts like marine invertebrates excrete nitrogen mainly in the form of ammonia but the elasmobranchs excrete urea. E. BOYLAND.

Biochemical determination of allantoin in urine. R. FOSSE, A. BRUNEL, and P. DE GRAEVE (Compt. rend., 1929, 188, 1632—1634).—In alkaline media, the allantoinase and urease of soya-bean extract transform allantoin into allantoic acid and destroy the urea; subsequent treatment with hydrochloric acid destroys the urease and liberates urea, which is then weighed as dixanthylcarbamide, from allantoic acid. In order to eliminate the urea formed from uric acid by the soya-bean extract (Nemec, A., 1921, i, 213), the uric acid is first removed by precipitation with acid mercuric sulphate. Preliminary determinations of the allantoin content of some animals' urine are recorded. C. C. N. VASS.

Ammonia coefficients of urine. R. GOIFFON (Bull. Soc. Chim. biol., 1929, 11, 531—542).—The application of the constants of Hasselbalch and others to the study of the renal regulation of the acid–base equilibrium is limited. F. C. HAPPOLD.

Origin of urinary ammonia. S. R. BENEDICT and T. P. NASH, jun. (J. Biol. Chem., 1929, 82, 673—678).—The work of Bliss (this vol., 339) and of

Embden and others (*ibid.*, 346) on ammonia formation and utilisation in the organism is criticised. The authors' previous view (A., 1922, i, 191) that urinary ammonia is formed in the kidney is confirmed, carbamide being regarded as the probable precursor.
C. R. Harington.

Purine bases in urine of dogs. H. Lethaus (Z. physiol. Chem., 1929, **183**, 98—102).—Dogs fed on a diet of meat and rice excrete uric acid, hypoxanthine, adenine, and xanthine. H. Burton.

Micro-determinations of carbon and nitrogen in fæcal material. A. Boivin and J. Roche (Bull. Soc. Chim. biol., 1929, **11**, 543—548).—A modification of the method of Nicloux is preferred to Pregl's micro-method for the determination of carbon in dried fæces, and the micro-Kjeldahl to the micro-Dumas method for the determination of nitrogen.
F. C. Happold.

Insulin in acromegalic diabetes. H. Ulrich (Arch. Int. Med., 1929, **43**, 785—794).—A review of the literature demonstrates that the view is unfounded that diabetes associated with acromegaly responds to treatment by insulin as well as does pancreatic diabetes. W. O. Kermack.

The cholesterol of the blood-plasma in epilepsy. M. Gosden, J. T. Fox, and W. R. Brain (Lancet, 1929, ii, 12—16).—Epilepsy is accompanied by a decrease in the cholesterol of the blood-plasma.
E. Boyland.

Influence of iodine on the excretion of creatine in exophthalmic goitre. W. W. Palmer, D. A. Carson, and L. W. Sloan (J. Clin. Invest., 1929, **6**, 597—608).—Administration of iodine diminished creatinuria. Chemical Abstracts.

Optimal hydrogen-ion concentrations in colloidal gold in the Lange test. H. Nicol (J.S.C.I., 1929, **48**, 100T).—The author concludes that a slightly alkaline sol is preferable. Dilute oxalic acid may be used to adjust the p_H without affecting the physical condition of the sol.

Early detection of mastitis by examination of milk. G. Roeder (Fortschr. Landw., 1928, **3**, 871—873; Chem. Zentr., 1929, i, 163).—Mastitis is accompanied by a higher, and then by a lower, p_H than that (6·3—6·6) of normal milk. Bromothymol-blue is used as indicator. A. A. Eldridge.

Experimental dehydration; chemical changes in the blood of the dog contrasted with those following obstruction of the cardiac end of the stomach. R. L. Haden and T. G. Orr (J. Exp. Med. 1929, **49**, 945—953).—In dehydration by intestinal obstruction and administration of sucrose, the blood-chlorides and the urine output are higher than in simple obstruction, whilst the total protein and non-protein-nitrogen are lower. E. Boyland.

Carbohydrate metabolism in parathyroidectomised dogs. C. I. Reed (Amer. J. Physiol., 1929, **89**, 230—238).—The tetany following parathyroidectomy is relieved by administration of dextrose, but during the tetany the dextrose tolerance is lower than normal. E. Boyland.

Effect of insulin on parathyroidectomised dogs. C. I. Reed (Amer. J. Physiol., 1929, **89**, 239—242).—Parathyroidectomy does not influence the effect of insulin on the blood-sugar, but insulin produces an increase in the blood-calcium and decrease in the blood-phosphate. E. Boyland.

Prevention of tetany of parathyroidectomised dogs. III. Ammonium chloride. I. Greenwald (J. Biol. Chem., 1929, **82**, 717—725).—Administration of ammonium chloride relieves tetany in parathyroidectomised dogs with coincident increased excretion of phosphorus, sodium, and potassium. The relief of tetany is probably due to diminished reflex excitability associated with the condition of acidosis. C. R. Harington.

Absorption of phosphorus in normal and rachitic children. G. Murdoch (Arch. Dis. Childhood, 1927, **2**, 285—301).—Increased serum-phosphate was observed on administration of sodium hydrogen phosphate to normal and rachitic children; addition of calcium lactate diminished the effect.
Chemical Abstracts.

Suprarenal insufficiency. IV. Blood-sugar in suprarenalectomised rats. L. C. Wyman and B. S. Walker (Amer. J. Physiol., 1929, **89**, 215—222).—Suprarenalectomy produced a marked fall in blood-sugar, but this could be maintained at a normal level by transplanted cortical tissue.
E. Boyland.

Serum-calcium of cats during fasting. S. Morgulis and A. M. Perley (Amer. J. Physiol., 1929, **89**, 213—214).—The serum-calcium of cats remained fairly constant during fasting.
E. Boyland.

Calcium and magnesium relationships in the animal. W. P. Elmslie and H. Steenbock (J. Biol. Chem., 1929, **82**, 611—632).—Administration of magnesium salts was without effect on the metabolism of calcium in rats on normal diets and on diets deficient in calcium; the severity of the rickets produced in rats by diets rich in calcium and low in phosphorus was not increased by simultaneous administration of magnesium. Therapeutic use of magnesium therefore appears to be without danger.
C. R. Harington.

Metabolism of sulphur. XVI. Diet and composition of hair in the young white rat. H. D. Lightbody and H. B. Lewis (J. Biol. Chem., 1929, **82**, 663—671).—The previous conclusion (this vol., 843) that cystine is utilised primarily for growth requirements and secondarily for the formation of hair is confirmed. The cystine and sulphur content of the hair of young rats was reduced by deficiency of cystine in the diet, no such reduction being observed in cases of retardation of growth by dietary deficiency of other amino-acids. C. R. Harington.

Nerve metabolism. V. Phosphates. R. W. Gerard and J. Wallen (Amer. J. Physiol., 1929, **89**, 108—120).—Rest in nitrogen causes a breakdown of the acid-labile and acid-stable forms of combined phosphate, to produce inorganic phosphate. This is reversed in oxygen. Stimulation in oxygen produces the same changes as occur with rest in nitrogen, but the change is not so great. E. Boyland.

Alleged toxicity of galactose. L. Randoin and R. Lecoq (Compt. rend. Soc. Biol., 1929, **101**, 355—357).—With a suitable diet pigeons are able to utilise galactose satisfactorily, when it forms the only sugar of the food. E. Boyland.

Origin and destination of cell-fat. J. Amar (Compt. rend., 1929, **188**, 1626—1628).—Biochemical, biological, and thermal reactions and clinical data are employed to support the view that lipogenesis takes place in the cytoplasm at rest, glycogenesis during muscular activity. C. C. N. Vass.

Behaviour of aminobenzoic acid in the body of lower animals. T. Kamei (J. Biochem. Japan, 1928, **10**, 189—195).—In the frog, *o*-, *m*-, and *p*-aminobenzoic acids are excreted (20%) unchanged. Neither uraminobenzoic nor aminohippuric acid was found. In the turtle the *m*- and *p*-compounds behave likewise, but of the *o*-compound only 3% appears in the urine. Chemical Abstracts.

Basal metabolism of inhabitants of the tropics. P. J. T. van Berkhart (Med. Dienst. Volks. Ned.-Indie, Reprint, 1929, 69 pp.).—The basal metabolism of Europeans and Malays living in the tropics is lower than that of Europeans living in temperate climates. F. C. Happold.

Basal metabolism of inhabitants of the tropics. C. Eykman (Med. Dienst. Volks. Ned.-Indie, Reprint, 1928, 4 pp.).—Polemical: A reply to van Berkhart (preceding abstract). F. C. Happold.

Hydrogen-ion concentration of the reproductive organs of the White Leghorn chicken. G. D. Buckner and J. H. Martin (Amer. J. Physiol., 1929, **89**, 164—169).—The mucosa of the upper part of the oviduct of an actively laying chicken has p_H 6·3—6·6 and that of the uterus and vagina has p_H 5·6—5·9. The semen of the vesicles of a cock is at p_H 7·3. The albumin of an egg has p_H 7·4 in the uterus, 8·2 when freshly laid, and 9·8 20 days after laying. E. Boyland.

Effect of p_H on the action of certain poisons. A. A. Ljubuschin (Zhur. exp. Biol. Med., 1928, **10**, 277—283). Chemical Abstracts.

Phosphorus poisoning in rabbits. A. Huruya (J. Biochem. Japan, 1928, **10**, 63—95).—The urinary nitrogen is increased in mild, and decreased in severe, intoxication; the urea fraction decreases, and the ammonia fraction increases, with the degree of intoxication. Injection of phosphorus causes increased excretion of sulphur. Affection of the kidneys is accompanied by high values for the blood-non-protein-nitrogen and -sulphate. Chemical Abstracts.

Detection of lead in body-fluids and tissues. D. Ganassini (Arch. Ist. Biochim. Ital., 1929, **1**, 105—112).—Addition to serum containing lead of a little 10% sodium sulphite solution gives an immediate precipitate of lead sulphite, insoluble in excess of the reagent. In cases of chronic lead poisoning, however, this test often fails, as the lead is fixed in the coagulum. The blood is then repeatedly treated, at boiling temperature, with a little nitric acid, and the filtered, slightly coloured liquid mixed with an equal volume of saturated sodium sulphite solution; within 12 hrs. lead sulphite settles. Urine containing lead sometimes deposits lead sulphite when treated with its own volume of saturated sodium sulphite solution. If a negative result is obtained in this way, 100 c.c. of the urine are boiled for a few minutes with 5 c.c. of nitric acid and excess (about 10 g.) of solid sodium sulphite is gradually dissolved in the solution; the appearance of a white precipitate after 12 hrs. renders probable the presence of lead. The washed precipitate should always be identified (1) by treating it with a solution of 1 g. of iodine and 2 g. of potassium iodide in 100 c.c. of water, the iodine converting the lead sulphite into the sulphate, with which potassium iodide gives lead iodide, or (2) by warming it on a microscope slide with hydrochloric acid and treating the dry residue with a crystal of potassium nitrite and a drop of a solution of 4 g. of sodium acetate and 2 g. of copper acetate in 100 c.c. of 10% acetic acid; black or brown cubes of the compound $K_2CuPb(NO_2)_6$ are thus formed. A rapid test for lead in urine consists in shaking 10 c.c. of the urine with 8—10 drops of hydrochloric acid, about 1 g. of powdered sodium sulphite, and a little zinc dust; provided that neither bismuth nor mercury has been administered, the appearance of a black precipitate indicates the presence of lead. Modified conditions are given for Mayençon and Bergeret's electrolytic test, in which the lead is deposited as metal by means of a platinum–zinc or platinum–aluminium couple. T. H. Pope.

Detection of bismuth in the inflammatory nodules after intramuscular injections. J. Leboucq (J. Pharm. Chim., 1929, [viii], **9**, 524—525).—Bismuth has been detected in the greyish nodules occurring in the gluteal region of a patient after intramuscular injection. E. H. Sharples.

Bismuth in the animal body. R. Vaurs (Bull. Soc. Chim. biol., 1929, **11**, 609—619).—Methods used for the detection of bismuth in urine are criticised. A method is described in which the urine is concentrated and organic matter destroyed by treatment with nitric and sulphuric acids. Calcium sulphate is removed, the filtrate neutralised with ammonia and acidified with hydrochloric acid, and bismuth precipitated as the sulphide. To remove copper the sulphides are redissolved in nitric acid and the bismuth is precipitated as basic carbonate. F. C. Happold.

Standardisation and stabilisation of mydriatics and myotics. E. E. Swanson, H. E. Thompson, and C. L. Rose (J. Amer. Pharm. Assoc., 1929, **18**, 446—450).—Atropine sulphate, homatropine sulphate, scopolamine hydrobromide, hyoscyamine sulphate, ephedrine and ψ-ephedrine and their sulphates have been biologically assayed by the cat's-eye method of Munch (J. Assoc. Off. Agric. Chem., 1927, **10**, 383). The results agree with those reported by Munch. Five tinctures of belladonna, all of which gave similar results by chemical assay, showed a variability of 1·5—8 times by the above method. This is probably due to the presence of more active alkaloids. E. H. Sharples.

Rate of absorption of cocaine hydrochloride when injected subcutaneously into rabbits. H. Sandquist and W. Hök (Svensk Farm. Tid., 1928, 32, 649). Chemical Abstracts.

Influence of ergotamine on the blood-sugar. G. Eda (J. Biochem. Japan, 1928, 10, 101—114).—Experiments on normal man and dogs do not justify the conclusion that ergotamine has a hypoglycæmic action, whereas in diabetes, or in depancreatised dogs, the blood-sugar is diminished. Chemical Abstracts.

Creatine. I. Effect of creatine on blood-sugar. R. M. Hill and I. H. Mattison. **II. Effect of creatine on rabbits.** W. A. Peabody and R. M. Hill (J. Biol. Chem., 1929, 82, 679—685, 687—692).—I. Subcutaneous or oral administration of creatine reduces the blood-sugar of fasting dogs and diminishes the rise in blood-sugar which would normally follow ingestion of dextrose. No toxic effects of creatine were observed, and it was impossible, by its use, to reduce the blood-sugar so much as to produce hypoglycæmic convulsions.

II. Creatine failed to produce hypoglycæmia in rabbits, nor did it exercise any toxic effect on the liver, as indicated by the power of this organ to deaminate glycine (cf. Blatherwick and others, A., 1928, 199). C. R. Harington.

Creatine and creatinine. I. N. Sato (Sei-I-Kwai Med. J., 1928, 47, No. 10).—Creatine, when administered to rabbits, is partly retained, partly converted into creatinine, and partly excreted in the urine. After oral administration, the creatine contents of the kidneys and liver are increased; that of the muscle at first increases and then decreases. Retention of creatine or creatinine is diminished when intravenous injection is substituted for oral administration. Chemical Abstracts.

Effect of diguanide and its derivatives on sugar metabolism. E. Hesse and G. Taubmann (Arch. exp. Path. Pharm., 1929, 142, 290—308).—Certain derivatives of diguanide when administered to normal or hyperglycæmic animals cause a lowering of the blood-sugar level. These compounds in their physiological behaviour resemble "synthalin" and in certain respects differ from insulin. In particular the curative effect of the administration of adrenaline or of dextrose is much less effective against the toxic action of these compounds than against that of insulin. W. O. Kermack.

Possible decomposition of 5-iodo-, 5-bromo-, 5-chloro-, and 3 : 5-dibromo-salicylic acids in the animal organism. C. Girod (J. Pharm. Chim., 1929, [viii], 9, 513—520).—The above acids, after oral administration to rabbits, are eliminated unchanged in the urine. They promote the production of glycuronic acid and are probably eliminated in association with this compound, as is salicylic acid. The following are described: 4-*chloro*-2 : 6-*di-iodophenyl acetate*, m. p. 127·5°; 4-*chloro*-2 : 6-*di-iodophenetole*, m. p. 69°; 2 : 4-*dichloro*-6-*iodophenol*, m. p. 63°; 2 : 4-*dichloro*-6-*iodophenyl acetate*, m. p. 65—66°; 2 : 4-*dichloro*-6-*iodophenetole*, b. p. 290—294°; 4-*bromo*-2 : 6-*di-iodophenol*, m. p. 128°; 4-*bromo*-2 : 6-*di-iodophenyl acetate*, m. p. 135°; 4-*bromo*-2 : 6-*di-iodophenetole* m. p. 75°; 2 : 4-*dibromo*-6-*iodophenol*, m. p. 104°; 2 : 4-*dibromo*-6-*iodophenyl acetate*, m. p. 106·5—107°; 2 : 4-*dibromo*-6-*iodophenetole*, m. p. 54°. E. H. Sharples.

Excretion of picric acid in the urine after different methods of injection into animals. V. J. Leszcynski (Russ. J. Physiol., 1929, 12, 205—210).—The daily output of picric acid through the urine following injection into the stomach subcutaneously, intravenously, or intraperitoneally in dogs, cats, and rabbits was determined by Gumbert's reaction. The excretion of picric acid by the animals, even when doses of 100—150 g. were injected, did not continue for so long a time as that recorded for man. The duration of the excretion depended not only on the method of injection, but also on the animal species. With dogs the longest period was observed after injection into the stomach, in cats after subcutaneous and intravenous injection, in rabbits after subcutaneous injection. Cats excreted picric and picramic acids over the longest period, rabbits over the shortest. Rabbits did not excrete picramic acid after intravenous and intraperitoneal injections, 5-gram doses of picric acid given intravenously to dogs and intraperitoneally to cats were rapidly transformed into picramic acid, whereas rabbits following intraperitoneal injection excreted a derivative of picric acid other than picramic acid. C. C. N. Vass.

Preparation of diastase. F. Winkler and F. Köck (Chem.-Ztg., 1929, 53, 457).—Green malt or the kernels of sunflower seeds are thoroughly bruised in a mortar and treated with chlorinated organic compounds until thoroughly disintegrated. The mass is digested with water and glycerol or a dilute "yatren" solution, the mixture sterilised and centrifuged, and the liquor siphoned off and filtered. The filtrate is treated with acetone, the precipitate separated after 24 hrs. by centrifuging, and the solution evaporated at 40° under reduced pressure. The resulting yellowish-white substance has a higher diastatic power than that obtained by the usual alcohol method. A. R. Powell.

Lactic acid formation in muscle extracts. IV. Comparison between dextrose and glycogen in respect of lactic acid formation and phosphoric ester accumulation. D. Stiven (Biochem. J., 1929, 23, 583—586).—The accumulation of phosphoric ester from dextrose is very small compared with that from glycogen in the muscle of the cat, even when the rate of lactic acid formation from the former is greater than that from the latter. Both the rate and extent of the lactic acid formation from dextrose are greater than from glycogen; there is, however, a great variation from one extract to another. This variation is not due to faulty technique, but to some factor as yet uncontrolled. S. S. Zilva.

Hydrolysis of *d*-glucosides of *d*- and *l*-methyl-*n*-hexylcarbinol with emulsin. S. Mitchell (J. Biol. Chem., 1929, 82, 727—730).—*Tetra-acetyl-β-methyl-*n*-hexylcarbinyl-*d*-glucoside*, from acetobromoglucose and methyl-*n*-hexylcarbinol with silver carbonate, has m. p. 95°, and yields, when hydrolysed with barium hydroxide, β-*methyl*-n-*hexylcarbinyl*-d-*glucoside.* The glucosides prepared thus from the *d*- and *l*-carbinols had $[\alpha]_{5461}^{17}$ $-37·8°$ and $-46·6°$, respectively; the former was hydrolysed by emulsin 8·4 times as rapidly as the latter. C. R. Harington.

Asymmetric hydrolysis of esters by enzymes. II. Configuration specificity of liver esterase of different animals and its dependence on concentration of the substrate. R. Willstätter, R. Kuhn, and E. Bamann (Ber., 1929, **62**, [*B*], 1538—1548; cf. A., 1928, 755).—The relative activities of the different liver esterases towards methyl butyrate are: dog 18·8, ox 18·8, man 24·5, sheep 49·5, horse 78·8, and rabbit 274·0. The substrates used are ethyl *r*-, (+)-, and (−)-mandelates. The initial rates of hydrolysis are measured at 25°. In the most concentrated solutions (0·096*M*), hydrolysis occurs to 1% or less, in 0·012*M* solution 1—4%, and in 10 times more dilute solution 4—30%. Reaction is directly proportional to the time and the change is zero-molecular. With esterase of sheep, dog, man, and rabbit the optimal substrate concentration of the (−)-ester is 0·024*M*; with increasing concentration the amount of acid formed decreases; with ox and horse esterase, maximum reaction is not attained in 0·096*M*-solution. Except in the case of sheep-liver esterase, maximal action towards the (+)-ester is not developed in 0·095*M*-solution. Only in the case of sheep-liver esterase is it possible to calculate the dissociation constants of the esterase-(−)-ester and esterase-(+)-ester from the maximal rates of reaction; the values agree nearly with those observed for pigs (*loc. cit.*). The optical activities of the mandelic acids obtained by partial hydrolysis of ethyl *r*-mandelate are determined for the various esterases with differing periods and substrate concentrations; the most striking observation is the dependence of the sign of rotation of the acid on the substrate concentration with the esterases of man and rabbit. H. Wren.

Disappearance of histamine from autolysing lung tissue. C. H. Best (J. Physiol., 1929, **67**, 256—263).—Lung tissue in the presence of toluene is able to destroy both naturally occurring and added histamine. This property is lost on heating at 90° for 4 min. E. Boyland.

Proteolytic enzymes in green malt. C. K. Mill and K. Linderstrøm-Lang (Compt. rend. Trav. Lab. Carlsberg, 1929, **17**, No. 10).—There are at least two proteolytic enzymes in an extract of green malt. The first, which is a protease, acts on gelatin, edestin, and egg-albumin peptone, and has in the decomposition of edestin at 40° an optimum p_H of 4·3, measured at 18°. The second enzyme is a peptidase which decomposes leucylglycine, and at 40° has its optimum action at p_H 7·6—7·9, measured at 18°. The peptidase is inhibited by phosphates and decomposes readily when the malt extract is kept at its natural reaction (p_H 5·9) at the ordinary temperature. C. Ranken.

Action of trypsin on caseinogen. H. W. Wahlteich (J. Biol. Chem., 1929, **82**, 737—749).—The digestion of caseinogen by trypsin has been studied at three different temperatures with varying concentrations of enzyme. Under all conditions, the appearance of the maximum proteose-nitrogen (*i.e.*, nitrogen precipitable with zinc sulphate) coincided with disappearance of the original substrate, and with an increase in the amino-nitrogen to about 10% of the total. The time taken to convert 10—12% of the total nitrogen into amino-nitrogen gives a useful measure of tryptic activity. Between 20° and 40° the rate of tryptic action is approximately doubled for 10° rise in temperature. C. R. Harington.

Influence of chemical reagents, especially of metallic salts, on the tyrosinase reaction. S. Takaoka (Keio J. Med., 1928, **8**, 165—190).—Zinc chloride accelerates the tyrosinase reaction. Salts which shift the p_H value to the acidic side generally inhibit the reaction. Salts which shift the p_H value to the alkaline side generally accelerate the second reaction (formation of black substance). In dilute solution, oxidising and reducing agents accelerate the first reaction (red coloration) and have an inhibiting effect, respectively. Inhibition is observed with alcohols and diamines. The first reaction is accelerated by pilocarpine and inhibited by brucine; the second is accelerated by morphine hydrochloride, quinine hydrochloride, or strychnine nitrate. Chemical Abstracts.

Enzymic inactivation of co-zymase. H. von Euler, K. Myrbäck, and E. Brunius (Z. physiol. Chem., 1929, **183**, 60—66).—The inactivation of co-zymase by castor-bean lipase (cf. Buchner and Klatte, A., 1908, i, 380) is not dependent on the enzyme, since inactivation also occurs with the enzyme-free preparation. Similarly, inactivation by pancreas is not due to pancreatic lipase. Inactivation is also brought about by dry liver powder (obtained by washing liver with acetone and alcohol) at p_H about 8 but not at p_H 4—5. Similar dry preparations from the stomach, intestine, and pancreas exert an analogous influence. The inactivation appears to be related to the fission of phosphate from the co-zymase preparation. The results of Raymond (A., 1928, 1402) on the extraction of co-zymase from yeast with water and toluene were not confirmed. H. Burton.

Alcoholic fermentation of amino-acids. E. Parisi [with B. Bernardi and F. de Meichsner] (Annali Chim. Appl., 1929, **19**, 234—239; cf. B., 1926, 169).—As the amount of amino-acids in molasses (beet) distillery slop is only slightly lower than that originally present in the molasses, these compounds cannot be utilised to any great extent by the yeast during fermentation. This conclusion is confirmed by Ehrlich (A., 1907, ii, 383). Experiments on the fermentation of sugar in solutions containing nitrogen as glycine, alanine, valine, leucine, *iso*leucine, α- or β-phenylalanine, glutamic acid, tryptophan, or asparagine show that, in the transformation of 15—16 g. of sugar into alcohol, at most 0·02 g. of amino-nitrogen is consumed by the yeast. T. H. Pope.

Nitrogen content of growing cultures of *Mycoderma* and of *Saccharomyces cerevisiæ*. L. M. Christensen (Plant Physiol., 1928, **3**, 61—

69).—The apparent nitrogen content of cultures on molasses depends on the p_H, time, and method of analysis. The true amount of nitrogen fixed is probably greater than that indicated.

Chemical Abstracts.

Metabolism of *Aspergillus oryzæ*. III. H. Tamiya (Acta Phytochim., 1929, 4, 227—295; cf. A., 1928, 1063).—An apparatus is described by means of which the respiration of fungi in gaseous systems of known composition can be measured. Maximum growth and respiration of *A. oryzæ* on Pfeffer's medium at p_H 5·5 was obtained in a mixture of 17% of nitrogen and 83% of oxygen, the oxidation quotient being 0·5—1·0. Removal of sugar from the medium caused an inhibition of growth, a decrease in the intensity of respiration, and a still larger decrease in fermentation, whilst the oxidation quotient rose to 1·3—2·0. Addition of more than $7·5\times10^{-3}$ mol. of potassium cyanide to the medium resulted in diminished growth and inhibition of respiration and fermentation in 15% of nitrogen and 85% of oxygen, whilst the oxidation quotient reached an abnormally high value. Under anaërobic conditions in the presence of potassium cyanide the mould showed no change in weight, but whilst the fermentation was diminished a stronger resistance against this inhibition was observed than under similar but aërobic conditions. The presence of carbon monoxide always caused an inhibition of growth under aërobic conditions, whereas the intensities of the respiration and fermentation processes were not inhibited. Under anaërobic conditions carbon monoxide neither activated nor inhibited fermentation. The synthetic quotient, which is measured by the ratio of the increase in weight of the mould (in g.) to the sugar used (in mg.), was in normal cultures 0·4—1·0; on removal of sugar or addition of carbon monoxide it was decreased.

Cytochrome was always observed in aërobic cultures, whereas in anaërobic cultures it was absent or only faintly detectable, the rate of its disappearance being retarded in the presence of potassium cyanide. C. C. N. Vass.

Dehydrase and glutathione in moulds. H. Tamiya (Acta Phytochim., 1929, 4, 297—311).—*Aspergillus oryzæ* grown on Pfeffer's medium containing 0·025% of methylene-blue caused a decolorisation at the commencement, but with the onset of autolysis the colour returned. Individual examination at p_H 7·6 of the dried mould, an extract of the mould obtained after boiling for 1 hr., a mould which had been washed with water for 24 hrs., and the medium freed from the mould showed that the reduction was not due to the mould alone. The strongest reduction was obtained when the dried mould and the medium were used together. Whilst the extract showed no reduction and the washed mould a diminished reduction, together these gave an increased reduction. Anaërobiosis caused a decrease in the reducing power of the mould which, however, fell less rapidly with age, whereas that of the culture medium varied with age, increasing to a maximum on the eighth day. The glutathione content of the dried mould determined by the method of Tunnicliffe (A., 1925, i, 752) was found to be 0·2—0·5%. Aërobic cultures showed a maximum glutathione content after 4 days, which gradually decreased, and no positive sodium nitroprusside reaction was obtained at the end of 5 months. Anaërobic cultures contained approximately one half of the glutathione content of aërobic cultures, but its rate of disappearance was much slower, glutathione being detectable at the end of 5 months. The glutathione content of the medium increased up to the eleventh day in aërobic cultures, when it reached the recorded glutathione content of blood (0·01—0·02%), whilst under anaërobic conditions, although the amount of glutathione formed was smaller, it remained unchanged for a longer period.

C. C. N. Vass.

Influence of carbon monoxide on the metabolism of moulds. H. Tamiya (Acta Phytochim., 1929, 4, 313—326).—The growth and intensity of respiration of *Aspergillus oryzæ* have been observed in varying concentrations of oxygen, nitrogen, and carbon monoxide. During short periods of growth, *e.g.*, 4 days, carbon monoxide does not inhibit respiration, but causes slight destruction of the living cells. C. C. N. Vass.

Biochemical synthesis of fumaric from pyruvic acid. A. Gottschalk (Z. physiol. Chem., 1929, 182, 311—312).—Contrary to the results previously described (A., 1926, 545; 1928, 804), and in agreement with Ehrlich and Bender's observations (A., 1928, 95, 804), the author has been unable to obtain fumaric acid during the growth of *Rhizopus nigricans* on a pyruvic acid–mineral salt or a lævulose-mineral salt medium. H. Burton.

Fungicidal action of sulphur. III. Toxicity of hydrogen sulphide and the interaction of sulphur with fungi. R. W. Marsh (J. Pomology, 1929, 7, 237—250).—Experiments are described showing the high toxicity of hydrogen sulphide to germinating spores of several species of fungi. The addition of powdered sulphur to spores of *Monilia fructigena* inhibits germination, whereas *Botrytis cinerea* is unaffected by this treatment. The same effect can be obtained when sulphur is placed on a flowering plant bearing these spores. These experiments are thought to indicate that sulphur is toxic to these fungi only by virtue of the hydrogen sulphide produced and that a fungus sensitive to sulphur is one which can reduce sulphur. E. A. Lunt.

Type III pneumococci. A. Stull (J. Biol. Chem., 1929, 82, 641—650).—The specific soluble carbohydrate of Heidelberger and Goebel (A., 1927, 77, 1114) could be isolated from an unbuffered culture medium after 18 hrs.' growth of type III pneumococci. The organisms were separated, dried, and extracted successively with a variety of solvents. The whole of the specific soluble carbohydrate (the only specific precipitating material found) was contained in the distilled-water extract of the fat-free material.

C. R. Harington.

Effect of tin on tubercle bacillus. N. Dos Santos (Compt. rend. Soc. Biol., 1929, 101, 383—384).—Stannous chloride in concentrations of 1 to

5000 does not affect the growth of the tubercle bacillus. E. Boyland.

Colorimetric and biological determination of the adrenaline content of the suprarenals of rabbits. M. Watanabe and H. Sato (Tohoku J. Exp. Med., 1928, **11**, 433—448).—With the cortical suprarenal substance of rabbits, the method of Folin, Cannon, and Denis gave a positive reaction, whilst the biological methods did not. For the total gland, this method gave higher values than did the biological or Suto and Inouye's method. Chemical Abstracts.

Determination of adrenaline in the suprarenal extract from oxen, pigs, cats, dogs, and rabbits. T. Sugawara (Tohoku J. Exp. Med., 1928, **11**, 410—432).—Biological and colorimetric methods were compared. The values obtained were, apparently, not related to the method of extraction. Adrenaline diffuses from the medulla to the cortex after extirpation of the gland, particularly on manipulation of the capsule. Chemical Abstracts.

Adrenaline and hyperglycæmia. G. S. Eadie (Amer. J. Physiol., 1929, **89**, 46—49).—The increased blood-sugar in adrenaline hyperglycæmia is derived from the liver, not from the muscles. E. Boyland.

Hormone content of the urine of the pregnant female. M. M. Maino (Arch. Ist. Biochim. Ital., 1929, **1**, 95—104).—Allen and Doisy's biological test shows that the ovarian hormone appears in the urine in amounts sufficient to cause œstrus in castrated experimental animals only at about the middle of the fourth month of pregnancy. During the first months of pregnancy the urine contains a hormone acting mainly on the ovary, in which it determines the appearance of mature follicles, hæmorrhage, and atresic corpora lutea. This hormone is undoubtedly different from the ovarian hormone and as it does not occur in appreciable proportions during non-pregnancy, its presence serves for the early diagnosis of pregnancy. T. H. Pope.

Dextrose–insulin equilibrium. J. P. Bouckaert, P. Denayer, and R. Krekels (Compt. rend. Soc. Biol., 1929, **101**, 511—512).—The amount of dextrose necessary to maintain the blood-sugar after insulin administration is relatively much less for large doses of insulin. E. Boyland.

Action of insulin on the carbamide of the blood. A. C. Marie (Compt. rend. Soc. Biol., 1929, **101**, 445—447).—Insulin reduces the high carbamide concentration produced by administration of adrenaline. E. Boyland.

Modification of insulin action in medulliadrenal-inactivated cats by post-pituitary extracts. E. M. K. Geiling, S. W. Britton, and H. O. Calvery (J. Pharm. Exp. Ther., 1929, **36**, 235—241).—Simultaneous injection of pituitary extract and insulin prevents, diminishes, or retards the hypoglycæmia and convulsions produced when insulin is administered in adequate doses to normal and medulliadrenal-inactivated unanæsthetised cats. Medulliadrenal-inactivated animals are the more sensitive to insulin and require larger doses of pituitary extract than normal animals to protect them equally against the insulin. Pituitary extract administered during insulin hypoglycæmia may abolish severe convulsions and muscular weakness without an appreciable rise in blood-sugar. Post-pituitary liquid and adrenaline produce hyperglycæmia in cats when the adrenal medulla was evacuated and the hepatic nerves were severed. This effect was much less than with normal animals. F. C. Happold.

Action of extract of pituitary on the blood-sugar after pancreatectomy. C. G. Imrie (J. Physiol., 1929, **67**, 264—269).—The injection of pituitrin up to 44 hrs. after administration of insulin to a depancreatised dog causes a rise in blood-sugar. If the pituitrin is given 70 hrs. after the insulin this rise does not occur. The extra sugar is derived from liver, not from muscle-glycogen. E. Boyland.

Standardisation of thyroid preparations. J. R. Mørch (J. Physiol., 1929, **67**, 221—241).—The value of thyroid preparations is determined by their effect on the carbon dioxide production of white mice under special conditions. It is claimed that the results are significant to within 33%. E. Boyland.

Occurrence of vitamin-*A* in blood and blood-serum of domestic animals, cow's milk, milk products, and foodstuffs. B. Rösiö (Z. physiol. Chem., 1929, **182**, 289—304).—The vitamin-*A* colour reaction (antimony chloride) has been applied to the blood-serum from the horse, cow, sheep, and goat. Quantitative measurements (obtained by matching the colour produced in a Lovibond tintometer) show that with increase in the age of the horse and cow the vitamin content decreases. Pregnant cows and mares show generally an increased value; this appears to depend somewhat on age. For cows the mean vitamin content is about three times as high as for horses. The vitamin content of cow's blood is one half that of the serum. The vitamin-*A* content of cow's milk increases with increase in the amount of fat present; a similar relationship is found for butter. Swedish turnip (rutabaga), white mangold, and soya meal give colour reactions, whilst turnip does not. H. Burton.

Vitamin-*B* from brewer's yeast. A. Seidell (J. Biol. Chem., 1929, **82**, 633—640).—On treatment of an aqueous solution of the antineuritic concentrate previously described (A., 1926, 644) with benzoyl chloride and sodium carbonate, followed by extraction with chloroform, much of the nitrogenous material passed into the chloroform, whilst most of the physiological activity remained in the aqueous solution. The latter was poured into 4 vols. of acetone, yielding a precipitate of salts together with 90% of the active principle; in this form, 0·15 mg. of nitrogen represents the daily protective dose for a pigeon. C. R. Harington.

Antineuritic and water-soluble *B* vitamins in beef and pork. R. Hoagland (J. Agric. Res., 1929, **38**, 431—446).—Dried lean pork, fresh and smoked hams, and dried lean beef have been tested on pigeons with respect to their contents in antineuritic and water-soluble *B* vitamins. The results indicate that dried lean pork is a good source of the antineuritic vitamin. E. A. Lunt.

Physiology of vitamins. VII. Hæmoglobin, solids, sugar, and chloride changes in the blood of vitamin-*B*-deficient dogs. C. J. Stucky and W. B. Rose (Amer. J. Physiol., 1929, **89**, 1—17).—The blood-sugar of vitamin-*B*-deficient dogs remained normal, whilst the blood-chloride fell sometimes to a marked extent; anhydræmia developed accompanied by an increase in the hæmoglobin content of the blood. Starvation occurs on account of inefficient utilisation of food and reduced water consumption. E. Boyland.

Vitamin action and surface activity. II. Antiscorbutic action of plant juices and their surface activity. N. E. Schepilevskaja (Biochem. Z., 1929, **208**, 334—351).—The antiscorbutic action of a number of plant juices (of turnip, beet, radish, carrot, cabbage, etc.) is shown to run approximately parallel with their surface activities. P. W. Clutterbuck.

Effect of drying and of sulphur dioxide on antiscorbutic property of fruits. A. F. Morgan and A. Field (J. Biol. Chem., 1929, **82**, 579—586).—Sun-drying or dehydration of untreated peaches caused destruction of their antiscorbutic properties; the latter were, however, not affected by drying if the fruit were first treated with sulphur dioxide. C. R. Harington.

Vitamin-*D* and fæcal reaction. A. L. Bacharach and H. Jephcott (J. Biol. Chem., 1929, **82**, 751—758).—A reply to the criticisms of Shohl and Bing (A., 1928, 1288) and Oser (this vol., 210) of the authors' method (A., 1928, 332) for the determination of vitamin-*D*. C. R. Harington.

Spectrographic examination of lipins. V. Brustier and L. Bugnard (Compt. rend. Soc. Biol., 1929, **101**, 420—421).—The total lipins extracted from a rabbit apparently contained ergosterol. E. Boyland.

Composition of bone. VI. Effect of massive doses of irradiated ergosterol. B. Kramer, M. J. Shear, and M. R. McKenzie (J. Biol. Chem., 1929, **82**, 555—557; cf. A., 1928, 1271).—No deviation from the normal was observed in the residual Ca : P ratio of the bones of growing rats as the result of administration of massive doses of irradiated ergosterol. C. R. Harington.

Antirachitic action of certain cholesterolic lipins of the snail (*Helix pomatia*). G. Mouriquand and A. Leulier (Compt. rend., 1929, **188**, 1701—1702).—An irradiated mixture of cholesterol and lipins derived from *Helix pomatia* possesses powerful antirachitic properties. C. W. Shoppee.

Vegetable assimilation and respiration. XX. Photosynthesis in green plants. G. E. Briggs (Proc. Roy. Soc., 1929, *B*, **105**, 1—35).—Experiments have been carried out on the determination of photosynthetic efficiency in the following portions of the visible spectrum: 4300—5100, 5100—5600, 5700—6400 Å., the efficiency for comparative purposes being defined as the volume of carbon dioxide reduced per unit of energy absorbed. For the plants tested, *Phaseolus vulgaris*, *Sambucus nigra*, yellow and green elm, the efficiency decreased with decreasing wave-length. Comparison is made of these with existing data and theoretical considerations are advanced showing that, contrary to Warburg and Negelein's conclusions, the number of quanta required for the reduction by the plant of a molecule of carbon dioxide increases discontinuously with increasing wave-length. E. A. Lunt.

Permeability of plant cells in relation to the action of mercury on seeds. A. Niethammer (Z. physikal. Chem., 1929, **142**, 309—319).—The occurrence of mercury in plants grown from seed which has been in contact with various organic mercury compounds has been investigated. In general inappreciable quantities of mercury appear in the plant. H. F. Gillbe.

Protochlorophyll. W. H. Eyster (Science, 1928, **68**, 569—570).—The work of Liro (Ann. Acad. Scient. Fennicæ, 1909, **1**) and others indicates that protochlorophyll is not a decomposition product, but is a pigment which develops independently of light and changes to chlorophyll on insolation, probably in the presence only of a specific enzyme. L. S. Theobald.

[Detection of germinable seeds by] determination of acetaldehyde [content] by Griebel's micro-method. A. Niethammer (Mikrochem., 1929, **7**, 227—230).—The acetaldehyde content is determined approximately, preferably after a preliminary swelling in water, by Griebel's method (A., 1928, 82). Non-germinable seeds contain little or no acetaldehyde. J. S. Carter.

Translocation of potassium in tomato plants and its relation to their carbohydrate and nitrogen distribution. G. Janssen and R. P. Bartholomew (J. Agric. Res., 1929, **38**, 447—465).—Tomato plants grown on a nutrient solution with low potassium content show an increase in the percentage of dry matter, and high total and soluble nitrogen contents. There appears to be an optimum potassium concentration conducive to the normal assimilation of carbohydrate compounds. E. A. Lunt.

Determination of inorganic nitrogen in plant extracts. A. C. Sessions and J. W. Shive (Plant Physiol., 1928, **3**, 499—511).—The aqueous extract is deproteinised with 10% acetic acid and concentrated to 500 c.c.; ammonia is determined in 50 c.c. by Folin's aspiration method after addition of saturated sodium carbonate solution (50 c.c.) and sodium chloride (5 g.). Sodium hydroxide (to 0·125*N*) and Devarda's alloy are added, and the ammonia is determined by aspiration. Chemical Abstracts.

[Moisture in] wheat grown under constant conditions. I, II. H. L. van de Sande-Bakhuyzen (Plant Physiol., 1928, **3**, 1—30).—Moisture determinations suggest that the imbibition capacity of the plasma-colloids, which is maintained by the growth hormones as long as a vegetative point is present, decreases, by the act of fertilisation, as soon as the growing point is virtually lost to the vegetative plant. Chemical Abstracts.

Influence of the malting process on the fat of barley. K. Täufel and M. Rusch (Biochem. Z., 1929, **209**, 55—61).—The fat of barley is composed chiefly of glycerides of palmitic, stearic, oleic, linoleic, and linolenic acids. During the process of germination of the grain there is a loss of almost 11% of dry material, about 12% of this loss being in the fat. It is chiefly the oleic acid which disappears from the fat. There is probably also some conversion of the oleic acid into stearic acid. Special biological significance is attached to the fact that there is formation and accumulation of unsaponifiable matter in the fat during the process of germination.

W. McCartney.

Cytological study of water-soluble and fat-soluble constituents of *Citrus*. J. Dufrenoy (J. Agric. Res., 1929, **38**, 411—429).—The natural colouring process of the *Citrus* fruit is concomitant with starch transference from the chloroplasts in the cells of the three upper layers in the peel. The fat bodies then develop in the chloroplasts and the orange pigment that gives the fruit its colour dissolves in the fat bodies. The same process can be effected artificially by treatment with ethylene. Excitation of the epidermal cells of the fruit by light freezing results in permanent injury of the cell and hence of the fruit. E. A. Lunt.

Catalase and oxidase of the tomato as influenced by the soil reaction. E. S. Haber (Iowa State Coll. J. Sci., 1928, **3**, 29—39).—The catalase was lowest with soil of p_H 6·5—7; soil reaction had no effect on oxidase. Catalase was highest in green mature fruits, and oxidase in ripe fruits. Chemical Abstracts.

Composition of pineapple plants. F. G. Krauss (Ernähr. Pflanze, 1928, **24**, 398—400; Chem. Zentr., 1929, i, 662).—Results of analyses of the pineapple plant at various stages of growth are recorded. The ash is high in potassium and silica.

A. A. Eldridge.

***Phytolacca*.** G. E. Jenkins (J. Amer. Pharm. Assoc., 1929, **18**, 573—576).—Alcoholic extract of air-dried poke root (*Phytolacca Americana*, Linné) (moisture content about 9·0%; ash 9·4%) contains a small amount of an essential oil, 0·21% of potassium nitrate, and 0·16% of a gum which gives characteristic tests for alkaloids. C. C. N. Vass.

Constituents of *Cæsalpinia Bonducella* nut (Flem). I. Bonducella nut oil. S. N. Godbole, D. R. Paranjpe, and J. G. Shrikhande (J. Indian Chem. Soc., 1929, **6**, 295—302).—Extraction of the dried kernels with light petroleum yields 20% of a pale-yellow oil, d_{15}^{25} 0·9215, n^{25} 1·4750, saponification value 199·5—200·5, iodine value (Winkler) 127, Hehner value 93. The oil-free kernels on further extraction with alcohol give saponin and a bitter glucoside, containing almost all the sulphur in the nut: when extraction is carried out with 2% hydrochloric acid, a *substance* (chars without melting at 295°) is obtained. Hydrogenation of the oil is possible with a nickel–pumice catalyst at 180°; poisoning of the catalyst occurs frequently as with mustard oils. As saturation of the oil proceeds the values of *n* decrease in almost a linear function. The percentage composition of the acids isolated from the oil is linoleic (61·4), oleic (21·6), palmitic (10), and stearic (5·79). Sitosterol is present in the unsaponifiable matter (1·5% of original oil). The oil has an inhibiting action on castor-seed lipase.

H. Burton.

Lobeline-like substance isolated from the roots of *Lobelia sessilifolia*, L. S. Kubota, S. Nakashima, and R. Ito (Chinese J. Physiol., 1929, **3**, 278—286).—A crystalline hydrochloride, m. p. 180—190°, possessing alkaloidal properties, has been isolated. Like that of lobeline, with which it may be identical, it acts as a respiratory stimulant.

C. C. N. Vass.

***l*-Asparagine in the fresh flowers of *Ulex europæus*, L.** M. Bridel (J. Pharm. Chim., 1929, [viii], **9**, 112—113).—See this vol., 477.

***iso*Sakuranetin from the flowers of *Pseudaegle trifoliata*.** S. Hattori (Acta Phytochim., 1929, **4**, 219—226).—When the dried flowers of *P. trifoliata*, Makino, are extracted with 50% alcohol, concentrated, and then boiled with 3% hydrochloric acid for 30 min., a dark brown substance separates on keeping. Purification from alcohol affords *iso*sakuranetin, m. p. 194—195° (Shinodo and Sato, this vol., 189), which gives a purplish-red colour with alcoholic ferric chloride. The following derivatives have been prepared: methyl ether, m. p. 117—118° (*loc. cit.*); *ethyl ether*, m. p. 115°, by the action of diazoethane; *acetyl* derivative, m. p. 114—115°; *benzoyl* derivative, m. p. 143°. Fusion with potassium hydroxide gives phloroglucinol and anisic acid. C. C. N. Vass.

Proteins of the ginkgo. M. Furuichi (Bull. Tottori Higher Agric. Sch., 1928, **1**, 105—132).—Ginkgo contains starch 69·6, protein 12, fat 3%; the ash of the seed contains K_2O 40·6, Na_2O 8·4, CaO 4·8, $Fe_2O_3+Al_2O_3$ 3·7, P_2O_5 21·6, SO_3 8·3, SiO_2 4·9%. Of the total nitrogen, 60% is present as a globulin, ginkgoin. The point of maximum surface tension observed when hydrochloric acid is added to an alkaline solution of the globulin, albumin, protamine, or glutelin corresponds approximately with that of maximum turbidity.

Chemical Abstracts.

Proteins of the soya bean. T. Tadokoro and K. Toshimura (Hokkaido J. Agric., 1928, **20**, 355—362).—The ash and phosphorus contents decrease, and the nitrogen content increases, in the order legumelin, glycinin, glutelin. The free amide-nitrogen decreases in the order glycinin, glutelin, legumelin. The melanin-nitrogen is highest in glycinin, the histidine-nitrogen in legumelin, and the lysine-nitrogen in glutelin. Glycinin is the most highly condensed protein present. Chemical Abstracts.

Special constituents of the soya bean. S. Muramatsu (Mem. Pub. Morioka Agric. Coll., 1928, 1—15).—The following compounds were isolated: a *hydroxy-acid*, $C_{50}H_{50}O_{20}$, m. p. 240°; lecithin (from the oil from skin and cotyledons, 0·64%; from the residue after extraction with ethyl alcohol, skin 0·07%, cotyledons 0·78%); a *sterol*, and an *alcohol*, $C_{24}H_{32}O_8$, m. p. 235°. Chemical Abstracts.

Phyto-pharmacology of leucines and cystines. D. I. Macht (J. Pharm. Exp. Ther., 1929, **36**, 243—

250).—The effects of leucine and cystine on the growth of *Lupinus albus* seedlings in nutrient solutions have been studied. The *l*-acids were pharmacologically more active than the *d*-acids in their action on growth. Combination of the stereoisomerides of both acids produced an effect on growth which could not be explained as a mean effect of the two components. F. C. Happold.

Occurrence of chlorates in a tomato soil. O. Owen (J. Pomology, 1929, 7, 270—275).—A case of disease similar in symptoms to the mosaic disease of the tomato was shown to be due to the presence of a toxic amount of chlorates in the soil. E. A. Lunt.

Pigments of red algæ. R. Lemberg (Naturwiss., 1929, **17**, 541).—The pepsin method of obtaining the pigment in a protein-free state is unsuitable because the chromoprotein from red algæ is less readily broken down than in the case of hæmoglobin. The pigment is best obtained by brief treatment with hot concentrated hydrochloric acid followed by extraction of the diluted solution by means of chloroform, air being excluded throughout the operations. Oxidation results in the formation of phycocyan from phycoerythrin pigments. The phycocyan pigment has been isolated in crystalline form from "Nori," a Japanese delicacy, but the phycoerythrin pigment has not yet been obtained pure. It is proposed to call the new pigments *phycobilins*. They are amphoteric, relatively strongly acidic, and easily esterified. With hydrogen chloride in chloroform, salts are formed which are readily hydrolysed by water. The phycobilins and their esters resemble the magnesium-free derivatives of chlorophyll in forming complex zinc and copper salts, soluble in organic solvents and characterised by intense fluorescence. Phycocyanobilin resembles bilicyanin in spectroscopic properties. The ease with which it is oxidised indicates the presence of a hydroxypyrrole ring. Phycocyanobilin crystallises from chloroform–benzene, in an atmosphere of carbon dioxide, as dark blue prisms reflecting red light. Provisionally, the formula $C_{34}H_{44}O_8N_4$ is given; methoxyl determinations on the methyl ester indicate the presence of two carboxyl groups. The pigments represent about 2% of the chromoprotein. R. A. Morton.

Dispersoid analysis by means of a diffusion apparatus. A. Nistler (Kolloidchem. Beih., 1929, **28**, 296—313).—The determination of particle size in a sol by means of diffusion analysis is recommended for biochemical purposes. A new diffusion apparatus for this purpose is described in detail and some results are given for a number of dyes. E. S. Hedges.

Micro-determination of protein. K. Samson (Biochem. Z., 1929, **208**, 262—273).—The centrifuge method for the determination of protein (precipitation in a graduated centrifuge tube and determination in terms of the volume of protein after centrifuging) is examined theoretically and a number of examples are given using different precipitating agents, times of centrifuging, etc., and the method is applied to the separate determination of albumin and globulin fractions of cerebrospinal fluid. P. W. Clutterbuck.

Van Slyke's method [for the determination of amino-acids]. L. Rosenthaler.—See this vol., 713.

Oxidation of dixanthhydrylcarbamide by dichromate; determination of carbamide. F. W. Allen and J. M. Luck (J. Biol. Chem., 1929, **82**, 693—701).—Luck's method (A., 1928, 1229) for the determination of carbamide is modified by oxidising the xanthhydryl compound with excess of potassium dichromate, the excess of oxidising agent being determined iodometrically. The method is applicable to urine, blood, and tissues, in the last case after clarification of the protein-free filtrate with copper sulphate and barium hydroxide. C. R. Harington.

Determination of nitrates and nitrogen [in organic material]. E. M. Emmert (Science, 1928, **68**, 457—458).—Nitrogen present as nitrate is determined by treating 1 g. of plant or animal tissue or 10 g. of soil with 25 c.c. of cold, 75% sulphuric acid and gradually distilling into 50 c.c. of chlorine dioxide solution kept yellow by bubbling through it a stream of this gas. The distillate is then boiled until colourless, neutralised, evaporated to dryness, and the nitrate determined by means of phenoldisulphonic acid. The remaining nitrogen in the sample is determined by the addition of 5 g. of potassium or sodium chlorate, distillation, and treatment as above. The final residue is neutralised with sodium hydroxide and the inorganic constituents are determined. The precautions necessary to avoid harmful explosions in the above method are detailed. L. S. Theobald.

Van Slyke's method for determination of chlorides. A. J. Eisenmann (J. Biol. Chem., 1929, **82**, 411—414).—Contrary to the statement of Wilson and Ball (A., 1928, 1269), Van Slyke's method for the determination of chlorides in its original form (A., 1924, ii, 271) gives accurate results. C. R. Harington.

Determination of chlorine ions in organic fluids. R. Calatroni and E. Tschopp (Biochem. Z., 1929, **208**, 274—278).—The hot deproteinised fluid is treated with excess of standard silver nitrate and, after separating the insoluble chloride by centrifuging, the excess of silver in the supernatant fluid is determined by treating an aliquot part with an aqueous solution of hydrogen sulphide in presence of gelatin as protective colloid. The silver sulphide formed is a very stable colloid and may be determined colorimetrically. The results agree fairly closely with those obtained on the same solution by Van Slyke's method, the variations being from ±0·5 to 1·5%. P. W. Clutterbuck.

Determination of chlorine in organs and foods. M. Birner (Z. ges. exp. Med., 1928, **61**, 700—706; Chem. Zentr., 1928, ii, 2582—2583).—The organic material is covered in a tall, narrow nickel crucible with 2—3 times the quantity of sodium hydroxide, and the mass is heated on the water-bath, the temperature being raised to 120° after addition of a small amount of potassium nitrate, and finally to a temperature not above 450°. After cooling, the mass is dissolved in water, filtered, and the chlorine determined by Volhard's method. Nitrite is removed by boiling after addition of silver nitrate, the last traces being oxidised with a few drops of permanganate solution. A. A. Eldridge.